

Measurement of small spin–spin splittings in the presence of chemical exchange: case of deuteriated water

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Abstract

A new implementation of a described data processing for measuring small scalar coupling constant J is proposed. It is applied particularly to situations where the coupling constant is around the linewidth at half-height, and in the presence of chemical exchange. This modified data processing uses only a simple “one-pulse” experiment instead of a series of spin echoes experiments required by the previous processing. The FID recorded in the one pulse experiment is used by a reconstitution program to generate a set of signals, which are analyzed in the time domain to obtain a spectrum where the scalar coupling constant is apparently multiplied by $n + 1$, where n is positive. The new processing is tested with simulated spectra. The coupling constant between proton and deuterium is measured in the proton spectrum of a solution of 80% of D_2O and 20% of H_2O . It was found to be $J = 1.54 \pm 0.01$ Hz. © 2003 Elsevier Science (USA). All rights reserved.

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1. Introduction

Scalar coupling constants are of considerable help for elucidation of structural and conformational problems [1–5]. For cases where these are around the value of the linewidth, the direct method of measurement (by locating peak maxima) breaks down [6]. Measurements can then lead to erroneous evaluation of spin–spin coupling due to interference and cancellation of signals [7]. Various methods [8–15] have been proposed to measure spin–spin coupling in this situation. The so-called method of J -doubling [9] is simple and easy to implement. The time domain signal is extracted, multiplied by $\sin(\pi J^* t)$, where J^* is a trial coupling. An automated search program detects the case where $J^* = J$. This method have been modified recently by Garza-Garcia et al. [16]. The modified J -doubling allows one to analyze 2D multiplets and to measure very small coupling constants. In the method described by Mahi and Duplan

[17], a set of signals obtained from spin echo experiments [18] is analyzed in the time domain by an integration program, to increase apparently all spin–spin coupling constants in the spectrum. The method is designed to extract long-range coupling constants in homonuclear and heteronuclear spin systems.

In this paper we apply this technique to measurements of very small coupling constants in the presence of chemical exchange [19,20]. Spin–spin coupling is very difficult to measure in this situation, because the chemical exchange leads to an additional broadening of the individual signals [20]. The latter are always very broad singlets. We also introduce substantial modifications into this technique. Its implementation will require the recording of only one “one-pulse” experiment instead of a series of spin echo experiments. The main difference between certain techniques such as J -deconvolution or J -doubling and the proposed method is that the latter does not require isolation of the signal in the time domain corresponding of the multiplet of interest. The signal corresponding to the whole signal is analyzed in the time domain and all couplings in the spectrum are apparently multiplied by the same factor.

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2. Description of the macroscopic magnetization

The evolution of the shape and width of the signal of a spin system in which the individual nuclei are moving from position to position in a random statistical manner, has been developed by Gutowsky et al. [21] and simplified by McConnell [22]. The description of this system is best developed by suitable modifications of the Bloch equations [23]. In our development we take account of the spin–spin coupling (in contrast with the analysis used in [22]) and we suppose also that the positions A, B are of two types of nuclei with different chemical shifts. We shall follow the same procedure as that proposed by McConnell [22]. We will consider that all proton nuclei remain in one position (A) where they are coupled to a deuterium nucleus of spin $+|I_z|$ until they make a sudden rapid jump to another position (B) where they are coupled to a deuterium nucleus of spin $-|I_z|$. The quantitative description of this system is given by the Bloch equations [24], which are suitably modified to take account of the possibility of exchange between A and B positions. One can find that the total complex magnetization $G(t)$, is given by:

$$G(t) = \frac{M^0 \exp\left(\left(i\omega_\delta - \frac{1}{T_2'}\right)t\right)}{2\pi\beta\tau_v} \left[(1 + \beta\pi\tau_v) \times \exp(\beta\pi t) + (\beta\pi\tau_v - 1) \exp(-\beta\pi t) \right], \quad (1)$$

where

$$\beta = \sqrt{\frac{1}{(\pi\tau_v)^2} - J^2}, \quad (2)$$

$$\frac{1}{T_2'} = \frac{1}{T_2} + \frac{1}{\tau_v} \quad (3)$$

ω_δ is the chemical shift frequency of the considered proton nucleus. τ_v is the mean lifetime in a given position. J is the spin–spin coupling constant between deuterium and the proton. T_2 is the transverse relaxation time.

So when a spin echo experiment is recorded for a delay τ , the observed magnetization will be given by [18]:

$$G(t, \tau) = \frac{g(t)}{2\pi\beta\tau_v} \exp\left(\frac{-\tau}{T_2}\right) \left[(1 + \beta\pi\tau_v) \exp(\beta\pi(t + \tau)) + (\beta\pi\tau_v - 1) \exp(-\beta\pi(t + \tau)) \right], \quad (4)$$

where

$$g(t) = M^0 \exp\left(\left(i\omega_\delta - \frac{1}{T_2'}\right)t\right). \quad (5)$$

Different cases have to be considered, following the value of the rate of chemical exchange $1/\tau_v$ compared to the quantity πJ .

In case of rapid exchange, τ_v is very small and we can write: $(1/\tau_v) \gg \pi J$. The magnetization $G(t, \tau)$ does not depend explicitly on J . One cannot measure the coupling

constant J using the described method. When the chemical exchange is slow ($1/\tau_v$ is sufficiently large compared with πJ) the situation is rather similar to that studied by the data processing described in [17].

2.1. Intermediate cases

Now let us examine the situations where $1/\tau_v$ and πJ are comparable.

2.1.1. Case where $(1/\tau_v) < \pi J$

In the case where $(1/\tau_v) < \pi J$ we have then $(1/\tau_v^2) - (\pi J)^2 < 0$ and from Eq. (4), $G(t, \tau)$ will be written as:

$$G(t, \tau) = g(t) \exp\left(\frac{-\tau}{T_2}\right) \left[\cos(\pi\beta'(t + \tau)) + \frac{1}{\beta\pi\tau_v} \sin(\pi\beta'(t + \tau)) \right], \quad (6)$$

where

$$\beta' = \sqrt{J^2 - \frac{1}{(\pi\tau_v)^2}}. \quad (7)$$

$G(t, 0)$ gives, by Fourier transformation, a doublet in the absorption mode, centered on the chemical shift frequency. By locating peak maxima in the absorption spectrum, one measures the quantity β' and not the spin–spin coupling constant J , as in the absence of chemical exchange. Experimentally one observes a multiplet where the shape and the number of the components depend on the rate of exchange. The multiplet may be partly or completely collapsed by these mechanisms of chemical exchange [20]. A single broad line is often observed.

2.1.2. Case where $(1/\tau_v) > \pi J$

In the situations where $(1/\tau_v) > \pi J$, $(1/\tau_v^2) - (\pi J)^2$ will be positive and the expression of $G(t, \tau)$ of Eq. (4) becomes:

$$G(t, \tau) = g(t) \exp\left(\frac{-\tau}{T_2}\right) \left[\text{ch}(\pi\beta(t + \tau)) + \frac{1}{\beta\tau_v} \text{sh}(\pi\beta(t + \tau)) \right]. \quad (8)$$

The Fourier transformation of $G(t, 0)$ (Eq. (8)) gives a single wide line, which corresponds to a combination of the lines given by the terms $\exp(\pi\beta t)$ and $\exp(-\pi\beta t)$ in the hyperbolic cosine and sine.

3. Application of the described data processing

We now can apply the data processing described in [17]. In this latter the authors describe a data processing

for extracting small scalar coupling constants when these are around the linewidth. A set of conventional spin echo experiment is recorded for various values of the delay τ of the echo. Recorded data are processed in the time domain, to obtain a post-treated spectrum where couplings are apparently multiplied by $n + 1$, n is positive. The analysis of signals $G(t, \tau)$ is based on the evaluation of the following integral:

$$G'(t) = \int_{-\infty}^{\infty} \int_0^T G(t, \tau) \exp(i\pi v(\tau - nt)) d\tau dv, \quad (9)$$

where n is a real positive, T is the maximum value of τ , and v is a trial coupling. One assumes that $G(t, \tau) = 0$ for $t > T$.

Since the integral $\int_{-\infty}^{\infty} \exp(i\pi v(\tau - nt)) dv$ is the Dirac Delta function $\delta(\tau - nt)$, Eq. (9) is equivalent to:

$$G'(t) = \int_0^T G(t, \tau) \delta(\tau - nt) d\tau \quad (10)$$

which gives, using the shifting property of the Dirac Delta function:

$$G'(t, \tau) = G(t, nt). \quad (11)$$

The idea is then to multiply the signal by a Dirac comb with respect to the second variable (τ). This multiplication results in a shifting of the frequency J of a component, by a quantity nJ . This component appears then at the frequency $(n + 1)J$ in the resulting spectrum. Thus one obtains a spectrum where all the scalar couplings are apparently multiplied by $n + 1$.

The effect of the shifting introduced by the Dirac comb can be interpreted by analyzing the 2D spectrum, obtained by performing the Fourier transformation of $G(t, \tau)$, with respect to t and τ , as in J -resolved spectroscopy [25,26]. Because of this shifting, one obtains the frequencies $(n + 1)J$ on the F_1 axis (instead of J without shifting), and $(\omega_s/2\pi) + (n + 1)J$ on the F_2 axis (instead of $(\omega_s/2\pi) + J$). The projection of the 2D spectrum on the F_2 axis gives the conventional proton spectrum where the apparent spin–spin splitting is $(n + 1)J$.

We will calculate the sum of Eq. (9), in the two situations examined previously, according to the rate of the chemical exchange $1/\tau_v$.

3.1. Intermediate chemical exchange

3.1.1. Case where $(1/\tau_v) < \pi J$

The calculation of $G'(t)$ of Eq. (9) is performed by taking $G(t, \tau)$ of Eq. (6). The evaluation of $G'(t)$ is again quite similar to that developed in [17]. The constant J is replaced here by the parameter β' . One obtains easily after calculation:

$$G'(t) = M^0 \exp(i\omega_s t) \exp\left(-\left(\frac{1}{\tau_v} + \frac{n+1}{T_2}\right)t\right) \times \cos(\pi\beta'(n+1)t). \quad (12)$$

The apparent spin–spin splitting is then increased, since it multiplied by the factor $n + 1$, and it is given by $J_{\text{app}} = (n + 1)\beta'$. In spite of the widening of the line by the chemical exchange, this increase reveals the fine structure of the multiplet. The measure of the real coupling constant J requires then the value of the mean lifetime τ_v (since $\beta' = (J^2 - (1/(\pi\tau_v)^2))^{1/2}$). This parameter can be deduced from measurements of the linewidths in the obtained multiplet. Indeed, in the triplet corresponding to the proton spectrum, the linewidth at half-height R_n , is given by (from Eq. (12)):

$$R_n = \frac{1}{\pi} \left(\frac{1}{\tau_v} + \frac{n+1}{T_2} \right). \quad (13)$$

Then R_n is measuring for various values of n . The plot of R_n as function of n is a line whose slope S and the ordinate at the origin R_0 , are given by:

$$S = \frac{1}{\pi T_2}, \quad (14)$$

$$R_0 = \frac{1}{\pi} \left(\frac{1}{\tau_v} + \frac{1}{T_2} \right). \quad (15)$$

Then by setting $T_2 = 1/(\pi S)$ in Eq. (15), one obtains:

$$\tau_v = \frac{1}{\pi(R_0 - S)}. \quad (16)$$

Then one can deduce the value of the coupling constant J , using the expression for β' (Eq. (7)).

Notice that the modified processing causes an increase of the linewidth, because of the term $\exp(-nt/T_2)$ (Eq. (12)). This last can be compensated by multiplying the signal by $\exp(\alpha nt)$, where $\alpha \approx (1/T_2)_{\text{average}}$.

3.1.2. Case where $(1/\tau_v) > \pi J$

In situation where $(1/\tau_v) > \pi J$, one finds easily by using the same calculation as in [17], that $G'(t)$ (Eq. (9)) is given by:

$$G'(t) = 2M^0 \exp(i\omega_s t) \exp\left(-\left(\frac{1}{\tau_v} + \frac{1+n}{T_2}\right)t\right) \times \left[\text{ch}(\pi\beta(n+1)t) + \frac{1}{\beta\pi\tau_v} \text{sh}(\pi\beta(n+1)t) \right]. \quad (17)$$

Fourier transformation of $G'(t)$ gives a single line, which becomes increasingly broad when n increases. One can perform a deconvolution of the signal $G'(t)$ to obtain the two component lines which correspond respectively to the terms $\exp(\pi\beta(n+1)t)$ and $\exp(-\pi\beta(n+1)t)$ in the hyperbolic cosine and sine (Eq. (17)). One easily finds that the linewidths at half-height of these two Lorentzian functions, obtained after deconvolution, are given respectively by:

$$R_1 = \frac{1}{\pi} \left(\frac{1}{\tau_v} + (n+1) \left(\pi\beta + \frac{1}{T_2} \right) \right), \quad (18)$$

$$R_2 = \frac{1}{\pi} \left(\frac{1}{\tau_v} + (n + 1) \left(\frac{1}{T_2} - \pi\beta \right) \right). \quad (19)$$

Hence we can get the sum and the difference of R_1 and R_2 :

$$R_1 + R_2 = \frac{2}{\pi} \left(\frac{1}{\tau_v} + \frac{n + 1}{T_2} \right), \quad (20)$$

$$R_1 - R_2 = 2\beta(n + 1). \quad (21)$$

Thus by measuring R_1 and R_2 for various values of n , one can deduce the mean lifetime τ_v using the expression of $R_1 + R_2$. The difference $R_1 - R_2$ gives the parameter β . Then the coupling constant J is deduced from the expression for β , since $\beta = ((1/(\pi\tau_v)^2) - J^2)^{1/2}$ (Eq. (2)).

4. Modification of the described data processing

In this section we modify the technique described by Mahi and Duplan [17] so that its application does not require the recording of a set of spin echoes experiments but only a simple one pulse experiment. The series of signals necessary to implement the method will be generated by processing experimental data (FID), recorded during the “one-pulse” experiment.

So a simple “one-pulse” experiment is recorded with TD points. The expression for the FID will be given by Eq. (1). Starting from the recorded FID (Fig. 1), one takes a set of N ($N < TD$) points which are saved in a file, and will be the first signal of the generated series. The other signals are generated by saving the same number of points (N) in different files and by carrying out a shift by p points each time, such as $\tau = p dt$ (Fig. 1), p is a positive integer and dt is the sampling period of the FID.

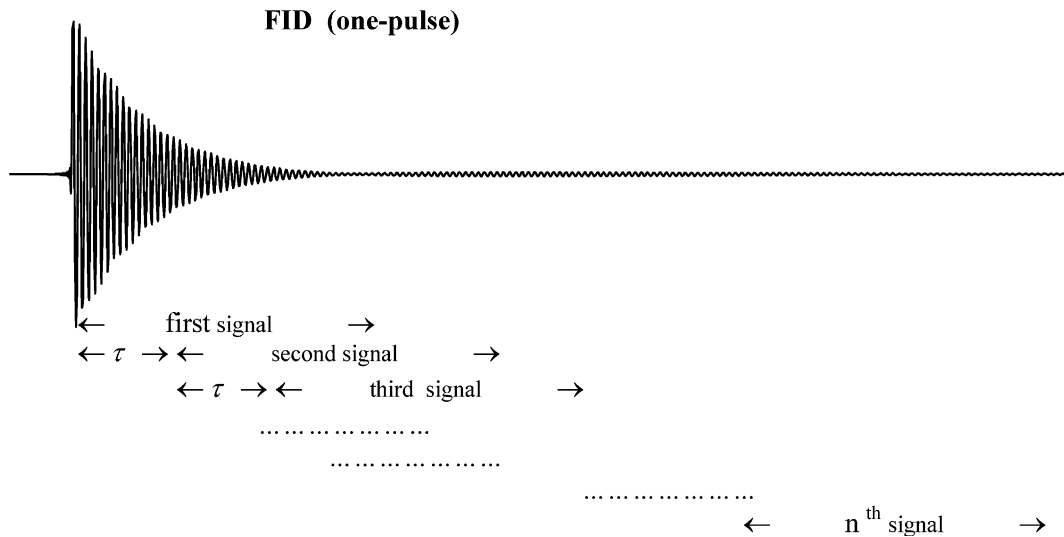


Fig. 1. A one-pulse experiment is recorded with TD points, and a set of signals is generated by saving N ($N < TD$) points of the original FID in various files. The first point in two successive signals is shifted by p points each time. The integer p is chosen such as $\tau = p dt$ (dt is the sampling period of the FID).

Then each generated signal will have the following expression:

$$G(t, \tau) = \frac{M^0 \exp(-\frac{t}{T_2} - \frac{\tau}{T_2})}{2\pi\beta\tau_v} \times \exp(i\omega_\delta(t + \tau))[(1 + \beta\pi\tau_v) \times \exp(\beta\pi\tau_v(\tau + t)) + (\beta\pi\tau_v - 1) \times \exp(-\beta\pi\tau_v(\tau + t))] \quad (22)$$

β has the same definition as in Eq. (4) ($\beta = ((1/(\pi\tau_v)^2) - J^2)^{1/2}$).

The phase of the chemical shift at $t = 0$ (in Eq. (22)) is $\phi_0 = i\omega_\delta\tau$. To remove the latter, and to obtain a signal similar to that obtained in conventional spin echo experiment, one multiplies each signal by $\exp(-i\omega_\delta\tau)$, for the corresponding value of τ . The aim of this multiplication is also to keep the chemical shift at its usual frequency in the resulting spectrum. $G(t, \tau)$ of Eq. (22) becomes then:

$$G(t, \tau) = \frac{g(t)}{2\pi\beta\tau_v} [(1 + \beta\pi\tau_v) \exp((\tau + t)\beta\pi\tau_v) + (\beta\pi\tau_v - 1) \exp(-(\tau + t)\beta\pi\tau_v)]. \quad (23)$$

The signals $G(t, \tau)$ (Eq. (23)) generated by this new process, will thus have the same expression as that given by the Eq. (4). They will be used in the data processing described in [17], in the various cases of the chemical exchange discussed above.

5. Simulations

5.1. Case where $(1/\tau_v) < \pi J$

A FID is simulated with 64k points as previously (using Eq. (1)). So the FID is simulated with 64k points

and a sampling period dt of $410 \mu\text{s}$. $J = 0.45 \text{ Hz}$, $\tau_v = 25 \text{ s}$ and $T_2 = 3.3 \text{ s}$, $J = 0.5 \text{ Hz}$. A reconstitution program generates a set of 90 signals using the simulated FID, and saves them in various files. Each signal contains 8k points. The beginning of the first signal coincides with that of the FID (Fig. 1). The points of the second signal are taken starting from the 200th point of the FID (here the parameter p is set to 200). The points of the third signal start at the 400th point of the FID and so on. The parameter τ is then $\tau = pdt = 0.082 \text{ s}$. The maximum value of τ is $T = 7.38 \text{ s}$. Then the phase at $t = 0$ of the chemical shift is suppressed in each generated signal. Signals are then given by Eq. (6). Finally an integration program uses the series of generated signals to evaluate the sum of Eq. (9), as described in [17].

The simple spectrum is shown in Fig. 2a. The resolution enhancement by an apodization function does not allow one to visualize the lines of the triplet. Then the generated signals are processed by setting $n = 3$ (Fig. 2b). One measures on the spectrum $J_{\text{appt}} = (n + 1)\beta'$ which equal to 1.78 Hz . The linewidth at half-height for the line at 4.75 ppm is measured for various values of the parameter n . And, using the method explained in paragraph III, we found the mean lifetime τ_v (calculated using Eq. (16)), to be 24.98 s . Then from the expression of β' one deduces the value of the constant J . We found $J = 0.45 \text{ Hz}$. This value is quite identical to that taken in the simulation ($J = 0.45 \text{ Hz}$).

5.2. Notice

For clarity and to obtain a simulated spectrum closely similar to the experimental one, we added a term in the expression of the simulated signal of Eq. (6), to represent the central component (for which the proton is coupled to a deuterium nucleus of spin $I_z = 0$) of the triplet.

5.2.1. Case where $1/\tau_v > \pi J$

The series of signals is generated as explained in the previous case. Their expression is then given by Eq. (8). One observes a single line which is a combination of two lines given by the terms $\exp(\pi\beta t)$ and $\exp(-\pi\beta t)$. The lines are also particularly broad because of the factor $\exp(-t/\tau_v)$. Generated signals are processed as previously. We obtain a line which becomes increasingly fine when n increases, as predicted by the theory. By deconvoluting the post-treatment signal, one obtains two lines. The measure of their linewidths at half-height allows one to calculate (using Eq. (20) and Eq. (21)) τ_v and then the coupling constant J . The value of the coupling measured by the data processing agrees well with that taken in the simulation of the FID.

6. Measurement of J in a solution of deuterium oxide

Let us consider now, a more delicate and more interesting case, that of D_2O in solution, where the cou-

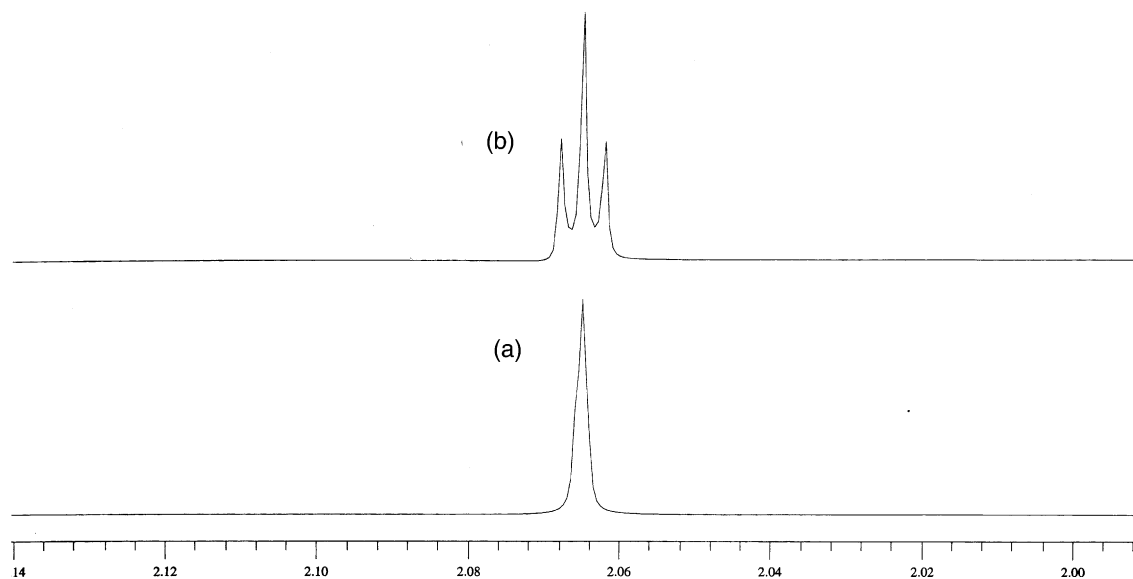


Fig. 2. Spectra simulated in the case where $(1/\tau_v) < \pi J$. A simple FID 64k points is simulated using the expression $G(t, \tau)$ of Eq. (6). The different parameters of simulation are $J = 0.45 \text{ Hz}$, $\tau_v = 25 \text{ s}$, $T_2 = 3.3 \text{ s}$. Then, a series of 90 signals is generated for 90 values of τ . Each one of the latter contains 8k points. (a) Conventional spectrum. (b) spectrum obtained by processing the set of generated signals by using the integration program, and by taking $n = 3$. The coupling is then apparently multiplied by $(n + 1)$. By locating peak maxima, one measures an apparent coupling of 1.79 Hz . One measures the linewidth at half-height of the line at 4.75 ppm for various values of n (see text) and calculates the mean lifetime τ_v and consequently the coupling constant J . It found to be $J = 0.45 \text{ Hz}$, a value which is quite identical to the value taken in the simulation.

pling constant J is around the linewidth at half-height, and only one broad line is ever observed. A one-pulse experiment is recorded with a solution of 80% of D_2O and 20% of H_2O . The signal is recorded for 1.86 s with 64k points, and a sampling period of 60 μs . Eight scans are averaged. As usual one observes a single line broadened by the effects of the chemical exchange phenomenon (Fig. 3a).

The FID thus recorded is used by the reconstitution program to generate a series of 90 signals. Each signal contains 8k points. The parameter τ is incremented by 0.0454 s (here the parameter p is set to 200). Each signal is multiplied by $\exp(-i\omega_\delta\tau)$ for its respective value of τ . ω_δ is measured in the spectrum.

The signals are then processed by the integration program for $n=3$. This multiplies apparently the splittings by 4 (Fig. 3b), and then gives a well defined spectrum; the line corresponding to the protons of H_2O at 4.80 ppm, and the triplet given by the proton of HOD, centered at 4.77 ppm. The apparent coupling constant, measured directly in the spectrum, is $J_{\text{app}} = 6.10$ Hz. This apparent splitting is also given theoretically by the factor $J_{\text{app}} = (n+1)\beta'$ (Eq. (12)), since this case corresponds to the situation where $(1/\tau_v) < \pi J$. To deduce the value of the coupling J from that of β' , one needs τ_v . The linewidth at half-height of the line at 4.75 ppm is measured for different values of n , and one plots R_n according to n . The slope (S) and the ordinate at the origin (R_0) are measured. Then by using Eq. (16) one

finds that $\tau_v = 0.231$ s, and consequently the constant J equal to $J = 1.54$ Hz. Various measurements of the scalar coupling with this method are realized on simulated spectra and on spectra of molecules which one knows the value of J (acetone-d6, dimethyl sulfoxide-d6, methanol-d4, ...) show that coupling constants are measured with an accuracy of ± 0.01 Hz.

We also measured this coupling by using a set of conventional spin echo, as described in [17], to compare the results given by the two implementations. We obtained the same value for J (1.54 Hz).

To study the effect of the noise to the measures of J in this modified treatment, we introduce more and more noise in the FID of origin, and we calculated the constant J each time. So the noise extracted from the FID is added to this latter, and signals are generated, as explained above. The coupling J measured with the modified processing is of $J = 1.54$ Hz. One repeats thus the same operation, by injecting more noise and measuring the constant J . The measured value remains the same (1.54 Hz) until the introduced noise is 20 times that of the original FID. Beyond this limit the lines in the resulting spectrum become rather broad, and one notes a variation between 2 and 8% of the value measured initially.

We think that the modified processing improves considerably the initial implementation [17] for two main reasons. First, the use of spin echoes requires a long duration of recording of experiments, whereas the

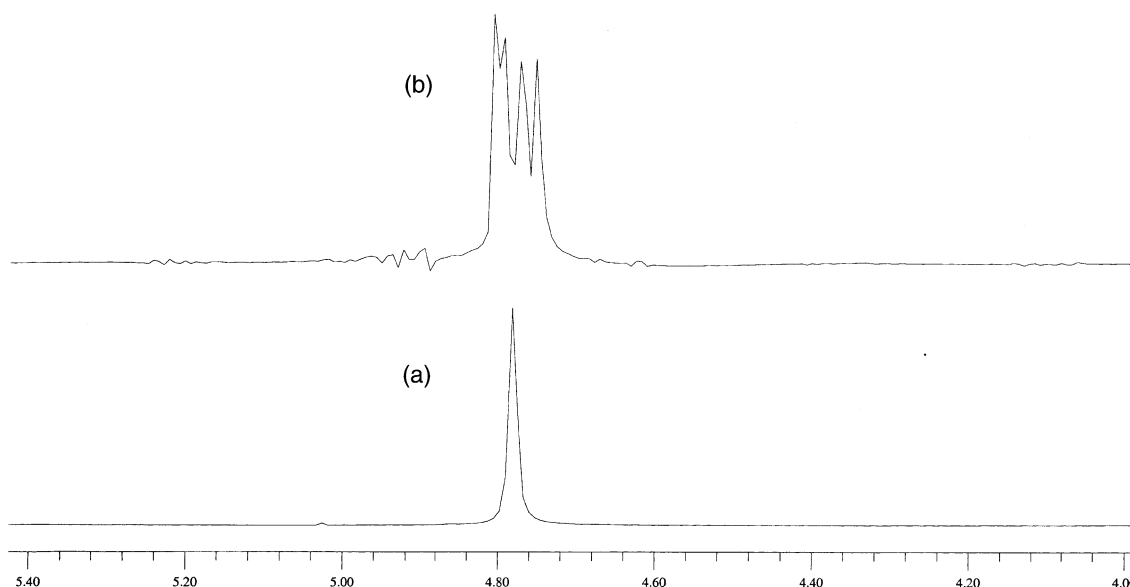


Fig. 3. Three hundred megahertz proton spectra of a solution of 80% of D_2O and 20% of H_2O , at 298 K. (a) Conventional spectrum recorded with 64k points, a sampling period of 60 μs . The spectrum is 8 averages and the acquisition time is of 3.93 s. (b) Post-treated spectrum obtained by processing 90 signals, generated starting from the FID and containing 8k points each one. The parameter p is equal to 200 and then τ is incremented by 0.012 s. The processing is performed by taking $n=3$. The spectrum shows the line corresponding to protons of H_2O at 4.80 ppm, and the triplet of HOD centered at 4.77 ppm. The apparent coupling constant measured in the spectrum is $J_{\text{app}} = 6.10$ Hz. By using the linewidth at half-height of the line at 4.75 ppm (see text) one finds that the real coupling constant is $J = 1.54 \pm 0.01$ Hz.

new processing needs a simple ‘one-pulse’ experiment. In addition the realization of an heteronuclear spin echo experiment requires the application of an inversion π -pulse to the two nuclei. The π -pulse applied to the proton and that applied to the deuterium must be simultaneous and must have the same length. In practice, this is not always easy to carry out.

The new implementation also makes it possible to avoid the effects of the imperfections of the π -pulses or small fluctuations of the temperature or the magnetic field, during the spin echoes experiments.

To improve the precision of the measure of the coupling J by the new implementation, it is however recommended, particularly when the signal-to-noise ratio is very weak, to record the FID with several scans and to choose $n \geq 2$ in the processing. Several measures of J for various values of n , must also be realized.

7. Conclusion

The new implementation of the described data processing proposed, requires a simple “one-pulse” experiment, and allows the observation and the measurement of very small coupling constants hidden in the linewidth, because of the chemical exchange phenomenon. The method allows to visualize, for the first time, the peak of the water and the triplet corresponding to the proton of HOD in the proton spectrum of the deuteriated water. A first experimental measure of the coupling constant J_{HD} is also realized. As in the original data processing, the new implementation causes an increase of the linewidth, but this can be perfectly eliminated by using an apodization function. The results obtained show that the modified method makes it possible to measure coupling constant J with a satisfactory precision. The FID must be recorded with several scans when the signal-to-noise ratio is very weak. The use of shifted extracts of the original FID is faster and easy to implement, and can be an alternative to the use of spin echoes experiments.

The described data processing can be used also to extract the coupling constants in some deuteriated solvents, where the knowledge of these constants can be useful to study the interactions between the solvent and complex molecules.

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