International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
IJCS 2018; 6(6): 537-540

Received: 13-09-2018
Accepted: 14-10-2018

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Investigaion of FID signals obtained by inversion recovery technique with and without albumin in H_2O-D_2O solutions

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Abstract
FID signals which are obtained by Inversion Recovery technique with and without albumin in H_2O-D_2O solutions were investigated. Measurements were carried out using a 400 MHz Avance Bruker ^{1}H-NMR spectrometer. FID signals were obtained from H_2O-D_2O solutions prepared in specific proportions. Additionally, the effects of pulse parameters on the signals were observed by changing the pulse repetition times. As a result, the Radiation Damping is increased with the increase of H_2O-D_2O amount. The Radiation Damping is reduced with the addition of albumin. The null point was not observed accurately in the present of Radiation Damping. In addition, to obtain a good signal the pulse delay times should be selected at appropriate intervals and, TR should be taken to $5T_1$.

Keywords: NMR, IR, FID, albumin, H_2O-D_2O

1. Introduction
The spin-lattice relaxation time (T_1) depicts the recovery of longitudinal magnetization after a perturbation. Knowledge of T_1 relaxation is required for the studies of the chemical exchange and the dynamics of spin systems. It is also demanded for the optimization of timings and nutation angle for data acquisition [1].
For many years, spin-lattice relaxation has always been measured by inversion-recovery (IR), saturation-recovery (SR), or related methods. However, it is known that the resolution in T_1 is limited in such measurements. Better signal-to-noise ratio (SNR) may improve the discrimination between T_1 values with the downside of longer acquisition times. The primary reason for such lack of T_1 resolution is that the magnetic resonance (MR) signal dependence on the relevant recovery time (recycle delay or inversion time) is smooth, not sharp [2].
In most NMR experimental methods, protons are detected in the acquisition dimension to take advantage of the inherent high sensitivity of these spins. The free induction decay (FID) collected at the end of each experiment is a mixture of signals from the protons in the molecule of interest and in the solvent molecules. The concentration of protons in the solvent can be thousands of times higher than those in the solute. This in turn affects the NMR spectra of the solute significantly. Standard NMR methods overlook the possibility that individual spins can influence the bulk nuclear magnetization of the whole sample, predominantly those of the water spins. Detection of the water resonances through a tuned circuit introduces an effect commonly known as radiation damping (RD), which is a manifestation of the combined spin system and the electronic resonance circuit assembly.
Although RD is an intrinsic physical phenomenon in all NMR experiments, the magnitude of the damping field depends on the QC (quality factor) value, the filling factor of the probe, and the bulk magnetic moment of the sample in correlation with the static field strength. RD is thus normally observed in experiments with high proton or fluorine concentrations at high fields [3-9].
The aim of this study is to investigate the radiation damping, repetition time (TR) and null point which affect FID signals obtained by IR technique with and without albumin in H_2O-D_2O solutions.

2. Material and Method
D_2O was purchased from Merck. 10% of H_2O and 90% of D_2O were used in all our measurements. 600 µL of each H_2O-D_2O solutions, prepared in the following ratios, were transferred into 5 mm NMR tubes and Free Induction Decay (FID) signals of each

measurement were obtained. Measurements were done by Avance Bruker 400 MHz ^{1}H-NMR spectrometer. In addition, pulse repetition times and solution ratios for each measurement were changed and thus the effects on the signal were observed.

3. Experimental Results

In this study, 25 different experiments were performed by changing the amount of albumin, inversion recovery delays and the amount of H_2O-D_2O solutions. 9 experimental results were shared in this article because all data would take a lot of space. The results were evaluated over 25 experiments.

3.1. Three different measurements using only D_2O solution

In the first measurement, only FID signal of D_2O solution was obtained (Fig.1). The repetition time (TR) was 5 s. The experiment was performed with 100 different inversion recovery delays ranging from 2 to 200 ms in increments of 2.

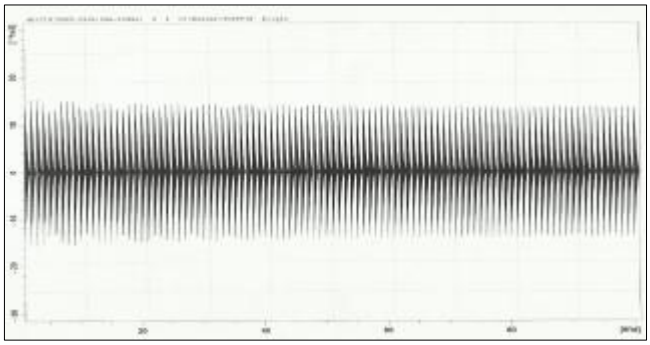

Fig 1: FID spectrum of D_2O solution.

The FID signal in Figure 1 shows that there is a Radiation Damping (RD). This is because the delay times are too short. In other words, the range of delays is insufficient. The D_2O also contains many protons which cause high signal strength.
In the second measurement, 0.2 g albumin was added to D_2O solution. FID signal was obtained (Fig.2). The repetition time (TR) was 5 s. The experiment was performed with 100 different inversion recovery delays ranging from 20 to 2000 ms in increments of 20.

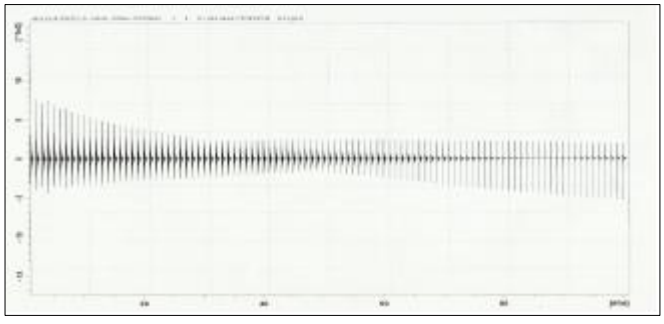

Fig 2: FID Spectrum of D_2O solution with 0.2 g albumin.

The FID signal in Figure 2 shows a normal spectrum appearance because the amount of albumin decreases the radiation dumping.
In the third measurement, the experiment was repeated by changing the inversion recovery delays ranging from 200 to 20000 ms in increments of 200 (Fig. 3).

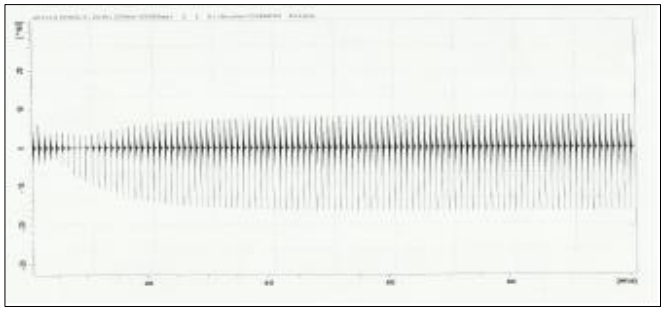

Fig 3: FID Spectrum of D_2O solution with 0.2 g albumin.

In Figure 3, the null point is immediately decayed. This shows that the inversion recovery delays range is too small and must be rearranged.

3.2. Two different measurements using 0.05 ml H_2O-D_2O solution

In the first measurement, 0.2 g albumin was added to H_2O-D_2O solution. FID signal was obtained (Fig.4). The repetition time (TR) was 5 s. The experiment was performed with 100 different inversion recovery delays ranging from 20 to 2000 ms in increments of 20.

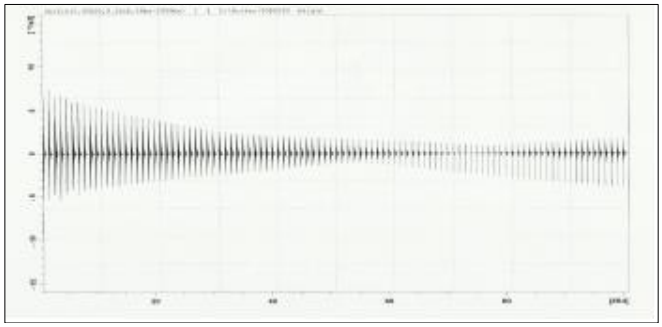

Fig 4: FID Spectrum of 0.05 ml H_2O-D_2O solution with 0.2 g albumin.

The spectrum in Figure 4 is similar to the spectrum in Figure 2. This shows that water protons are dominant although 0.2 g albumin was added.
In the second measurement, only the delay list (150 to 15000 ms) was changed by keeping all other values the same (Fig. 5).

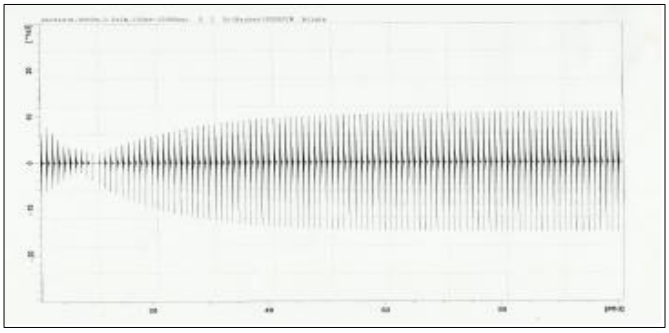

Fig 5: FID Spectrum of 0.05 ml H_2O-D_2O solution with 0.2 g albumin

The spectrum in Figure 5 is similar to the spectrum in Figure 3. But RD in Figure 5 is more than the RD in Figure 3. This is because we used H_2O which has many protons.

3.3. Two different measurements using 0.1 ml H_2O-D_2O solution

In the first measurement, 0.2 g albumin was added to 0.1 ml H_2O-D_2O solution. FID signal was obtained (Fig.6). The repetition time (TR) was 5 s. The experiment was performed with 100 different inversion recovery delays ranging from 20 to 2000 ms in increments of 20.

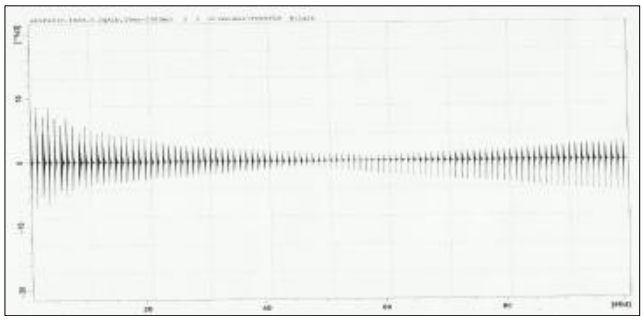

Fig 6: FID Spectrum of 0.1 ml H_2O-D_2O solution with 0.2 g albumin.

In the second measurement, only the delay list (100 to 10000 ms) was changed (Fig. 7).

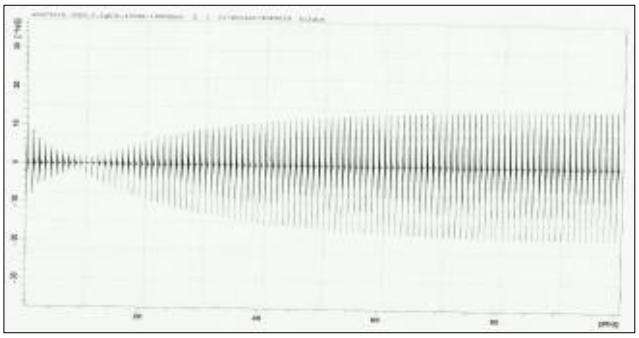

Fig 7: FID Spectrum of 0.1 ml H_2O-D_2O solution with 0.2 g albumin.

The spectrum in Figure 6 and 7 is similar to the spectrum in Figure 4 and 5, respectively. The effect of albumin was seen as a signal decrease in figure 6.

3.4. Two different measurements using 0.3 ml H_2O-D_2O solution

In the first measurement, 0.2 g albumin was added to 0.3 ml H_2O-D_2O solution. FID signal was obtained (Fig.8). The repetition time (TR) was 5 s. The experiment was performed with 100 different inversion recovery delays ranging from 20 to 2000 ms in increments of 20.

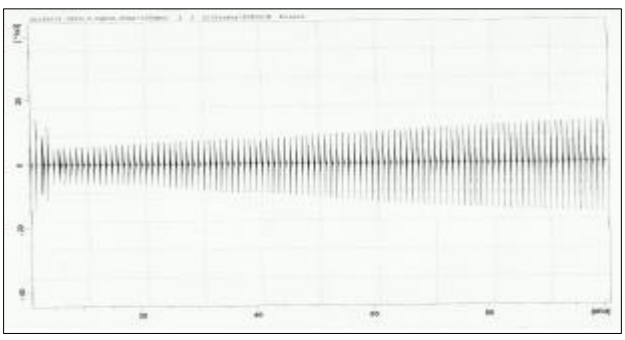

Fig 8: FID Spectrum of 0.3 ml H_2O-D_2O solution with 0.2 g albumin.

The null point was not observed in Figure 8. Inversion recovery delays must be expanded to the left side.

In the second measurement, only the delay list (100 to 10000 ms) was changed (Fig. 9).

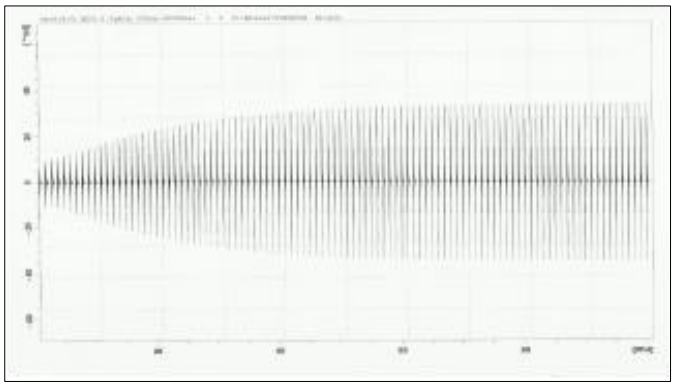

Fig 9: FID Spectrum of 0.3 ml H_2O-D_2O solution with 0.2 g albumin.

Figure 9 shows that radiation damping in the spectrum is too much. This is because there are many water protons. Besides, inversion recovery delays are insufficient.

4. Conclusion

The precision of T_1 measurement depends on many factors, including the pulse sequence, the signal-to-noise ratio, the number and value of the delay times, and TR. The effect on precision of changing one parameter depends on what else changes. Radiation damping is commonly assumed to affect signals only in a narrow frequency range close to the solvent resonance. In addition to the complications it poses in selective excitation of solvents and solvent signal suppression [10], Sobol *et al*. [11] have demonstrated how RD can influence signals with frequencies differing by several kHz from the solvent signal. During multi-pulse NMR experiments, the magnetic fields caused by the RD related field can become time dependent enabling the system to be nonlinear and influence the resonance frequency positions of all the nuclei in the sample.

One topic that has received rather less attention is the effect of RD when a probe is not at exact electrical resonance [12]. Traditionally, detuning of the probe has been used as a method of reducing the effects of RD, in a trade-off against signal-to-noise ratio. Detuning reduces the line broadening effects of RD both by reducing the induced current, and by reducing the angle between the precessing magnetization, and the secondary radiofrequency field generated by the coil. Even slight detuning has been shown to introduce unexpected effects in multiplet patterns [13]. The null point value varies depending on parameters such as T_1 and TR [7].

In our results, large amount of water causes the increase of radiation dumping. Increasing the amount of albumin causes a decrease in radiation dumping. Presence of radiation damping prevents obtaining the null point. If the TR is not selected as $5T_1$, the null point may not be detected exactly and a good signal will not be obtained.

Another implication of our results is that once the longest delay time has been set in IR method, TR should be set just enough longer than the longest delay time to allow data acquisition. Setting TR significantly longer than the longest delay time increases the measurement time without improving accuracy or precision [2, 14, 15].

5. References

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