About the NMR Relaxation times T1 and T2. Procedure to Fill the Reference Cell

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Abstract

In this note we review the effect of the different factors able to affect T1 and T2 values. The choice of the water used for the calibration of the ^{3}He polarized target NMR is explained. The procedure to fill properly the reference cells is detailed. The characteristics of the water used to fill are provided. A first goal of this study was to simplify the NMR water calibration analysis by equalizing the two telaxation times T1 and T2. In particular by using ^{17}O free water. However data extrapoled from ref [4] show that T1=T2 cannot be reach anyway and is not worth to used free ^{17}O water. We used de-oxygenated water to be able to compare our T1 measurement to the world data.

Contents

1 The longitudinal (*T1*) and transverse (*T2*) relaxation times

The two relaxation times *T1* and *T2* are inputs for the Bloch equations [1]. These are used to fit the NMR water signal more accurately than with a Lorentzian shape (see section 2) in order to provide a NMR signal calibration.

2 Expected values

We should have *T1*=*T2* for a correlation time τ_c (see definition in [1] p 271) shorter than the Larmor period of the proton spin ([1] p 324, [2] page 126). Nevertheless *T2* could be shorter than *T1* ([1] p326, [2] p 126, [3],[4]) because of the scalar coupling between the proton spin and the ^{17}O spin (This coupling splits the proton resonnance. The water signal is no more made of a single Lorentzian line but of two (the second line, although very weak, induces a broading of the signal).

[4] p 379 gives $\frac{1}{T2} - \frac{1}{T1} = 0.125\ \mathrm{s}^{-1}$ but this does not take into account the rf field influence on *T2* [4] p377, [2] p 127.

$\frac{1}{T2} - \frac{1}{T1}$ depends also on the water pH and the rf field magnitude. The previous 0.125 s^{-1} difference, reducing the signal magnitude by 1.5% [2], takes into account only the ^{17}O splitting effect.

3 Determinations of *T1* and *T2*

3.1 Longitudinal relaxation time *T1*

3.1.1 Indirect determinations

[2] p126 averages the magnitude of the up and down signals (the average being very *T1*-dependant[1]) and compares with numerical integrations of the Bloch equations. The result for E154 was $T1 = 2.4 \pm 0.3$ s at 20 ± 2^oc. The temperature dependance of *T1* is broadly 0.4 s each 5^o.

One did not know the amount of O_2 solved in the E154 water cell. [2] did not compare the result with the world available value of *T1* (2.95 s at 20^o) because of his dependance with O_2 solved in the water. For the experiment E94-010 we need to use de-oxygenated water to allow such a comparison.

(for a similar method to get *T1*: see also [5]. The result for E142 was $T1 = 1.8 \pm 0.4$s.)

3.1.2 Direct measurements

[2] (p 126) did also some *T1* measurements using saturation and recovery methods.

[1] the average is very *T1*-dependant but not very $\frac{1}{T2} - \frac{1}{T1}$-dependant [2] p129, [6] p 84.

3.2 Transverse relaxation time *T2*

[2] (p127) measured *T2 via* the spin echo method ([1] p58). [4] and [7] did their measurements *via* the "adiabatic half passage" method.

The *T1* and *T2* measurements done at Princeton in [2] show that ^{17}O is the main responsible for the difference between the two relaxation times (the effects due to inpurities in small amount (ions, [4] p 380) and deuterium [4] p 376 are small).

4 Effect of the rf field

Taking into account the rf field effect, the equation (2) p377 of [4] reduces the difference $\frac{1}{T2} - \frac{1}{T1}$ to : $\frac{1}{T2} - \frac{1}{T1} = 0.033\ \mathrm{s}^{-1}$ ([2], [6]) . This is the definitive result used in E154 for the polarimetry calibration.

This difference has negligible effect on the lorentzian shape [2] p 127 but reduces by 0.4 % the water signal amplitude.

5 Sensitivity of the difference $\frac{1}{T2} - \frac{1}{T1}$ to the pH and the ^{17}O amount

The previous paragrapher shows that the difference is quiet sensitive to the rf field magnitude. The other quantities affecting this difference are described below.

5.1 pH

Around pH=7 a change of 10 % on the pH induces a change of 0.01 s^{-1}. That is a $\frac{1}{T2} - \frac{1}{T1}$ change of 8 % [4].

Note. This change depends of the ^{17}O amount of the water. For exemple it reach 60 % for a 0.20 % ^{17}O amount.

5.2 ^{17}O amount.

A change of 10 % of the ^{17}O induces a change of 0.015 s^{-1} that is a change of 10 % on the difference $\frac{1}{T2} - \frac{1}{T1}$ (from a curve extrapolating the data of [4]. The curve slope makes this dependance broadly linear around 0.037 % of ^{17}O).

6 Procedure used to filled and seal the water cell

We chose to use de-oxygenited and de-ionized water with the natural amount of ^{17}O. The inpurities on the glass cellS have the more dramatic effects thus we took care of a good cleaning of the cellS. As the cellS were just made a simple cleaning was sufficient: we fill them three times with the de-oxygenited and de-ionized water used for cleaning in the accelerator polarized source. Then the cells are cleaned three times with acetone and rinsed three times with pure water. The cells are then filled with the same water. Its resistivity was 17.93 ± 2 MΩ/cm for the 25 cm cell and 18.06 MΩ/cm for the 40 cm cell. The O_2 and air content is not know but is negligible since we did not see the water bubbled under vaccum. The cells should have been sealed under vaccum to remove the remaining air but the short filling pipe of the references cell did not allow such a process.

All the expertise and materials were provided by Larry Phillips.

7 Conclusions

- We need de-ionized water.
- To allow a comparison with available data we need to use de-oxygenated water (or at least to know the amount of solved O_2). The effect of using de-oxygenated water is to decrease the water signal magnitude (see fig 4.17 p 87 of [6]), however in a negligeable amount.
- About ^{17}O : We know the correction to give to *T2* [4] and it seems to be reliable (following the direct measurement of the relaxation times done at Princeton). The presence of ^{17}O did not decrease much the signal (0.4%). It has no impact on the average up and down signal and on the reasonnace line shape. The purpose of using de-oxygenated, de-ionized, ^{17}O free, pure water was to simplify the NMR water calibration analysis in equalizing T1 and T2. The extrapolation of the reference [4] data shows that even without ^{17}O we could not reach *T1*=*T2* anyway. A change of 10 % in the ^{17}0 amount makes a change of 10 % on the difference $\frac{1}{T2} - \frac{1}{T1}$. We removed the solved gas in the water by bubbling it under low pressure and there is no reason to change the ^{17}O amount dramatically by this method. Thus we are able to do the ^{17}O correction in taking the natural amount of the isotope. However if we choose to use ^{17}O free water, one should be aware that the ^{17}O tends to come back to is natural amount of 0.037 % due to exchange with the water present in the air. This should not occur ewith full filled water cells.
- The impact of the incertainty on $\frac{1}{T2} - \frac{1}{T1}$ is not known since the errors in [2] and [6] were estimated in comparing, first: the deviation between the measurement and the numerical integration results; second: the two methods used to analyse the water signal [2] p130. However it seems the incertainty comes mainly from the relaxation time sensitivity to the environement (we should need precise measurements of *T1* or *T2*).
- De-ionized and de-oxygenated water is available at Jefferson Lab. It will also provide cell cleaning, filling and sealing (see Larry Phillips, Phillips@cebaf.gov).

- Water without ^{17}O should be available at Dajak Laboratories and Isomet Corporation [4] p379.

References

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