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Relaxation
Can T_2 Be Longer Than T_1?

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The basic equations describing the decay of the magnetization vector in the transverse plane and its growth along the longitudinal axis, after a pulse, are briefly examined for very simple systems that obey the extreme narrowing condition, and relax in the absence of radiation damping. It is shown that in these cases, the vector does not simply tip backwards with a constant magnitude, retracing the path it followed during the pulse. It is mathematically proven that if T_2 is equal to or less than twice T_1, then immediately after a pulse, the vector first shrinks and then grows back to its initial magnitude while it tips back toward the longitudinal axis, instead of simply retracing its path. It is also shown that if T_2 is greater than this threshold value, then at some point during the relaxation, the magnitude of the resultant will exceed its starting value, a situation apparently not consistent with our present understanding of the laws of physics.

INTRODUCTION

It is well known that after a pulse, the excited nuclei relax back to the lower energy level to re-establish the Boltzmann distribution. There are many books and articles that describe some of the details of this relaxation; some of the classics are by Abragam (*1*) and by Pople, Schneider, and Bernstein (*2*). However, many of the explanations in elementary textbooks are incorrect.

The discussions in this article will be limited to only those cases in which relaxation can be accurately described by the Bloch equations, shown below. For a recent review, see Ref. (*3*).

$$\frac{dM_{xy}}{dt} = -\frac{M_{xy}}{T_2}$$

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}$$

Hence, the following mathematical treatment is applicable only for systems in which both the longitudinal and transverse relaxations can be described by exponentials. For example, one reviewer pointed out that for cases that are outside of the fast-motion regime, and in which $I > 1$, each $|m_I|$ state can have a distinct value of T_1 and T_2. If the line-shape is not Lorentzian, then the decay is non-exponential, and T_2 may have only an operational definition, analogous to the definition of a half-life for a chemical reaction that is not first-order. Similarly, longitudinal relaxation is not always governed by a first-order rate law, in which case T_1 is not always well-defined either. We shall also restrict the discussion to systems in which cross-polarization, polarization transfer, etc., are either non-existent or negligibly small. That is, we will limit our discussions only to systems in which no mechanisms, except simple relaxation, are available for increasing the magnitude of a net magnetization vector. A final limitation is that radiation damping must be insignificant. This will be mentioned again. However, even with all these restrictions imposed, this discussion will be applicable to the vast majority of proton and carbon-13 high-resolution samples being run under standard conditions.

Many elementary textbooks incorrectly describe the relaxation of the net macroscopic magnetization vector (M_0) in the rotating frame, as a simple tipping back to the z axis, from the xy plane. This is depicted in Fig. 1, where M_0 is first shown being tipped away from the z axis onto the xy plane during the pulse (A), and then simply reversing its path during relaxation (B). The right-hand rule (*4*) was used for these figures. In Fig. 1A, M_0 is shown tipping toward the xy plane while maintaining a constant magnitude. The time elapsed during this period is on the order of 10 μsec, and is equal to the pulse-width. This time is very short compared to most relaxation processes in liquids and gases; hence, the vector is correctly depicted as one that is not changing during this time. However, in the typical high-resolution case, the relaxation processes that tip the vector back take much longer and are on the order of seconds; hence, the vector does not maintain a constant magnitude as shown in Fig. 1B. Instead, it changes its length while returning to the z axis. It is my experience that diagrams similar to Fig. 1B appear mostly in the early literature on magnetic resonance imaging (MRI). It is important to note here that radiation damping results in a tilting of the vector magnitization toward its equilibrium position while the length of the vector remains unchanged. That is, Fig. 1B correctly depicts relaxation due exclusively to radiation damping. For further details of this process, see page 73 of Ref. (*1*).

Figure 1. (A) Correct representation of a net magnetization vector being tipped during a pulse. (B) **INCORRECT** representation of a net magnetization vector relaxing in the absence of radiation damping.

THE MISCONCEPTION

Because of the widespread use of illustrations similar to Fig. 1B, many practicing spectroscopists have taken this explanation to be literally correct for the general case. Yet, it defies their common experiences gained from operating a spectrometer. For example, it is not unusual to acquire a carbon-13 FID for 1 to 3 s. For an acquisition time (AQ) of this length, many spectroscopists will allow for relaxation by employing a pulse delay (PD) of 5 to 10 s between the end of the acquisition time and the beginning of the next pulse. This is especially true if a rather large tip angle is used, e.g., 60° to 90°.

An AQ of 1 to 3 s is generally used because the typical T_2^* encountered for carbon-13 signals is such that almost all (95%) of the signal has disappeared after that time. If AQ is extended beyond that period, then only noise will be collected. This means that if Fig. 1B correctly depicts the relaxation of M_0, then in 1 to 3 s, when the component of M_0 in the xy plane (M_{xy}) and the signal have decayed to zero, M_0 is completely realigned along the z axis. If that is true, then why is PD set to 5 to 10 s? What is the relaxation time supposed to accomplish if the relaxation is already complete? Why not pulse immediately after the signal disappears? It is clear that typical operating techniques and the ideas depicted in Fig. 1B represent a paradox.

SIMPLE OBSERVATIONS OF RELAXATION

Scientists first make an observation—then they attempt to explain it. Following this procedure, we observe that after a pulse, the signal gradually disappears, i.e., exponentially decays. This signal can even be heard if the FID frequency is in the audio range, and if it is fed to a loudspeaker instead of to the computer. The sound will be similar to that heard when a high-quality crystal wine glass is gently tapped with a dinner fork. Furthermore, we observe that if we wait long enough ($> 5T_1$), the entire process can be repeated with exactly the same results.

From the first observation, we conclude that M_{xy} is exponentially decaying. From the second observation, we conclude that the component of M_0 along the z axis (M_z) is growing. Both processes are called relaxation, even though one is a decay and the other is a growth.

From the solutions of the Bloch equations, the magnitudes of M_{xy} and M_z at any time are given by Eq. [1] and Eq. [2], where T_2^* and T_1 are the time constants for the decay and growth, respectively.

$$M_{xy} = M_0 \exp(-t/T_2^*) \quad [1]$$

$$M_z = M_0[1 - \exp(-t/T_1)] \quad [2]$$

Plots of the magnitudes of M_{xy} and M_z as a function of time after a 90° pulse, are shown in Fig. 2, where M_0 has been set equal to unity.

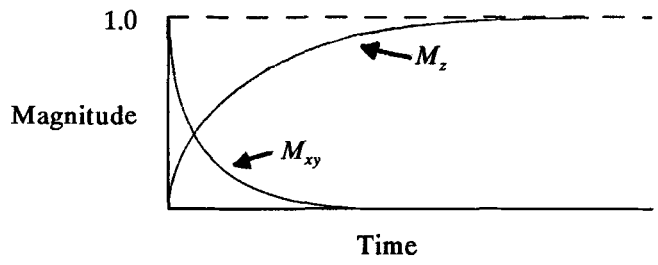

Figure 2. Plots of the magnitudes of the transverse (M_{xy}) and longitudinal (M_z) components of a net magnetization vector, as a function of time during relaxation, for the case where $T_2^* < T_1$.

HOW DOES M_0 RETURN TO THE Z AXIS?

This question can best be answered by calculating the vector sum of M_{xy} and M_z as a function of time for a simple spin system. For a typical case encountered in carbon-13 NMR spectroscopy, where $T_2^* << T_1$, the plot is shown in Fig. 3. The resultants were calculated using 1 and 15 s for T_2^* and T_1, respectively, and for the points in time that would show the resultants at 10° increments from the xy plane. Table 1 lists the times used to construct the figure, as well as the corresponding magnitudes of the resultants. In the figure, the small straight lines at each

10° increment represent a magnitude of 1.0. Note that the tip of the resultant *does not trace a quarter-circle*, which is shown by the dashed line, on its way back to the z axis. Instead, it first shrinks from its maximum length, reaches a minimum, and then grows back to its maximum length after at least $5T_1$.

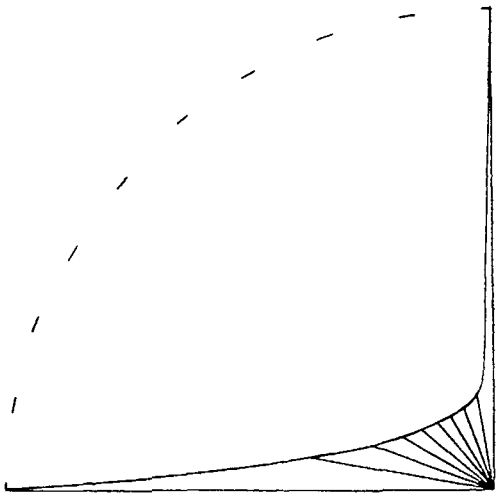

Figure 3. Plot of the resultants of M_{xy} and M_z at specific points in time for the case when T_2 = 1 s and T_1 = 15 s.

TABLE 1
Date Used to Construct Figure 3

Angle	Magnitude	Time (s)
0°	1.000	0.00
10°	.372	1.00
20°	.261	1.40
30°	.213	1.69
40°	.188	1.94
50°	.176	2.18
60°	.174	2.44
70°	.180	2.79
80°	.203	3.35
90°	1.000	∞

Contrary to common belief, the tip of the resultant will not follow the dashed line *even if* T_2^* *equals* T_1! This case is shown in Fig. 4, which was constructed from Table 2. For this case, both time constants were set to 1 s. The tip of the vector traces a *straight line*, not a circle. Equation [1] and Eq. [2] can be used to help explain why it traces a straight line. If T_2^* equals T_1, and if M_0 is set to unity, then at any point in time

$$M_z = 1 - M_{xy} \quad [3]$$

$$y = b + mx \quad [4]$$

Equation [4] is the general form for any straight line, where b and m represent the y intercept and the slope, respectively. When this equation is compared with Eq. [3], it can be seen that the intercept on the z axis should be 1.0, and that the slope should be -1.0.

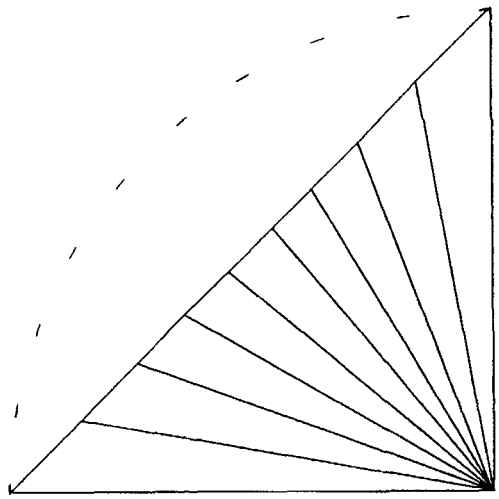

Figure 4. Plot of the resultants of M_{xy} and M_z at specific points in time for the case when T_2 = 1 s and T_1 = 1 s.

TABLE 2
Data Used to Construct Figure 4

Angle	Magnitude	Time (s)
0°	1.000	0.000
10°	.864	.162
20°	.780	.310
30°	.732	.456
40°	.710	.609
50°	.710	.785
60°	.732	1.01
70°	.780	1.32
80°	.863	1.90
90°	1.000	∞

CAN T_2 BE LONGER THAN T_1?

In my experience, most spectroscopists believe that T_2 can be equal to, or less that T_1, but cannot be greater. This belief is probably the result of the widespread acceptance of the statement, "T_2 can be equal to, or less than T_1 because all processes that lead to a T_1 relaxation also lead to a T_2 relaxation." Further, it has been shown that when the antisymmetric component of the shielding tensor is zero by symmetry, T_2 is not greater than the maximum of 0.857 T_1. For leading references to this ratio, see Ref. (*5*).

It is worth mentioning here that two reviewers commented that an error frequently appears in the literature, even though this misconception is not the central theme of this article. The error stems from confusing "relaxation rate," which is $1/T_1$ or $1/T_2$, with the "time constant" for the relaxation, T_1 or T_2, respectively. Using this inverted definition, it would appear that it is relatively easy for "T_2" to be greater (not longer) than "T_1".

Figure 5 and Table 3 represent the case when T_2 = 1 s, and T_1 = 0.5 s, i.e., when T_2 is twice as long as T_1. In this case, the assumption was made that the applied field, B_0, is perfectly homogeneous, i.e., that T_2' is infinitely long, making T_2^* equal to T_2, as shown in Eq. [5]. Here, the overall rate ($1/T_2^*$) of decay in the transverse plane is equal to the natural rate ($1/T_2$) plus the rate ($1/T_2'$) due to the inhomogeneity of the B_0 field. The symbols T_2^*, T_2, and T_2' are the time constants for the respective decays. The assumption made here prevents the magnetization vector from artificially decaying faster because of the inhomogeneous applied field.

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'} \qquad [5]$$

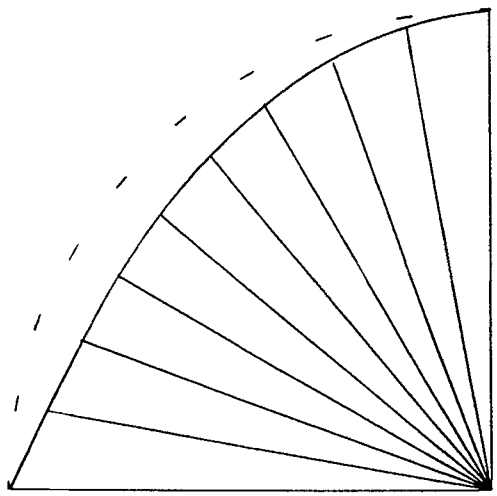

Figure 5. Plot of the resultants of M_{xy} and M_z at specific points in time for the case when T_2 = 1 s and T_1 = 0.5 s.

TABLE 3
Data Used to Construct Figure 5

Angle	Magnitude	Time (s)
0°	1.000	0.000
10°	.929	.088
20°	.888	.181
30°	.869	.285
40°	.868	.408
50°	.884	.565
60°	.914	.783
70°	.952	1.12
80°	.986	1.77
90°	1.000	∞

Even for this case, the resultant still shrinks immediately after the 90° pulse, reaches a minimum, and then grows back to its maximum value. However, note that the magnitude of the resultant does not exceed 1.0 at any time. According to this treatment, T_2 can be twice as long as T_1. Similar tables and plots show that if $T_2 > 2T_1$, then at some time the magnitude does exceed 1.0. Figure 6 and Table 4 show a case when T_2 is three times as long as T_1. Here, the magnitude of the resultant exceeds 1.0, and this is clearly a situation that seems to contradict our present understanding of the laws of physics, although claims to the contrary have been reported by Skinner (*6*, *7*). But at or below the threshold $T_2 = 2T_1$, the mathematical treatment presented above will allow for T_2 to be greater than T_1. This is only one example of the beauty of mathematical representations for physical phenomena; it can often tell a scientist what to seek, even if a physical picture cannot.

In fact, Frank A. L. Anet and coworkers (*5*) have clearly demonstrated experimentally that T_2 can be longer than T_1. Their relaxation data for the olefinic carbons of tetrachlorocyclopropene in toluene-d_8 at -89° C, show that the T_2/T_1 ratio is 1.16! A more detailed description of this experiment, as well as a very comprehensive paper on the T_2/T_1 ratio, will be presented by Frank A. L. Anet and Daniel J. O'Leary, in a forthcoming issue of this journal.

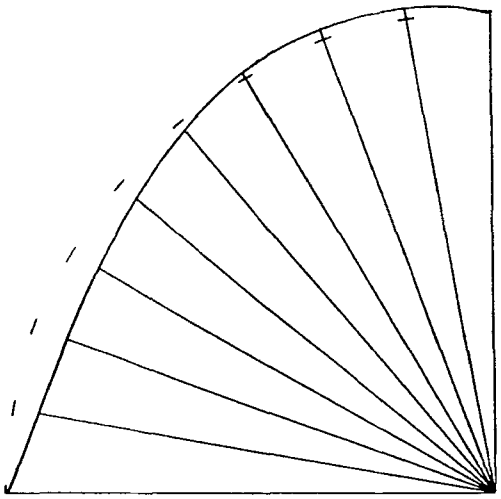

Figure 6. Plot of the resultants of M_{xy} and M_z at specific points in time for the case when T_2 = 1 s and T_1 = 1/3 s.

TABLE 4
Data Used to Construct Figure 6

Angle	Magnitude	Time (s)
0°	1.000	0.000
10°	.956	.060
20°	.936	.129
30°	.936	.210
40°	.952	.316
50°	.980	.463
60°	1.01	.686
70°	1.02	1.05
80°	1.01	1.74
90°	1.000	∞

SUMMARY

It is a common misconception that after a pulse, the net magnetization vector simply tips backwards toward the z axis, while maintaining a constant length. Instead, under the normal conditions when T_2^* is less than T_1, the resultant first shrinks, and then grows back toward its initial value as it tips back toward the z axis. This behavior is clearly shown by examining the basic equations that describe both the decay of the magnetization in the xy plane and its growth up along the z axis. From these equations, the magnitudes of the xy and z components, as well as their vectors sums, can be calculated as a function of time. This same behavior is demonstrated even when T_2^* is equal to T_1 — the resultant still does not maintain a constant value of 1.0 as it tips back.

The resultant does not exceed 1.0 at any time during the relaxation if the T_2/T_1 ratio does not exceed 2. However, experimental evidence has been obtained that shows that the ratio can be greater than 1.

ACKNOWLEDGMENTS

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REFERENCES

1. A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, Oxford, 1961.

2. J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance*, McGraw Hill, New York, 1959.

3. J. D. Roberts, "The Bloch Equations. How to Have Fun Calculating What Happens in NMR Experiments with a Personal Computer," *Concepts Magn. Reson.*, **1991**, *3*, 27-45.

4. D. D. Traficante, "Phase-Sensitive Detection — Part I: Phase, Gates, Phase-Sensitive Detectors, Mixers, and the Rotating Frame," *Concepts Magn. Reson.*, **1990**, *2*, 151-167.

5. F. A. L. Anet, D. J. O'Leary, C. G. Wade, and R. D. Johnson, "NMR Relaxation by the Antisymmetric Component of the Shielding Tensor: A Longer Transverse than Longitudinal Relaxation Time," *Chem. Phys. Lett.*, **1990**, *171*, 401-405.

6. H. M. Sevian and J. L. Skinner, "T_2 can be Greater than $2T_1$," *J. Chem. Phys.*, **1989**, *91*, 1775-1782.

7. B. B. Laird and J. L. Skinner, "T_2 can be Greater than $2T_1$ even at Finite Temperature," *J. Chem. Phys.*, **1991**, *94*, 4405-4410.