

M.Sc Chemistry



Inorganic Special Paper Semester IV

Course – 4101 B

Course Title – Spectral Techniques in Inorganic Chemistry

By – Dr. Vartika

NMR Spectroscopy (Cont...)



What is NMR Relaxation?

In the context of nuclear magnetic resonance (NMR), the term relaxation indicates the process by which the magnetic atomic nuclei reach thermal equilibrium with the chaotic molecular environment. In NMR, this process can be very slow, requiring between a fraction of a second to many minutes, depending on the sample and the environmental conditions. To NMR spectroscopists, relaxation is a friend, since it generates the nuclear magnetisation from which all NMR signals are derived; at the same time, relaxation can be a foe, since it limits how long any different forms of spin order last. For many years, it was generally thought that relaxation was intrinsic to the sample, and could not readily be manipulated or overcome. However, recent experiments have shown that in some cases the nuclear spin systems may be held in special configurations called long-lived states that are to some extent protected against relaxation

Relaxation Processes

Types of Relaxation Processes

Spin-Lattice Relaxation Processes

Also Known as :

- ❖ T_1 Relaxation
- ❖ Longitudinal Relaxation
- ❖ Along the axis of the external M.F
- ❖ Thermal Relaxation
- ❖ Spins interacting with the surrounding environment
- ❖ The signal builds up along the Z-axis due to T_1 relaxation

Spin-Spin Relaxation Processes

Also Known as :

- ❖ T_2 Relaxation
- ❖ Transverse Relaxation
- ❖ Perpendicular to the external M.F
- ❖ Spins interacting with other spins
- ❖ The signal decays to zero in the X-Y plane due to T_2 relaxation

Spin-Lattice (T_1) Relaxation

Spin-lattice relaxation occurs by transfer of energy to the surroundings (heat); dipolar coupling to other spins. Results in recovery of M_z to 63% of original value. Since molecule contains magnetic nuclei, the random nuclear motion will cause these nuclei to give rise to fluctuating magnetic fields. When this field is properly phased (to match precessional frequency) and properly oriented, a nucleus which is in an upper spin state can be relaxed to the ground state by imparting its excess energy to the lattice as rotational and translational energy. This mechanism for spin-relaxation is referred as nuclear-dipolar interaction. The total energy of the system is unchanged by this process, and the efficiency of the relaxation mechanism depends upon (a) magnitude of the local fields (b) the rate of fluctuation of the local fields. A quantity referred to as the spin-lattice relaxation time, T_1 , can be defined to indicate the rate of this process. A large value for T_1 , indicates an inefficient relaxation process, and a long lifetime for the excited state. In the absence of other effects, a sharp line results as predicted by equation:

$W \propto 1/t$, when T_1 is large.

- ❖ Gain and loss of magnetization in the z-direction.
- ❖ NMR lines are *at least* as wide as specified by the Heisenberg Uncertainty Principle broadening due to inherent lifetime of spin states (the actual width is governed by T_2).
- ❖ For most spin 1/2 nuclei T_2 is between 0.2 and 50 seconds.

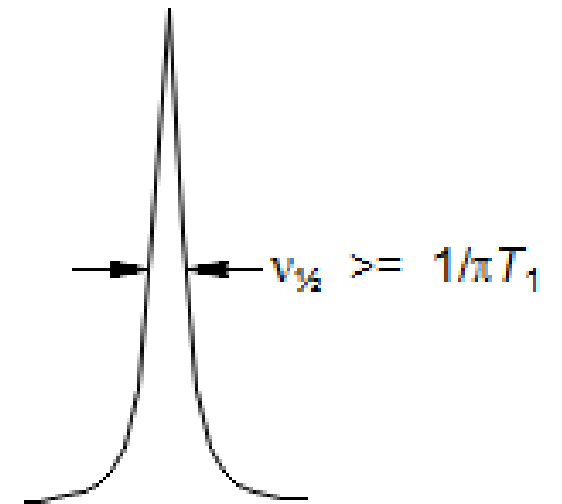
$$\Delta E \cdot \Delta t = h/2\pi$$

$$h\delta\nu \cdot \delta t = h/2\pi$$

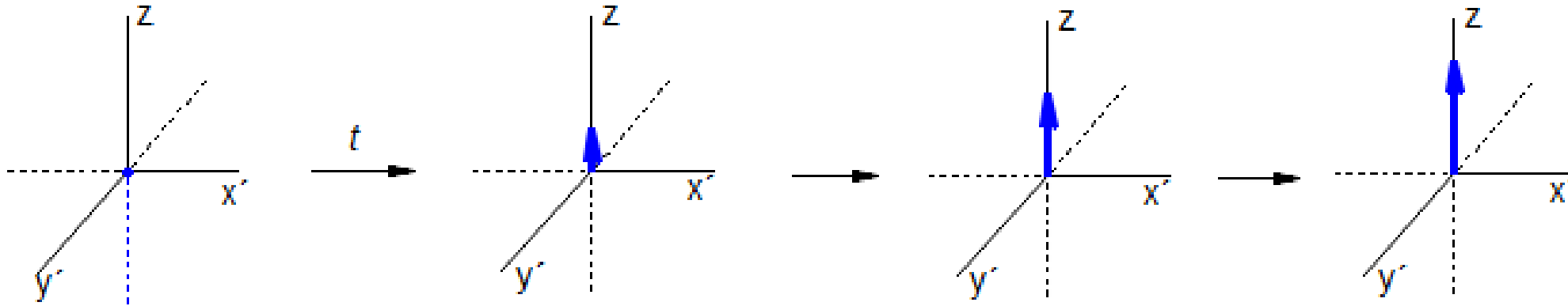
$$\nu_{1/2}/2 \geq 1/2\pi T_1 \quad (\text{Half-width at half height})$$

$$\boxed{\nu_{1/2} \geq 1/\pi T_1} \quad (\text{Width at half height})$$

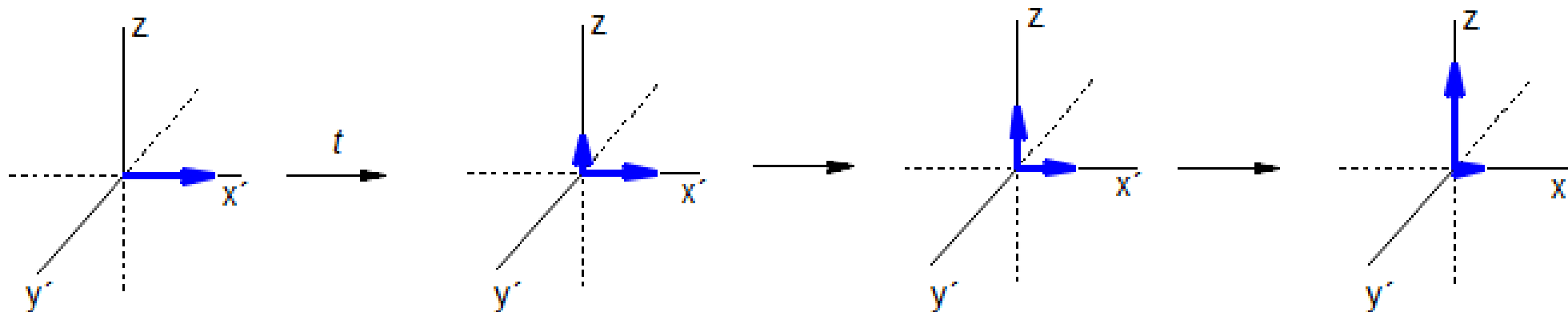
Broadening due to paramagnetic impurities is a special case of T_1 broadening



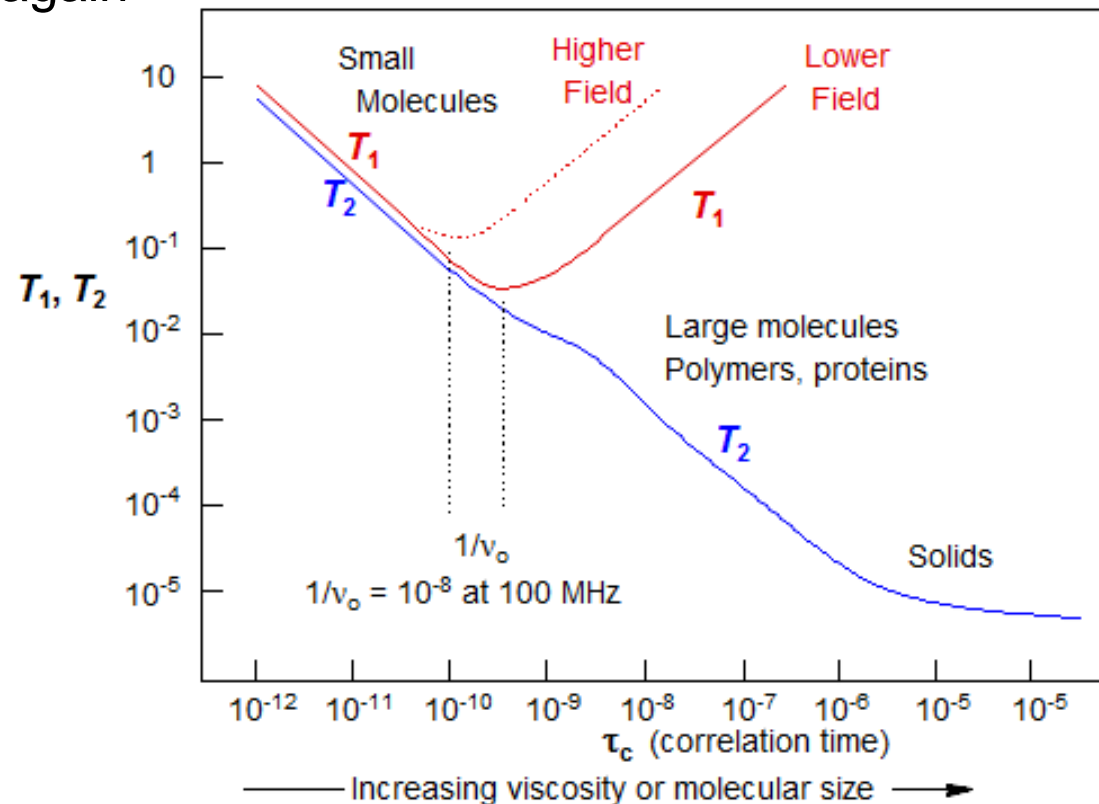
Place unmagnetized sample in magnetic field: establishment of the normal Boltzmann equilibrium between the α and β spin states has a first order rate constant of $k = 1/T_1$: $M_z = M_\infty (1 - e^{-t/T_1})$



Or apply a 90° pulse, and watch the magnetization return to the z -direction: $M_z = M_\infty (1 - e^{-t/T_1})$



The rate of spontaneous relaxation of nuclear spin orientations is almost zero. T_1 relaxation is caused by transient magnetic fields (usually due to molecular motion) at the Larmour precession frequency. In most situations T_1 relaxation is optimal if the average rate of molecular reorientation in space is at the Larmour precession frequency. In mobile liquids near room temperature the average rates of molecular rotation are several orders of magnitude higher than ν_0 , so only a very small fraction of the motions are at the proper frequency, leading to very inefficient relaxation (long T_1). For larger molecules and more viscous solutions molecular motions become slower and more efficient relaxation results (T_1 shortens). However, at some point the average molecular motions become slower than ν_0 , and T_1 becomes longer again



FigL Behavior of T_1 and T_2 as a function of correlation time for spin $\frac{1}{2}$ nuclei relaxing by the Dipole-Dipole mechanism. τ = Molecular correlation time: the time it takes the average molecule to rotate one radian

Causes for broadening in Spin-Lattice Relaxation

- ❖ Nuclear-Dipolar interactions
- ❖ Paramagnetic substances
- ❖ Interaction of quadrupole nuclei with fluctuating electric-field gradients (which arise from the motion of polar solvent molecules and solute molecular vibrations)

Spin-Spin (T_2) Relaxation

Heisenberg Uncertainty Principle broadening due to lifetime of spin coherence - gain and loss of magnetization in the x,y-direction.

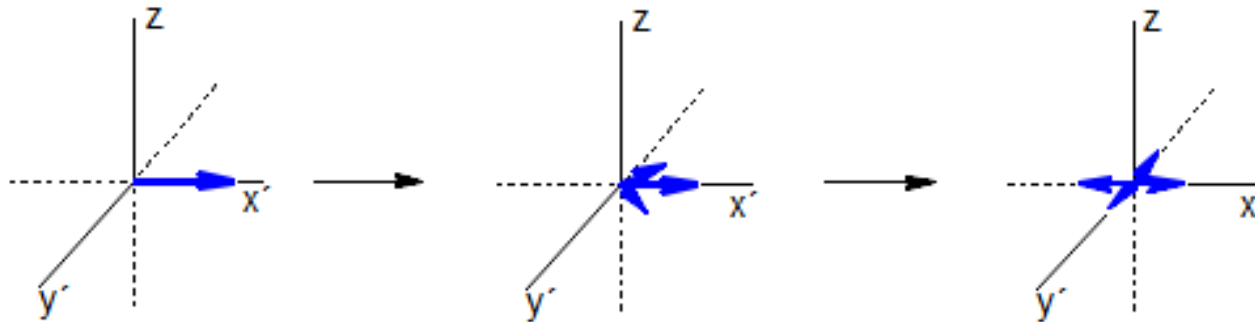
$$\nu_{1/2} = 1/\pi T_2$$

$$T_2 \leq T_1$$

For protons, T_2 is usually between 1 and 10 seconds

$$T_2 = 1 \text{ sec, } \nu_{1/2} = 1/\pi = 0.3 \text{ Hz}$$

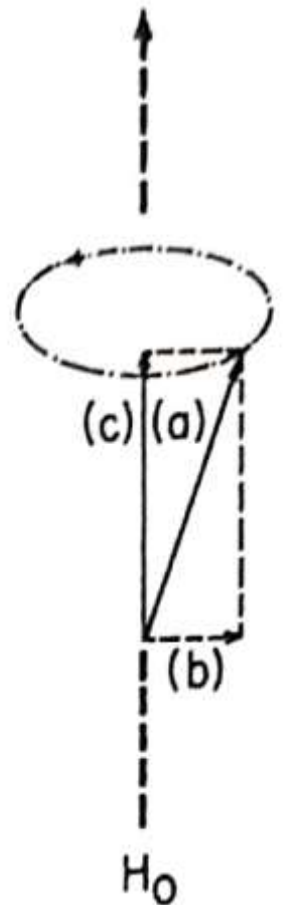
$$T_2 = 10 \text{ sec, } \nu_{1/2} = 1/10 \cdot \pi = 0.03 \text{ Hz}$$



- ❖ T_2 relaxation is caused by transient magnetic fields (usually due to molecular motion) at any frequency. Thus T_2 keeps getting shorter as molecular reorientation rates slow down
- ❖ T_2 relaxation is also caused by swapping of chemical shifts or coupling constants due to chemical exchange or interconversion of conformations. Line broadening due to chemical exchange provides an important tool for measurement of the rates of a variety of molecular processes
- ❖ A third source of T_2 relaxation is interconversion of spin states of a quadrupolar nucleus coupled to it

Reasons for broadening in Spin-Spin Relaxation

1. At the nucleus being examined, the static component of another nucleus causes a slight variation in the effective field at this nucleus. The contribution to the effective magnetic field by this second nucleus. Since the effect drops off sharply with distance, only neighbouring molecules will have an appreciable effect on the effective field. A variation in the environment of nuclei undergoing the NMR transition exists because of the random arrangements of neighbouring molecules. This results in a range of energies over which the transition can occur, and a broad line results.
2. Broadening in T_2 results from the variation in the applied field H_0 over the same dimensions. The observed spectrum is a superposition of several spectra corresponding to the different values of H_0 in the different parts of the sample.
3. If the rotating component of a neighbouring molecule has a frequency equivalent to the Larmor frequency of the nucleus undergoing the transition, this rotating component can induce a transition of the neighbouring nucleus to a different spin. The nucleus inducing the transition simultaneously undergoes a change in its spin state in this process. This decreases the lifetime of the excited state and result in broadening.



Larmor Frequency (a) and the rotating and (b) static (c) component

Conclusion

- ❖ $T_2 \leq T_1$
- ❖ T1 and T2 are routinely equivalent for most NMR experiments
- ❖ NMR Linewidths $\sim 1/T_2$ for spin $\frac{1}{2}$ nuclei
- ❖ NMR spectra of solids are very broad because T_2 is short.
- ❖ Because of the very broad lines usually observed when solid spectra are examined, most inorganic applications are carried out on gases, liquids, or solutions.

Suggested Reading Links

<https://www.ias.ac.in/article/fulltext/reso/020/11/0986-0994>

<https://www.chem.wisc.edu/areas/reich/nmr/08-tech-01-relax.htmj>

<http://mriquestions.com/what-is-t1.html>

<http://mriquestions.com/what-is-t2.html>

Thank you!

