

## Relaxation process: [H. Kaur - spectroscopy] ①

Relaxation process involve non-radiative transitions by which a nucleus in an upper transition state returns to the lower spin state. Two kinds of relaxation processes are spin-spin relaxation, spin-lattice relaxation.

### spin-spin relaxation or transverse relaxation ( $T_2$ )

This is effected by the mutual exchange of spins by two precessing nuclei in close proximity to one another. With each precessing nucleus, there is an associated magnetic field vector component rotating in a plane perpendicular to the main field. If this small rotating magnetic field is the same as is required to induce a transition in the neighbouring proton, then mutual exchange of spin takes place. This mutual exchange of spins shortens the life time of an individual nucleus in the higher state. In other words, it involves the transfer of energy from one nucleus to the other. There is no net loss of energy. The spread of energy among the nuclei concerned

in line broadening, which makes ~~the~~ NMR spectra of solids. The relaxation time is denoted as  $T_2$ . Its value is very small for crystalline solids or viscous liquids ( $10^{-4}$  s) and thus prevents the use of such samples for high resolution work.

spin-lattice relaxation (or longitudinal relaxation)  
Spin lattice relaxation is defined as the process whereby  $z$ -component of magnetization ( $M_z$ ) returns to its equilibrium value  $M_z^0$ . This is also termed as longitudinal relaxation because the decay of magnetization occurs along the longitude ( $z$ -axis) of the NMR experiment.

The NMR experiment is sustained because the neighbouring magnetic nuclei in motion can produce oscillatory fields with the same frequency and phase as that of the exciting nucleus. Thus, the energy may pass from the exciting spins to the surrounding environment (the lattice) so that the nuclei can return to the lower spin state and be available for another spin excitation of  $H_0$ . This mechanism is known as spin-lattice relaxation. The rate constant for this first order decay process is  $T_1$ , the spin-lattice relaxation time. This spin lattice relaxation time ( $T_1$ )

is a measure of the rate of build up of nuclear spin polarization in the direction of the external magnetic field and can be used in distinguishing nuclei located towards the tail end of a big molecule from the rest.

There are a number of mechanisms which can contribute to spin-lattice relaxation in a molecule.

- (i) dipole-dipole relaxation ( $T_{1DD}$ )
- (ii) spin-rotation relaxation ( $T_{1SR}$ )
- (iii) quadrupolar relaxation ( $T_{1Q}$ )
- (iv) scalar coupling ( $T_{1SC}$ ) and
- (v) chemical shift anisotropy ( $T_{1CSA}$ ).

Each of these combine to produce an overall spin-lattice time  $T_1$ .

$$\frac{1}{T_1} = \frac{1}{T_{1DD}} + \frac{1}{T_{1SR}} + \frac{1}{T_{1Q}} + \frac{1}{T_{1SC}} + \frac{1}{T_{1CSA}}$$

Relaxation rates are reciprocals of the corresponding relaxation times.

chemical shifts: [Anamalai DD notes]

The precise value of Larmor frequency for a given nucleus depends upon its electronic environment in which it is present. The magnitude of the magnetic field at the nucleus, is due not only to the applied field of the electrons and the other

② nuclei. All the electrons have spin angular momentum and all but 's' electrons have orbital angular momentum magnetic dipole moments are associated with these angular momenta. In most of the molecules the electronic ground states are non degenerate and there is no electronic or spin angular momentum. Hence in the absence of external magnetic field the 's' electrons usually do not contribute anything to the magnetic field felt by the nucleus.

However, when an external magnetic field is applied, the molecular electronic wave function is perturbed giving rise to an electronic contribution  $H^1$  to the magnetic field at the nucleus. In general  $H^1$  will have different values at different nuclei. The field  $H_c^1$  at  $i$  the nucleus produced by the perturbed electrons is proportional to the strength of the applied field  $H_0$  and is given by

$$H_c^1 = - \sigma_i H_0$$

where  $\sigma_i$  is a symmetric second order tensor. This equation thus defines the shielding tensor  $\sigma_i$  at the center. It is always possible to choose  $x, y$  and  $z$  axes at the nucleus.  $\sigma_i$  is diagonal then the diagonal values being given by  $\sigma_{xx}^i, \sigma_{yy}^i$  etc. In a liquid or gas molecules rotate

rapidly and we have to consider the mean value of  $\sigma$ . It is found that average of  $\sigma_i$  turns out to be  $[\sigma_{xx} + \sigma_{yy} + \sigma_{zz}]$  so that

$$H_i = -\sigma_i H_0$$

and the actual field at the nucleus

$$H_i = H_0 + H_j \text{ or}$$

$$H_i = H_0(1 - \sigma_i)$$

where the quantity  $\sigma_i$  is called the screening or shielding constant.

It has been shown by Ramsay using perturbation theory that  $\sigma_i$  is made up of two terms  $\sigma_d$  called the diamagnetic positive term and  $\sigma_p$  the paramagnetic negative term. For molecular protons  $\sigma_d$  exceeds  $\sigma_p$  and  $\sigma_H$  is positive for a single nucleus  $i$  with shielding constant  $\sigma_i$  the Hamiltonian becomes.

$$H_i = -g_i \frac{e}{2Mc} H_0$$

$$H_i = -g_i \frac{e}{2Mc} H_0 (1 - \sigma_i) I_{z_i}$$

The eigen function of  $H_i$  are called eigen function of  $I_{z_i}$  and its eigen values are

$$-g_i \frac{e}{2Mc} H_0 (1 - \sigma_i) M_{i, i}$$

For a molecule with several nuclei with

(b) non zero spin, every nucleus will interact with  $H_0$  and hence the  $H_i$  has to be averaged over all nuclei is  $\sum_i H_i$ .

Since the total Hamiltonian is the sum of the Hamiltonians of the individual nuclei, the eigen functions will be the product of individual eigen functions and the sum of the eigen energies of  $H_i$  are

$$E = -\frac{e}{2Mc} H_0 \sum_i g_i (1 - \sigma_i) M_{z,i}$$

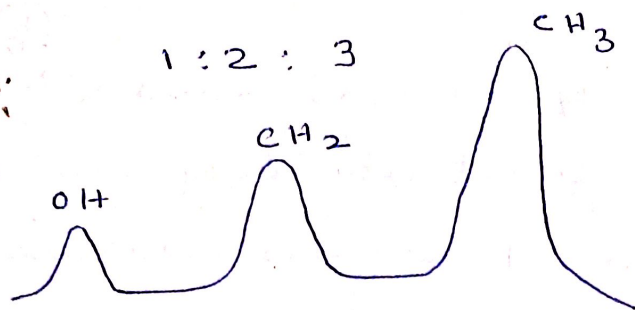
and the selection rules are

$$\left. \begin{aligned} \Delta M_{z,i} &= \pm 1 \\ \Delta M_{z,j} &= 0 \quad j \neq i \end{aligned} \right\} i = 1, 2$$

Thus the selection rule allows only one nuclear magnetic moment to change its orientation in a transition. The frequencies of the NMR line is given by

$$\nu_i = \frac{e}{2Mc h} H_0 g_i (1 - \sigma_i) \quad i = 1, 2, \dots$$

Identical nuclei in chemically equivalent environment in the molecule have the same ~~frequency~~ values of  $g_i$  and  $\sigma_i$  and have the same NMR transition frequency. Identical nuclei in chemically different environments have the same  $g_i$  values but different values of  $\sigma_i$  have NMR transition frequencies lying close together. Non identical nuclei have different values of  $g_i$  and their NMR frequencies as well, separated.



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consider for example the proton of ethyl alcohol  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{C}^{12}$  and  $\text{O}^{16}$  do not contribute as they have zero spins. There are three kinds of protons and each has its own values of  $\sigma$  and gives rise to three distinct signals of relative intensity 1:2:3 (OH, CH<sub>2</sub>, CH<sub>3</sub>)

We see from the expression for  $\nu_i$  that for a fixed value of  $H_0$  the resonance frequency depends on  $\sigma$ . Usually NMR spectra are observed with fixed radio frequency at a value  $\nu$  while  $H_0$  is varied. Under these conditions the value of  $H_0$  required for resonance of the nucleus is

$$H_{ei} = \frac{h \nu_{\text{spect}}}{\frac{e}{2mc} g_i (-\sigma_i)} \quad \text{--- (1)}$$

The change in NMR transition frequency at fixed  $H_0$  due to the shielding of a nucleus by the electrons of a molecule is called the chemical shift. The chemical shift is observed only in gases and liquids but not in solids. The chemical shift cannot be determined with high accuracy. Hence chemical shifts are measured relative to the shift in some standard

compound.

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The separation b/w the resonance of two nuclei with different shielding constant is proportional to  $\Delta \nu_{\text{spect}}$ . To express chemical shift in a form independent of the value of  $\Delta \nu_{\text{spect}}$  the quantity  $\delta_i$  is defined as -

$$\delta_i = (\sigma_{\text{ref}} - \sigma_i) \times 10^6 \text{ ppm} \quad \text{--- (2)}$$

where  $\sigma_{\text{ref}}$  and  $\sigma_i$  are the shielding constants for the standard reference and for the nucleus  $i$ . All chemical shifts values are expressed in parts per million. From the above definition,  $\delta_i$  is +ve for  $n$  nuclei, less shielded than the reference nuclei -

we can write @ combining (1) and (2)

$$\delta_i = \frac{h \Delta \nu_{\text{spect}}}{\left(\frac{e}{2mC}\right) g_i} \left( \frac{H_{\text{ref}} - H_{\text{oi}}}{H_{\text{ref}} H_{\text{oi}}} \right) \times 10^6 \text{ ppm}$$

since  $\sigma_i$  is generally small we can write

$$\delta_i = \frac{H_{\text{ref}} - H_{\text{oi}}}{H_{\text{ref}} H_{\text{oi}}} \times 10^6 \text{ ppm}$$

we can also write in terms of frequency.

$$\delta_i = \frac{\text{chemical shift } (H_z) \times 10^6}{\text{observation frequency } H_z} \text{ (ppm)}$$

generally the chemical shift lines shows multiplet structure due to the phenomenon of spin coupling. This is due to the mutual interaction b/w nuclei within a molecule -