

Singlet States in solution NMR

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One of the research projects in the NMR methodology laboratory at IIT Delhi deals with extending the lifetime of nuclear spin states in NMR, which is normally restricted by longitudinal relaxation time " T_1 ". This is achieved by creating states that are immune to the major relaxation mechanism, intramolecular dipole-dipole relaxation, in liquids, which results in exceptionally large lifetimes. It was demonstrated that these states, generally known as singlet states, have decay constant " T_{LLS} " which, in some cases is some orders of magnitude longer than longitudinal magnetization " T_1 " i.e. $T_{LLS} > T_1$. T_{LLS} was shown to be up to 36 times longer than T_1 . [1] This is strict and true for a system comprising two coupled spin-1/2 nuclei in liquid state NMR where the dipolar relaxation mechanism is dominant. However in more extended spin systems, the spins present in the close vicinity to these spins pair forming singlet states creates other dipolar relaxation sources to which these states are not immune. It was found that even in multi-spin systems, these singlet states have long lifetime provided that some conditions are met.

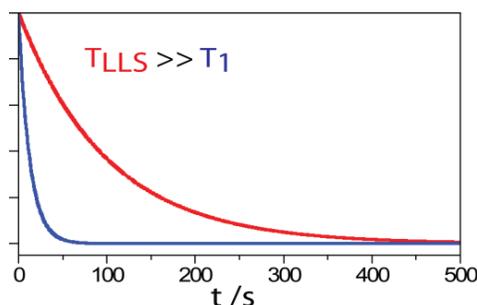


Fig1. Intensity Vs Time plot for comparing the lifetime T_{LLS} and T_1 .

For a homonuclear pair of coupled spins-1/2, the quantum state of a spin pair is expressed as a superposition of four Zeeman product states $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\alpha\rangle$ and $|\beta\beta\rangle$ where the label " α " denotes the angular momentum of $1/2\hbar$ along the magnetic field direction and " β " denotes the opposite angular momentum of $-1/2\hbar$. Under the condition of magnetic equivalence, these four states are combined to form one singlet state $|S_0\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)$ (having total nuclear spin $I=0$) and three triplet states $|T_{+1}\rangle = |\alpha\alpha\rangle$, $|T_0\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle)$ and $|T_{-1}\rangle = |\beta\beta\rangle$ (having total nuclear spin of $I=1$) that are the eigenstates of nuclear spin Hamiltonian (see Fig.1). The long lifetime of singlet state is often explained by symmetry considerations. The singlet state is *antisymmetric* whereas three triplet states are *symmetric* w.r.t spin exchange. The immunity of singlet state to the major intra-molecular dipole-dipole relaxation mechanism is due to the fact that both have different symmetry, so will not affect each other whereas the three triplet states have same symmetrical nature as that of this mechanism, so are strongly affected resulting in fast population equilibration of these states.

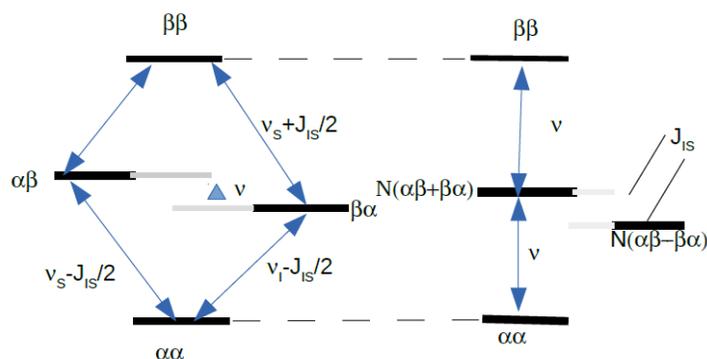


Fig.2 Graphical representation of energy level diagrams for creation of singlet states in liquid NMR.

Earlier some evidence is available regarding excitation of these states in dihydrogen molecule, but their excitation in magnetically equivalent spin-1/2 pair is not possible until last decade which sees some beautiful experiments published by the group of M. H. Levitt et. al.[2,3] for creation of these states in small molecules in liquid state NMR which opens a new perspectives for studying many processes which are earlier limited by the lifetime of Zeeman magnetization. Singlet states have been utilized for studying slow molecular motions and molecular transport,[4,5] the storage and transport of hyperpolarized nuclear spin order[6,7], and as a probe for local molecular geometry and dynamics[8,9]. In our group, we basically are extending the applications of these long-lived states in various fields of bio-molecular NMR.

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