

TEST 3 – RELAXATION and DYNAMICS

1. Table below shows results of inversion recovery experiment used for measurement T_1 relaxation time.

- Use simple law of first order kinetic and derive the time dependence of detected signal S .
- Based on data in attached table calculate the relaxation time $T_1=1/k$.

t (s)	0	0.1	0.5	0.9	1.3	1.7	2.1	2.9
S	-129.7	-93.4	7.6	62.6	93.4	109.5	118.9	126.4

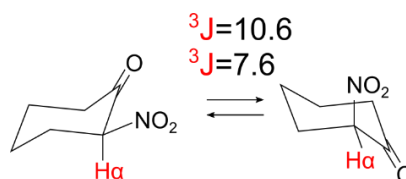
- Which parameter of NMR experiments in general is related to value of T_1 ?
- Explain why degassing of sample can increase substantially the T_1 value?

2. To demonstrate quantitatively NOE effect, assume pair of interacting spin I and S . The time dependence of z -magnetisation (I, S) on actual population of both spins is expressed by equation:

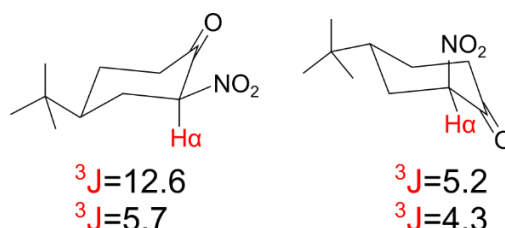
$$\frac{dI}{dt} = -\sigma(I - I_0) - \rho(S - S_0), \quad \frac{dS}{dt} = -\sigma(S - S_0) - \rho(I - I_0)$$

Let's assume that population of spin S is selectively saturated and after mixing time τ . Explain the meaning of constants σ and ρ . Try to estimate the NOE enhancement ($I-I_0/I_0$) of signal at the condition of initial-rate limit. Both spins are of the same type so signal intensity without perturbation is proportional to I_0 .

3. The following example demonstrate the calculation of free energy change associated with conformational change of 2-nitrocyclohexanon moiety based on weighted average of $^3J(H\alpha)$ coupling constant. Consider following $ax \leftrightarrow eq$ transition:

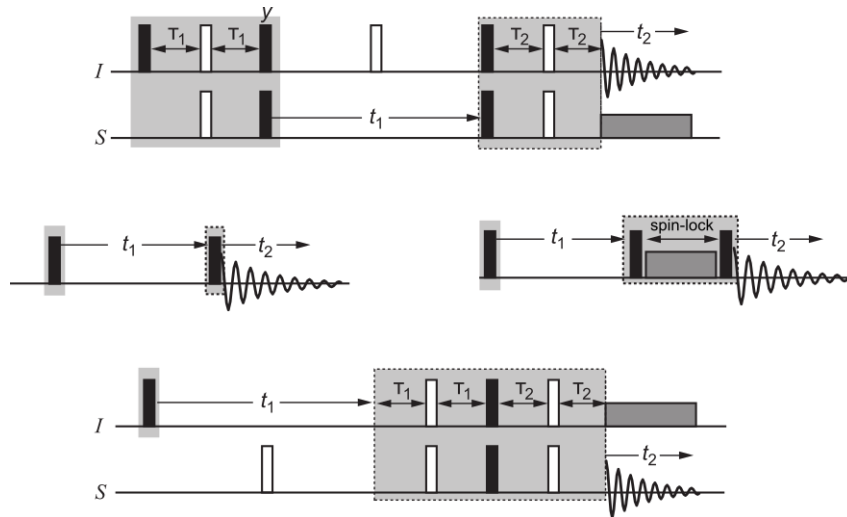


To get extreme values of spin-spin coupling constant use data from conformationally hindered system:



- Based on averaging of pure J values estimate abundance of both conformers.
- Estimate the difference in free energy.

4. In attached diagram of basic 2D experiments try to identify the type of experiment and indicate in each pulse sequence following basic blocks: P (preparation), E (evolution of frequency encoding), M (mixing, transfer of magnetisation) and A (acquisition). Some of experiments utilize also spin echo or decoupling module, show them as well.



5. DOSY experiments employs gradients of magnetic field to encode the position of diffusing molecule within NMR tube. The extend of translation motion within incremented time period is manifested by dephasing of magnetisation which is detected. Analyse 4 attached artificial gradient sequences and draw for each of them a vector model/resulting total signal intensity demonstrating the principle of the DOSY measurement.

