Role of nuclear spectral diffusion as the measure of disorder in materials

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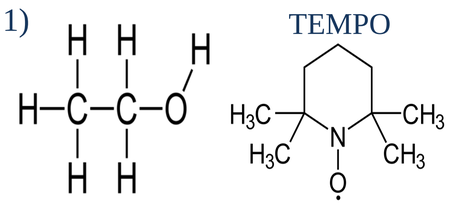
Aim- to investigate the role of nuclear spectral diffusion as the measure of disorder in the materials using constant time CPMG dynamical decoupling

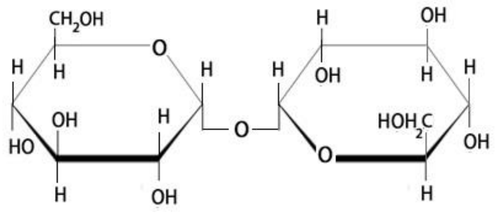
Method- pulsed EPR experiments perfomed using X-band (9.6 GHz) Bruker ELEXSYS 580 spectrometer
- experimentally determining phase memory relaxation time T_m

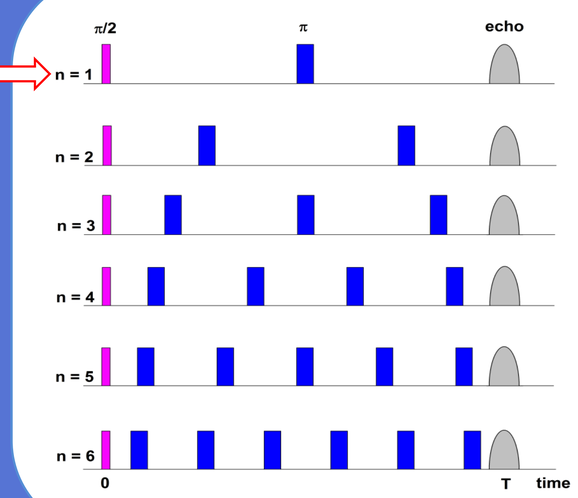
Samples : 1) ethanol doped with nitroxyl radical TEMPO
2) γ irradiated trehalose

1) TEMPO

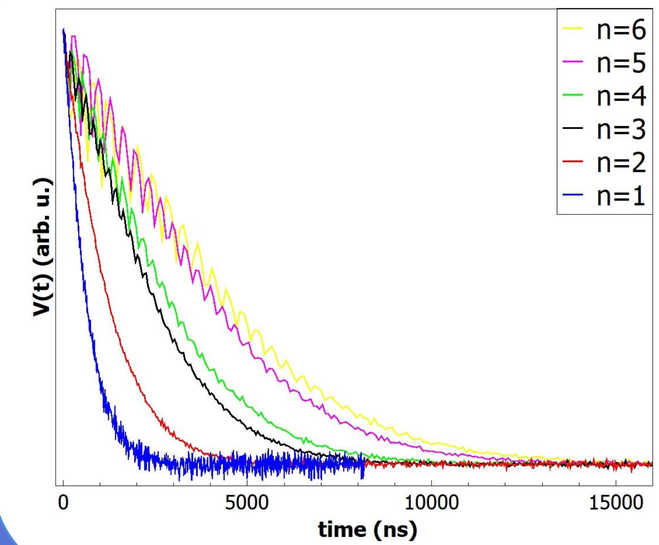


2)

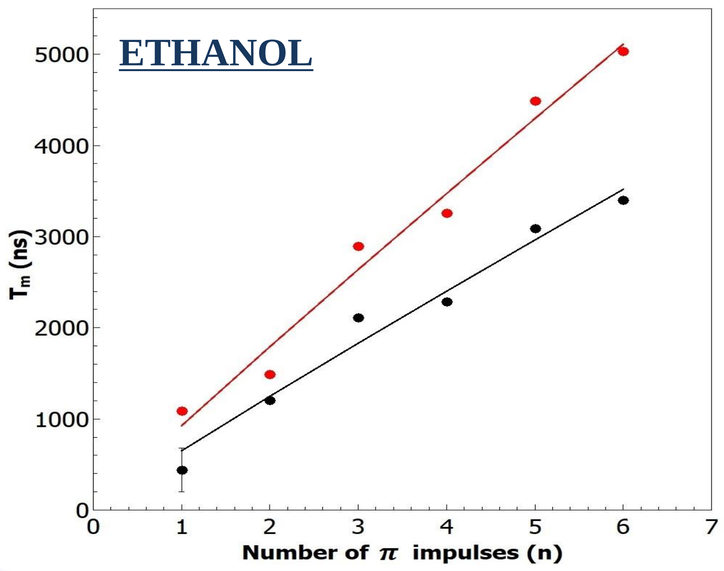




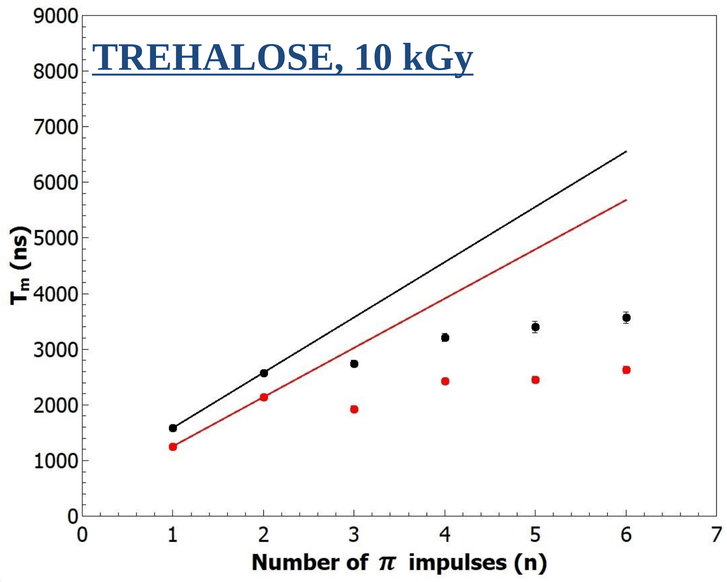
Dynamical decoupling control protocol: constant time Carr-Purcell-Meiboom-Gill (**CPMG**) pulse sequences with varying number n of π pulses ($n = 1, \dots, 6$). [1,2]

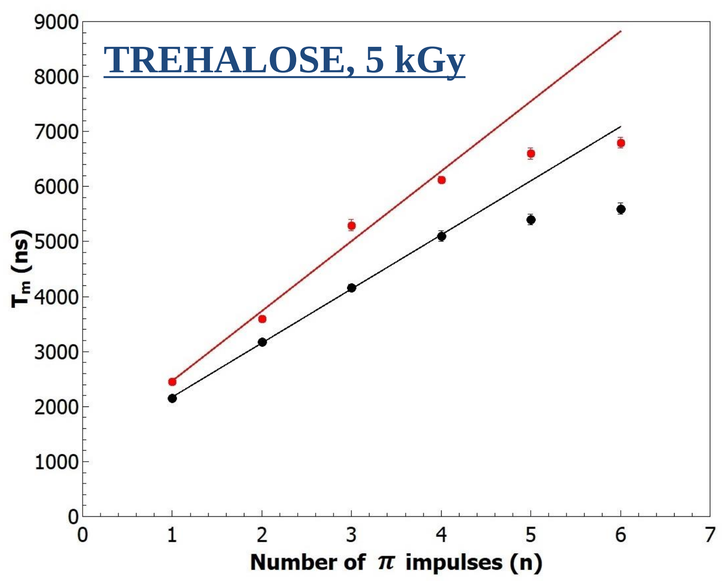


Typical electron spin-echo time decay signal acquired using constant-time CPMG pulse sequence with varying number n of π pulses ($n = 1, \dots, 6$) measured at 20 K for TEMPO incorporated in glassy ethanol.



T_m as a function of the number of π pulses in CPMG pulse sequence measured at 20 K for glassy (red) and crystaline (black) ethanol doped with TEMPO (0.5 mM).





T_m as a function of the number of π pulses in CPMG pulse sequence measured at 20 K for trehalose samples irradiated with the dose of 5 (right) and 10 kGy (left). Black (red) symbols refer to crystalline (glassy) trehalose.

-linear increase of T_m with number n of refocusing pulses

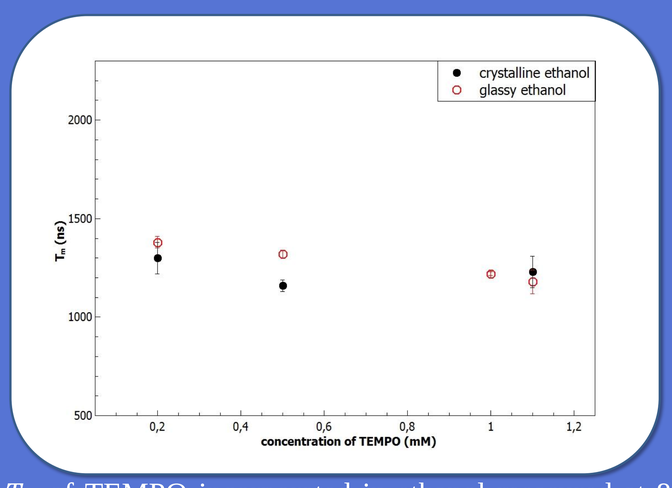
-T_m is determined using stretched exponential decay: $V(t) \propto exp\left[-\left(\frac{t}{T_m}\right)^s\right]$

-larger stretched exponent for glassy sample than for crystalline samples

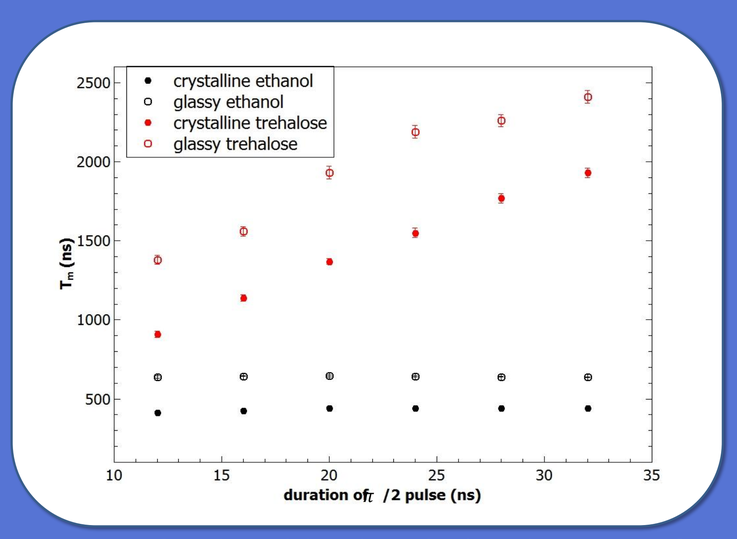
-increase of T_m with n is not linear, saturation effects for $n \geq 2$ for 10 kGy samples, for $n \geq 4$ for 5kGy samples

-T_m is determined using mono-exponential decay: $V(t) \propto exp\left(-\frac{t}{T_m}\right)$

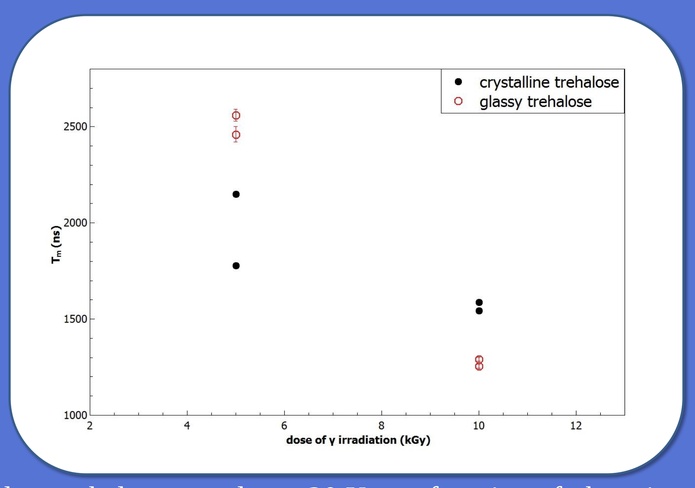
-ratio T_m(glassy)/T_m(crystalline) depends on the applied irradiation dose



T_m of TEMPO incorporated in ethanol measured at 80 K as a function of its concentration.



T_m as a function of duration of $\pi/2$ pulse measured at 40 K for trehalose (red) and ethanol (black) for CPMG sequence with $n = 1$ (Hahn echo).



T_m measured on trehalose samples at 20 K as a function of the γ irradiation.

Ethanol:
-no dependence of T_m on the concentration of paramagnetic centres
-no dependence of T_m on the duration of the refocusing pulses

Nuclear spectral diffusion (**NSD**) is the most important mechanism in electron spin decoherence in ethanol samples. [4]

Trehalose:
-T_m depends on the concentration of radicals in samples produced by γ irradiation
-T_m depends on the duration of the refocusing pulses

Instantaneous diffusion plays the important role in electron spin decoherence in trehalose samples.

The obtained experimental data are the basis for further theoretical studies of the molecular dynamics models in a disordered material since dynamic properties of nuclear spins, which are detected through the hyperfine interaction, directly reflect dynamic properties of the observed material.

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[1] H.Y. Carr, E.M. Purcell, Phys. Rev. 94 (1954) 630.
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[3] W.L. Ma, G. Wolfowicz, N. Zhao, S.S. Li, J.J.L. Morton, R.B. Liu, Nat. Commun. 5 (2014) 4822-31.
[4] J. Jurec, B. Rakvin, M. Jokić, M. Kveder, J. Non-Cryst. Solids, 471 (2017), 435.