*Polarised Nucleon Targets for Europe, 2nd meeting, Bochum 2005*

# Temperature dependence of nuclear spin-lattice relaxations in liquid ethanol with dissolved TEMPO radicals

*H. Štěpánková, J. Englich, J. Kohout, M. Pfeffer*

*J.Černá, V.Chlan, V.Procházka*

*E. Bunyatova*[*]

*Faculty of Mathematics and Physics, Charles University Prague, Czech Rep.*

[*] *Joint Institute for Nuclear Research Dubna, Russia*

- Introduction, NMR in ethanol
- Experimental results (spectra and relaxations)
- Summary

## Introduction

**Proton/neutron target materials**

alcohols + stable nitroxyl radicals

*criteria:* polarization as high as possible

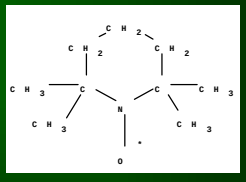
x

relaxation rate as long as possible

technical requirements (*T*, *B*, chemical stability)

**Current study**

ethanol + TEMPO



NMR spectra and spin-lattice relaxation in the liquid state

System is interesting from the point of view of hydrogen bonding (molecular structure and dynamics of water and simple alcohols)

## Introduction

### Nuclear magnetic resonance (NMR)

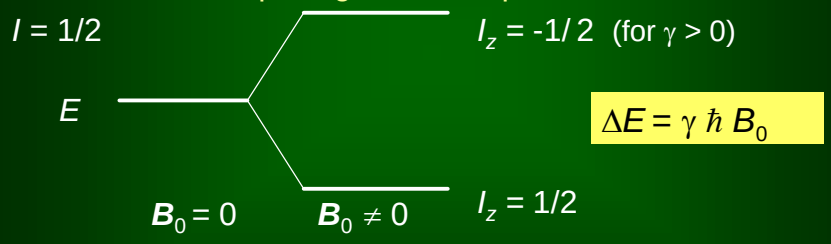
Nucleus with nonzero total angular momentum **(spin)** $\boldsymbol{I}$

nonzero magnetic dipolar momentum $\mu = \gamma \hbar \boldsymbol{I}$

($\gamma$ …gyromagnetic ratio)

In a static magnetic field $B_0 \parallel z$ energy depends on $\mu_z$

Zeeman splitting … $2I+1$ equidistant levels




Radiofrequency field induces transitions if $\omega_{rf} = \gamma B_0$

(Larmor frequency)

Resonating nucleus = probe sensitive to the local static field $B_0$

## Introduction

### High resolution NMR in liquids

$^{1}$H spectra

$^{13}$C spectra

**Chemical shift** - different resonant frequencies from nuclei in nonequivalent positions in a molecule due to the different shielding of external field by electrons

**J-coupling** - splits lines into multiplets due to the neighbour nuclei coupled via chemical bonds

**Direct dipol-dipol interaction** between nuclei - not seen in the spectra of liquids (averaged to zero)

**Linewidth** (homogeneous)~$1/T_2$

**Chemical exchange** - may broaden the lines or reduce the number of lines

**Paramagnetic atom** in the neighbourhood may cause a shift due to the contact Fermi interaction (dipolar interaction in liquids is averaged to zero)

## Introduction

### High resolution NMR in liquids

Spin-lattice ($T_1$) relaxation

Relaxation is induced by fluctuations $b(t)$ of local fields:

$K(\tau) = < b_x(t).b_x(t+\tau) > \sim < b_x(t)^2 > \exp(-\tau / \tau_c)$

$T_1^{-1}$ is determined by the spectral density of K(τ) at $\omega_0$, ($2\omega_0$ …)

$J(\omega) \sim 2\tau_c / (1 + \omega^2 \tau_c^2)$

$\tau_c$ …*correlation time*

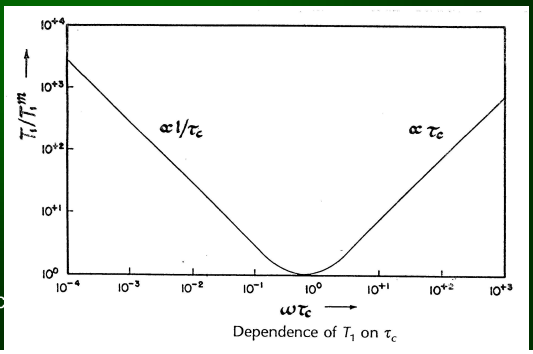
Minimum $T_1$ at $\tau_c \sim 1/\omega \sim 1/B$

$T \downarrow$ … $\tau_c \uparrow$

left … extreme narrowing

higher flexibility → shorter $\tau_c$

→ longer relaxation



Dependence of $T_1$ on $\tau_c$

## Introduction

### High resolution NMR in liquids

*Various relaxation mechanisms*

Diamagnetic samples: direct dipolar interactions

Relaxation due to electron spin: dipolar interaction

Fermi contact interaction

*Electron relaxation seen by nucleus - electronic correlation time* $\tau_s$

*Various kinds of atomic and molecular motion:*

rotation ($\tau_r$) – modulates dipolar relaxation

translational diffusion ($\tau_t$) – no adduct formation - modifies both contact and dipolar relaxation, non Lorentzian J

chemical exchange ($\tau_m$) – mean time for the adduct of the two chemical moieties

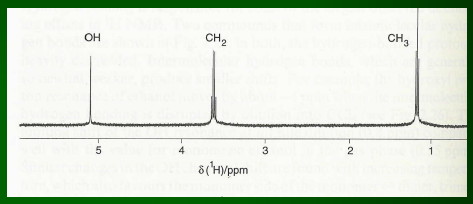
Anisotropic motion. Internal motions.

Concentration, temperature, field dependences

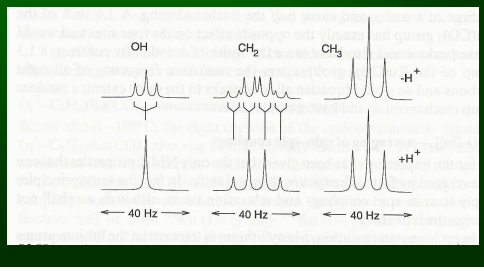
## Introduction

### High resolution NMR in ethanol $CH_3CH_2OH$

$^1H$ spectra: 3 signals
$^{13}C$ spectra: 2 signals



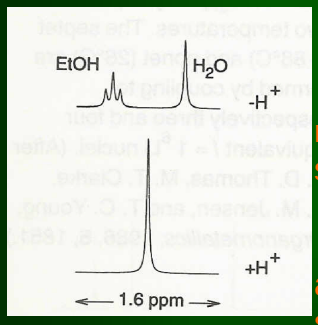

Line splittings due to the J - coupling - dependence on pH - chemical exchange




## Introduction

### High resolution NMR in ethanol $CH_3CH_2OH$

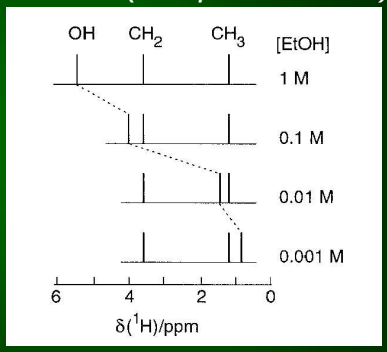
ethanol + water




neutral solution

acidic solution

ethanol in $CCl_4$
*(non polar solvent)*

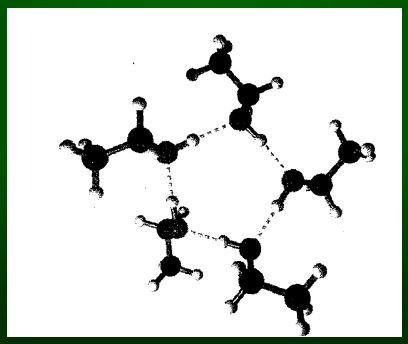


## Introduction

### High resolution NMR in ethanol $CH_3CH_2OH$

Hydrogen bonds, donor/accepor

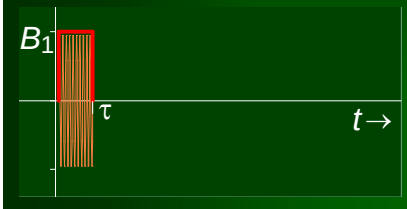
Formation of clusters (linear/cyclic) similarly as in water, but more simple (not the extended 3D clusters common to water), lifetime of the O-H covalent bond (and probably also the hydrogen bond) is relatively long

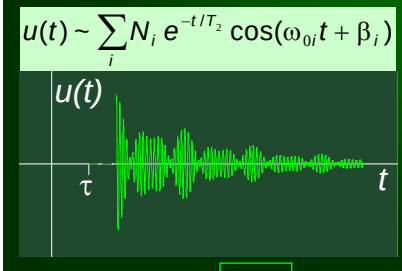


## Pulsed NMR experiments - spectra

### FID = free induction decay

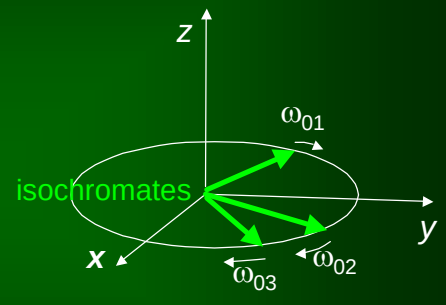
Distribution of Larmor frequencies,
inequivalent sites of resonating nuclei $\omega_{01}$, $\omega_{02}$, $\omega_{03}$, ...

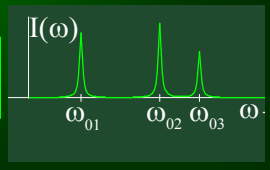



FID

FOURIER TRANSFORM

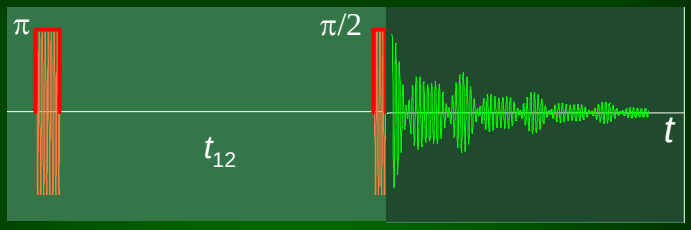



SPECTRUM

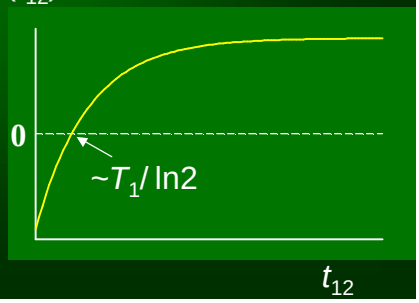
## Pulsed NMR experiments - spin-lattice relaxation ($T_1$)

### Inversion recovery




Proton relaxations **$^1$H**

Carbon relaxations $^{13}$C {$^1$H}




For individual spectral lines:

$I(t_{12}) = I(\infty)\ (1\text{-A.exp}(-\ t_{12}/T_1))$

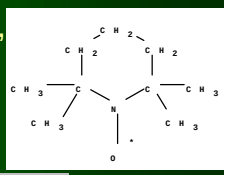
## Experimental

NMR BRUKER AVANCE 500 spectrometer

$B_{external}$ = 11.7 T ( 500 MHz for $^1$H, 125 MHz for $^{13}$C)

Ethanol absolute for analysis, >99.9%, FM 46.07, Merck

TEMPO = 2,2,6,6 tetramethylpiperidin-1-yloxy,
98%,FM156.25, Aldrich



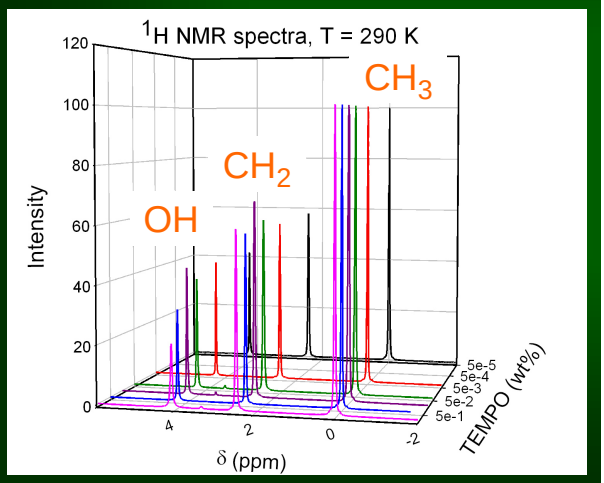
degassed samples, sealed, Ar atmosphere

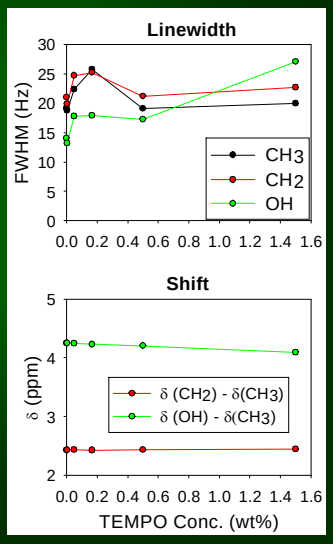
| Sample | TEMPO (wt%) | H2O (mol %) |
|---|---|---|
| #0/2 | 0 | 0.3 |
| #1/2 | 0.0050 | 0.2 |
| #2/2 | 0.050 | 2.6 |
| #5/2 | 0.170 | 2.3 |
| #3/2 | 0.50 | 0.2 |
| #4/2 | 1.50 | 3.9 |

(0.5 wt% of TEMPO~ 25mM)

## Results

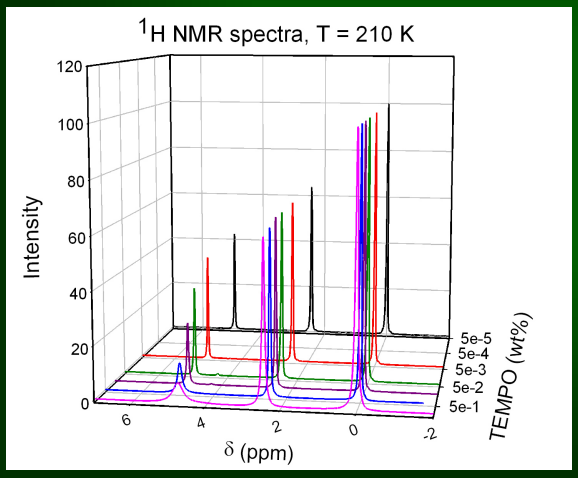
### Spectra $^1$H at 290K – all samples

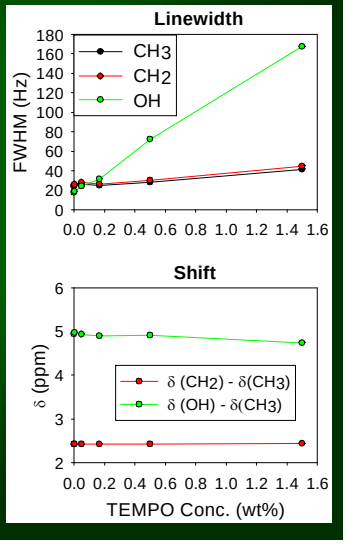



## Results

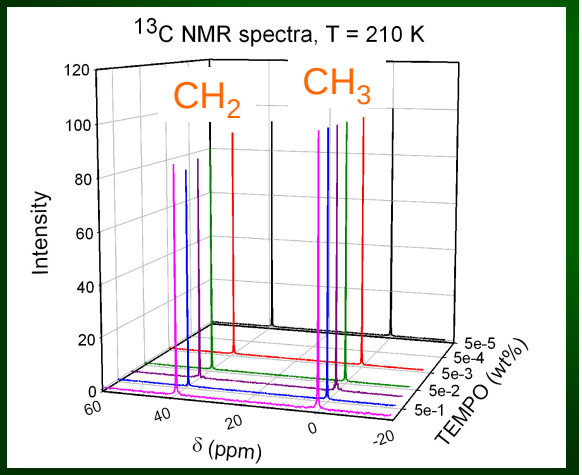
### Spectra $^1$H at 210K – all samples

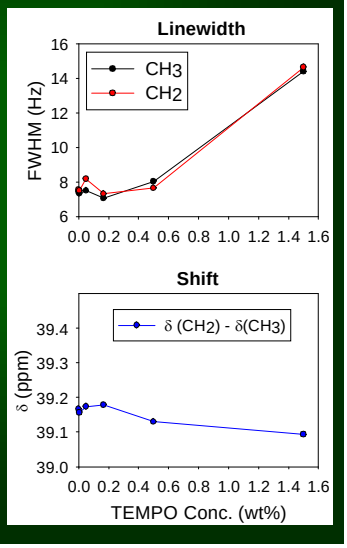


# Results

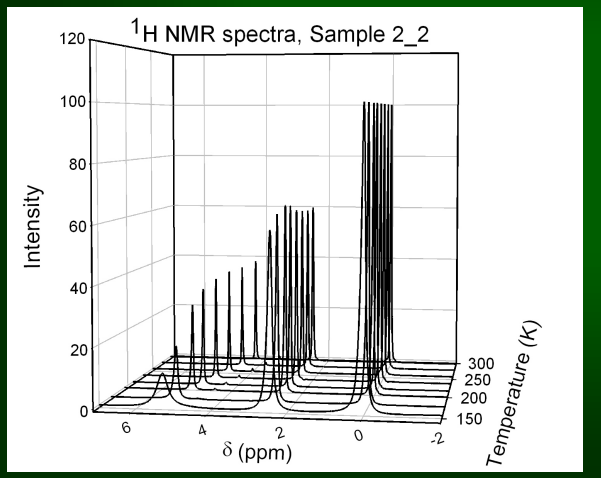
## Spectra $^{13}C$ at 210K – all samples

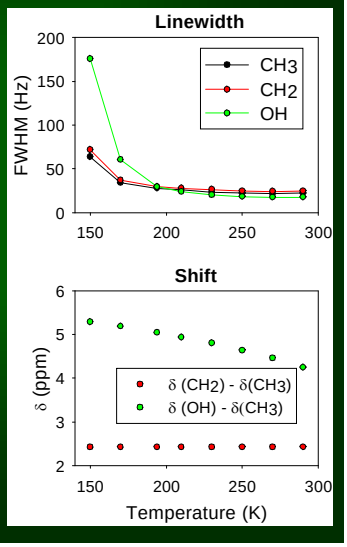



# Results

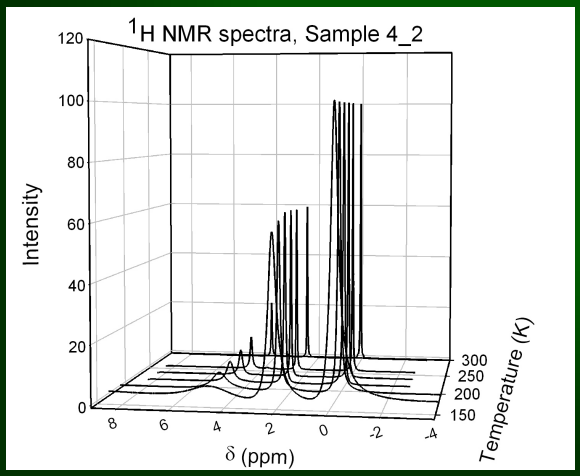
## Spectra $^{1}H$ – sample #2/2 (0.05wt%) at various temperatures

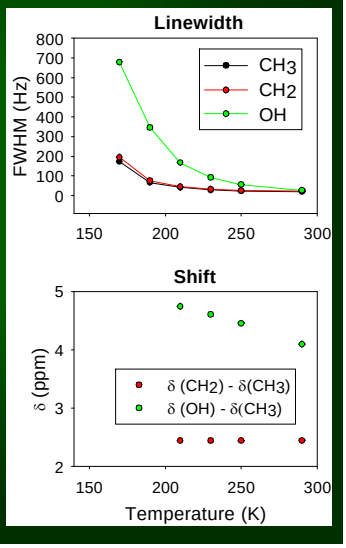


## Results

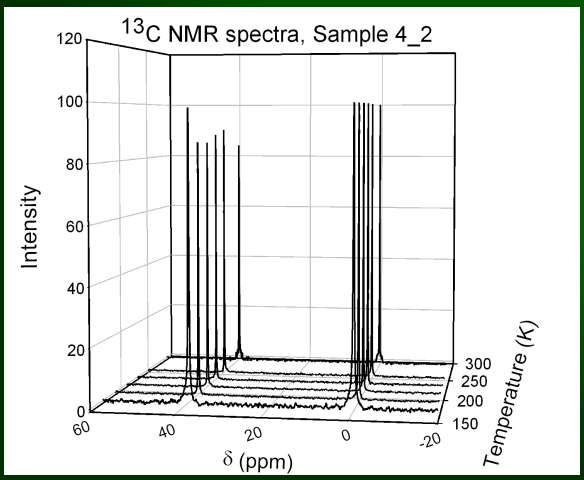
### Spectra $^{1}H$ – sample #4/2 (1.5 wt%) at various temperatures

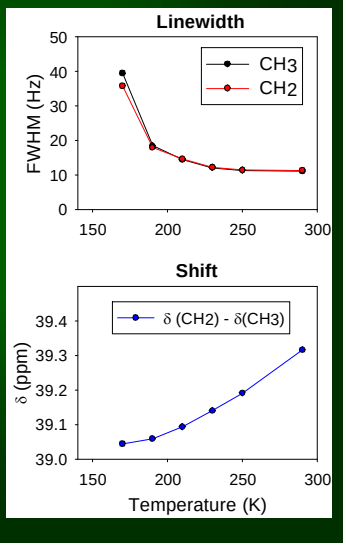



## Results

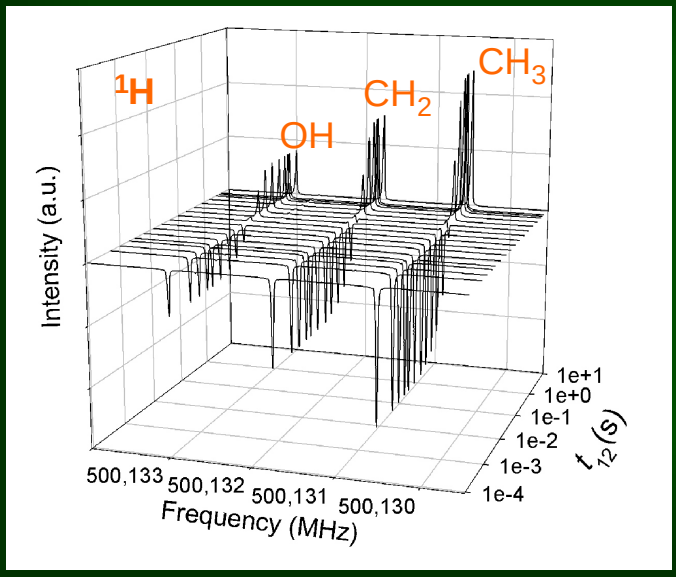
### Spectra $^{13}C$ – sample #4/2 (1.5wt%) at various temperatures



## Results

Inversion recovery - #2/2 (0.05wt%) at 210K




$T_1$ values

$^1$H

OH … 0.14 s

CH2 … 0.65 s

CH3 … 0.69 s

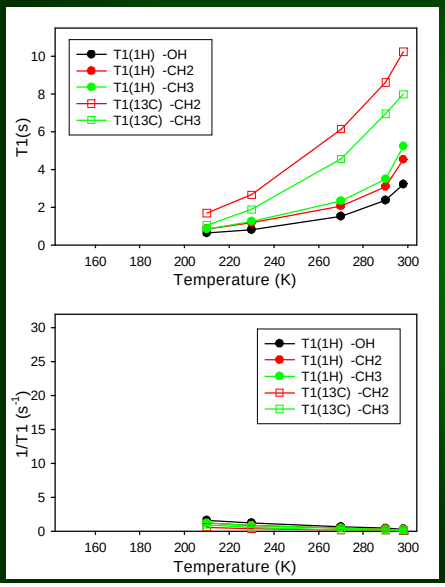
$^{13}$C

CH2 … 1.34 s

CH3 … 0.92 s

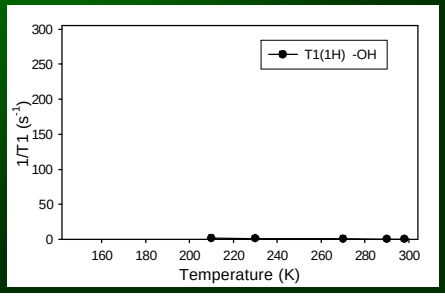
## Results

### Relaxation times and rates



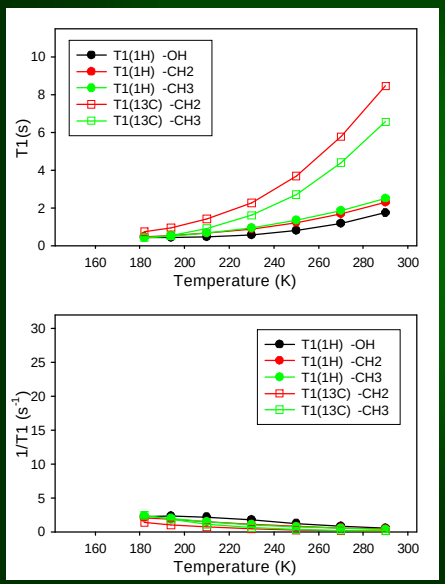

sample: #0/2

**0wt%**



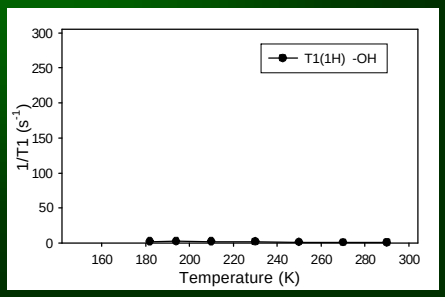
# Results

## Relaxation times and rates



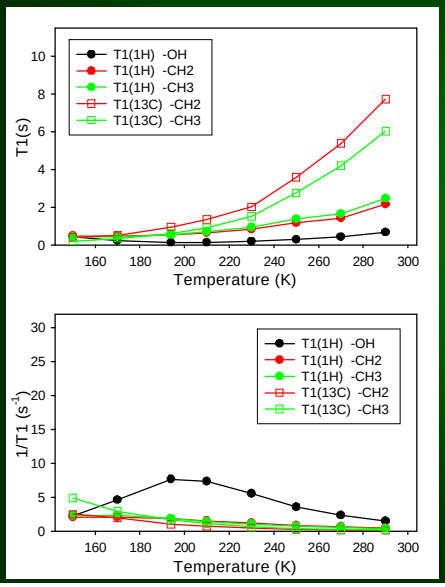

sample: #1/2

**0.005wt%**



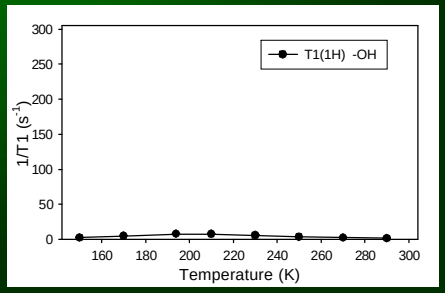

# Results

## Relaxation times and rates



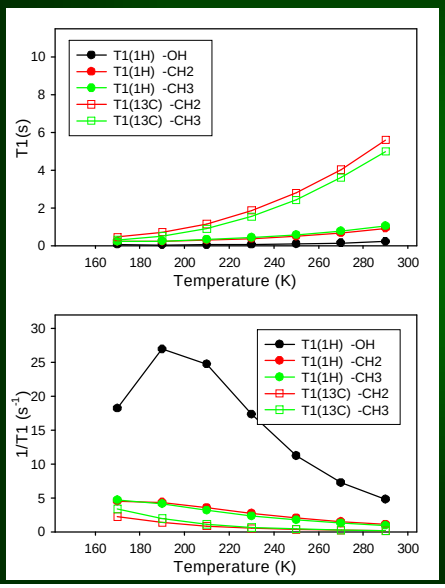

sample: #2/2

**0.05wt%**



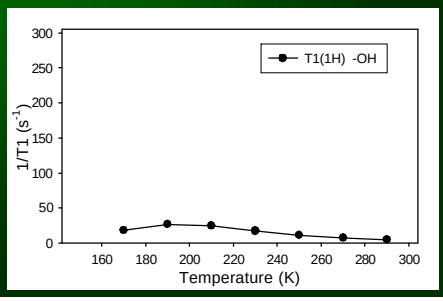
# Results

## Relaxation times and rates



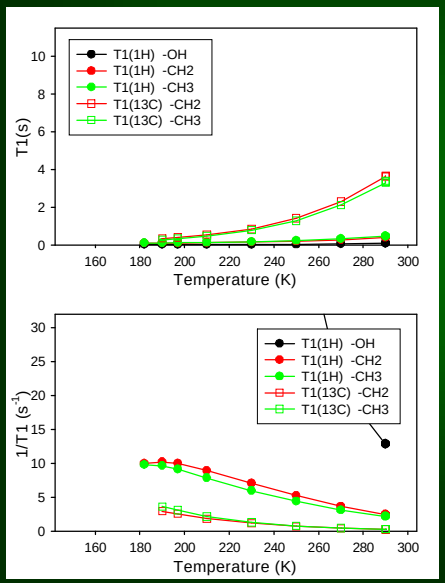

sample: #5/2

**0.167wt%**



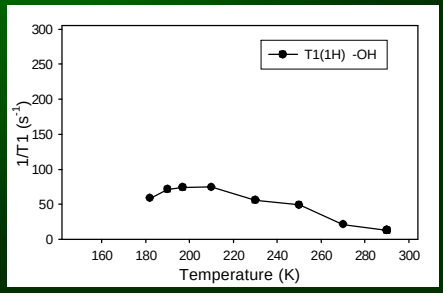

# Results

## Relaxation times and rates



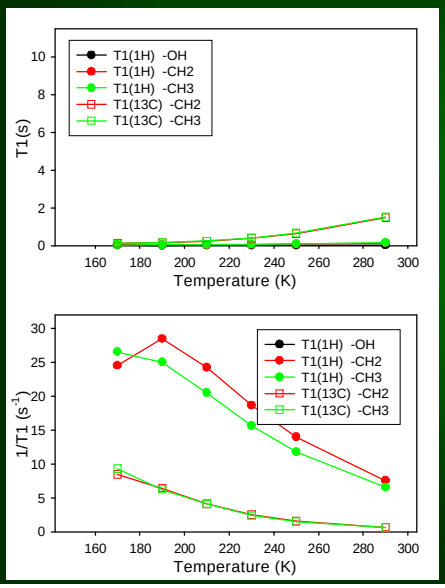

sample: #3/2

**0.5wt%**



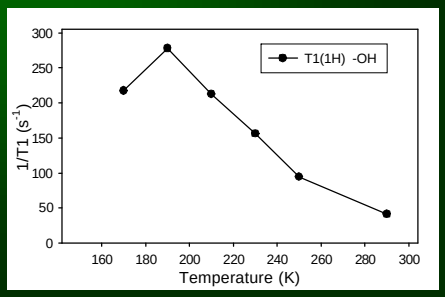
# Results

## Relaxation times and rates




sample: #4/2

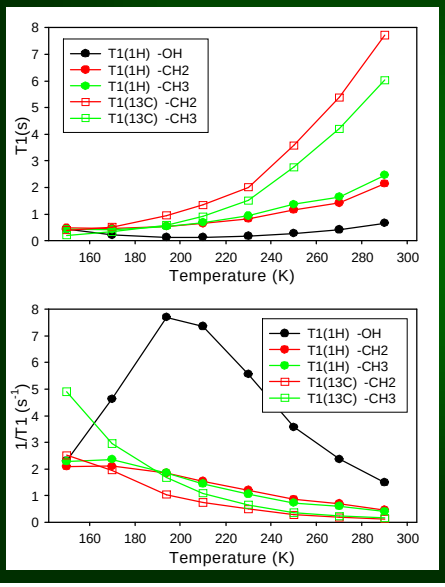
**1.5wt%**



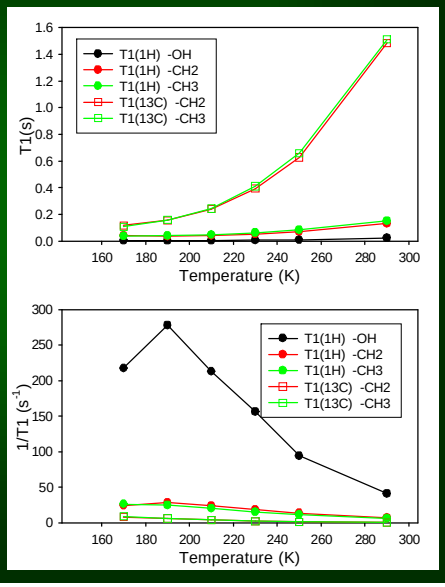

# Results

## Relaxation times and rates

**0.05wt%**



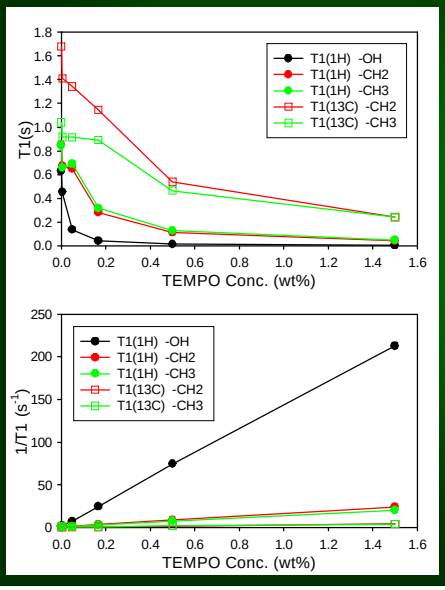

**1.5wt%**



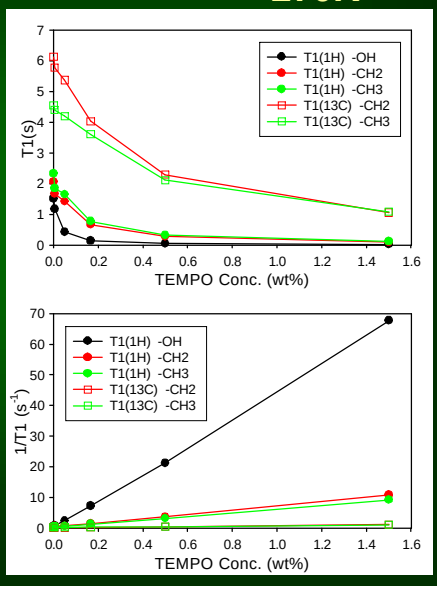
## Results

### Relaxation times and rates

**210K**




**270K**




## Summary

- **Strong and linear dependence of proton and carbon relaxation rates $T_1^{-1}$ of ethanol on TEMPO concentration**
- **Strong dependence of relaxation rates $T_1^{-1}$ on temperature, maximal proton relaxation rate at ~200K**
- **Besides the relaxation rates the doping affects also chemical shift and linewidth**
- **The most pronounced effect of doping is seen for OH protons – a role of hydrogen bonds between OH group of ethanol and the oxygen of TEMPO**