*Polarised Nucleon Targets for Europe, 3rd meeting, Rech 2006*

# Prague NMR activities

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- NMR in alcohols with TEMPO, liquid state

  (analysis of $^{1}H$, $^{13}C$ relaxations in ethanol +TEMPO solutions)

- On the way to lower temperatures (solid state)

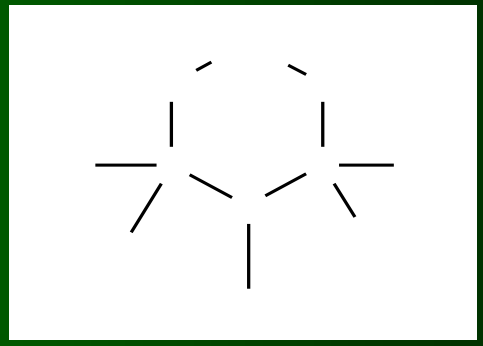
# Ethanol + TEMPO, high resolution NMR in solution

**Interactions between electron and nuclear spins:**

- are known to achieve high polarization of the nuclear spin system in processes of dynamic nuclear polarization
- give rise to effective relaxation mechanisms for excited nuclear spins

**Stable nitroxyl radicals:**

- spin labels for ESR experiments
- paramagnetic probe in NMR



**Ethanol:** interesting from the point of view of

- molecular structure and dynamics,
- forming and properties of intermolecular hydrogen bonds in polar liquids (water, simple alcohols)

# Ethanol + TEMPO, high resolution NMR in solution

NMR spectra and spin-lattice relaxations $T_1$ in the liquid state

*- first experimental results reported previously*

NMR BRUKER AVANCE 500 pulse spectrometer

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

six samples with 0 -1.5 wt% of TEMPO in $CH_3CH_2OH$

temperature range 160-290 K

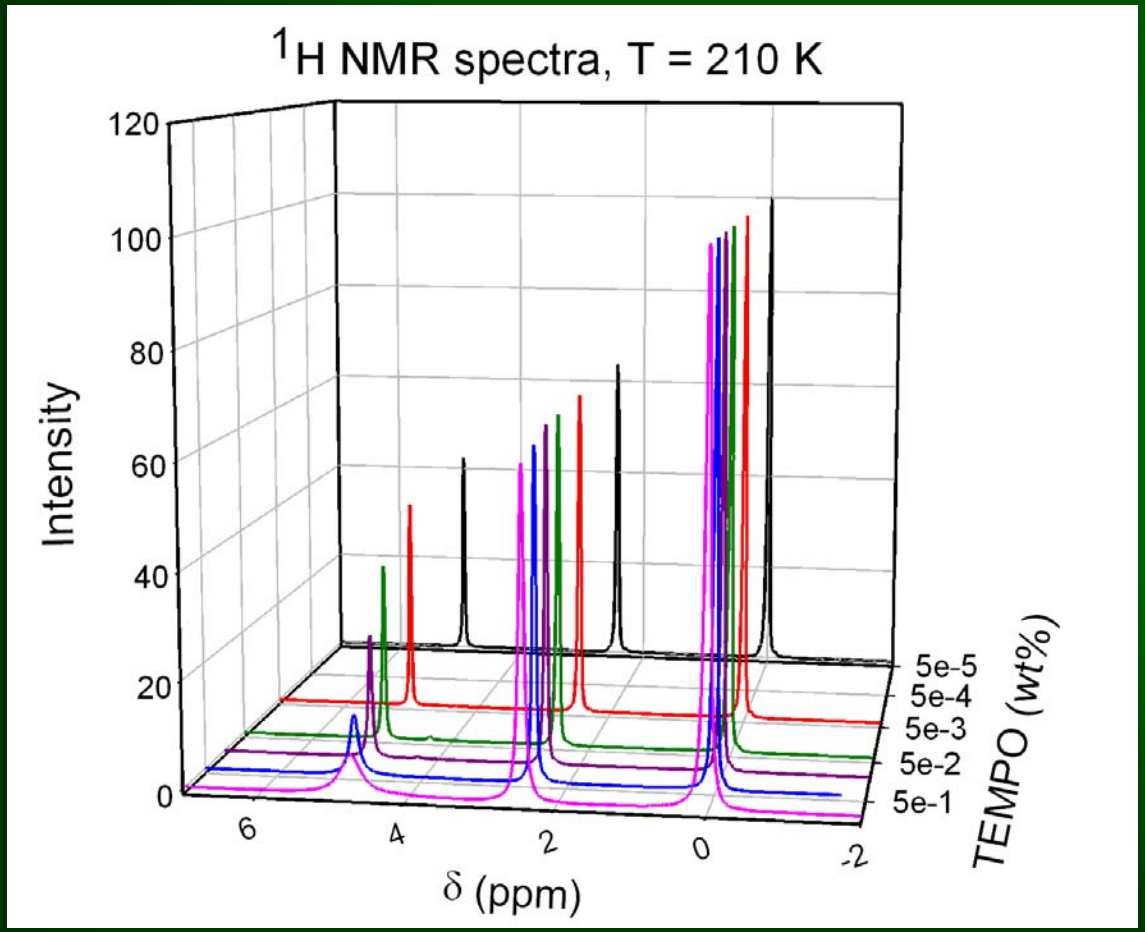
NMR of ethanol:

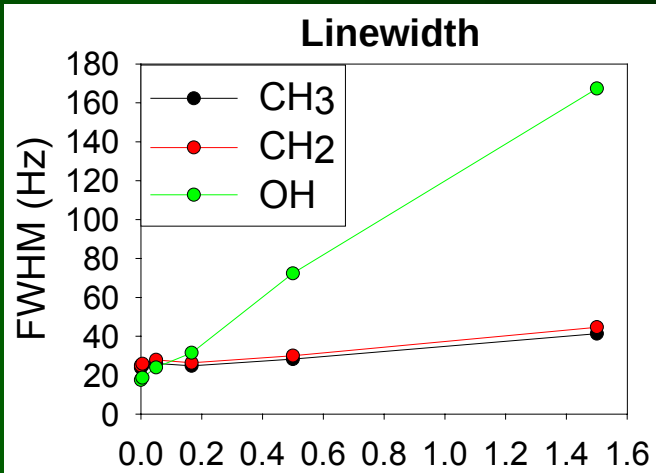
$^{1}H$ spectra: 3 signals

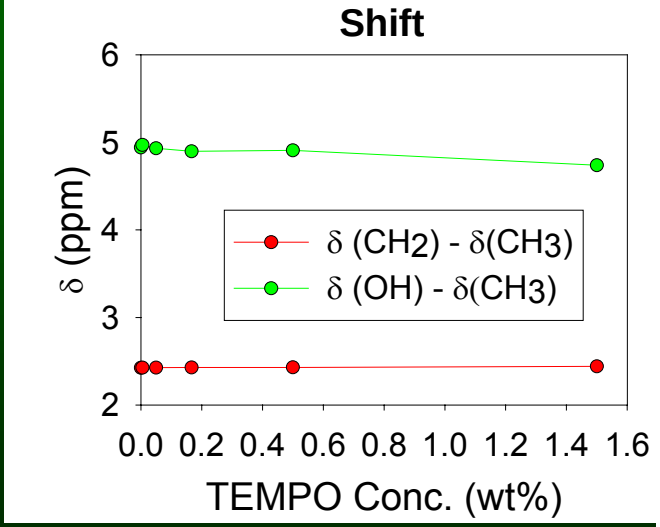
$^{13}C$ spectra: 2 signals

# Ethanol + TEMPO, high resolution NMR in solution

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

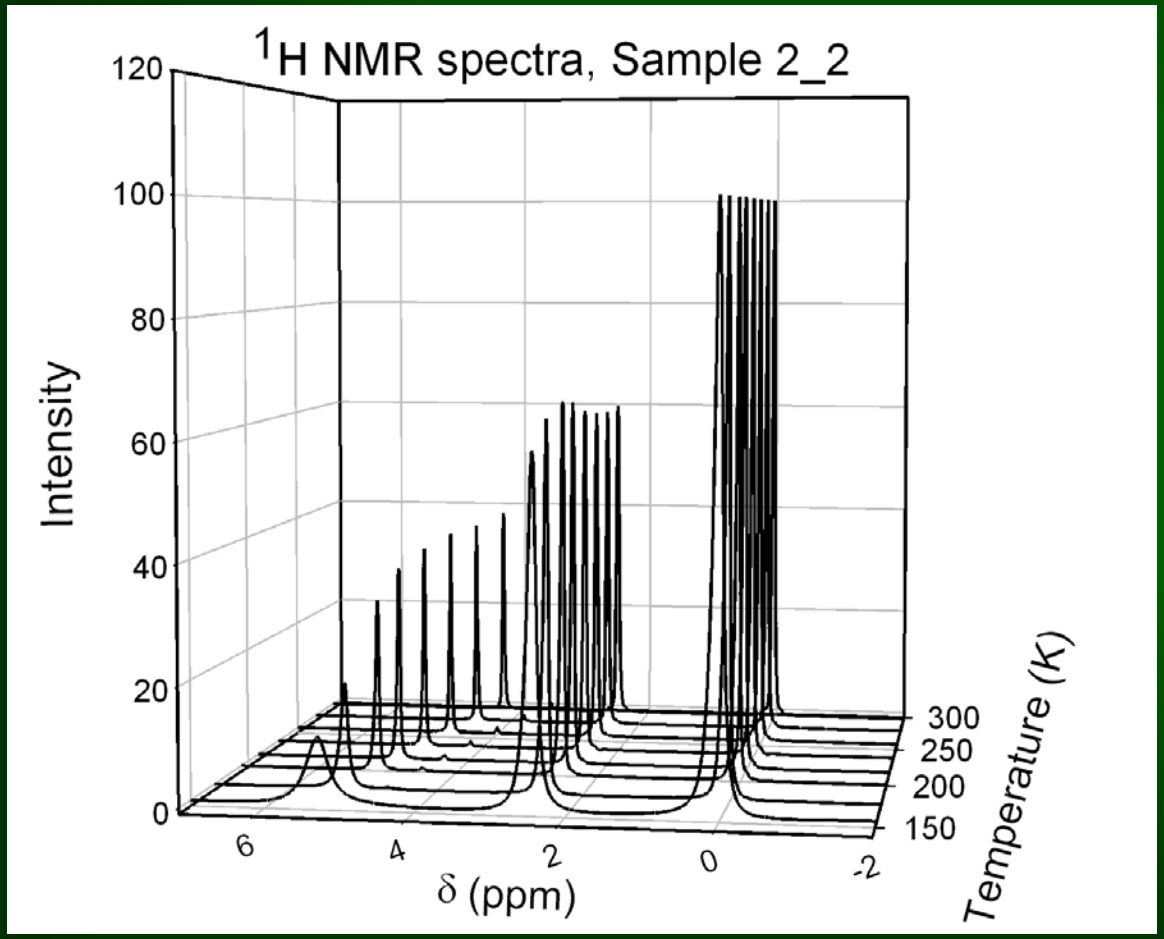


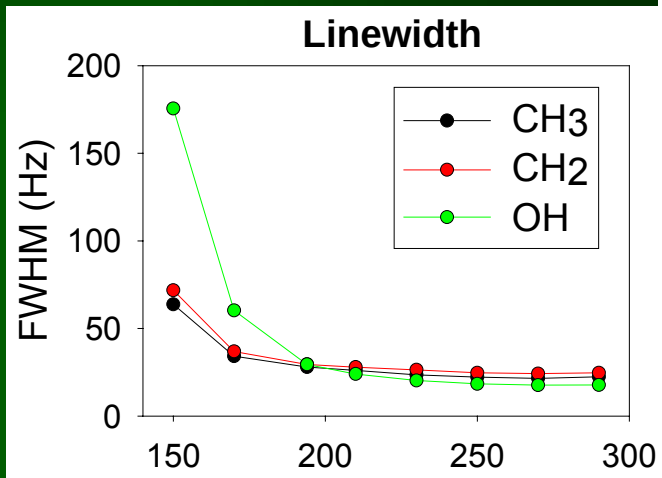



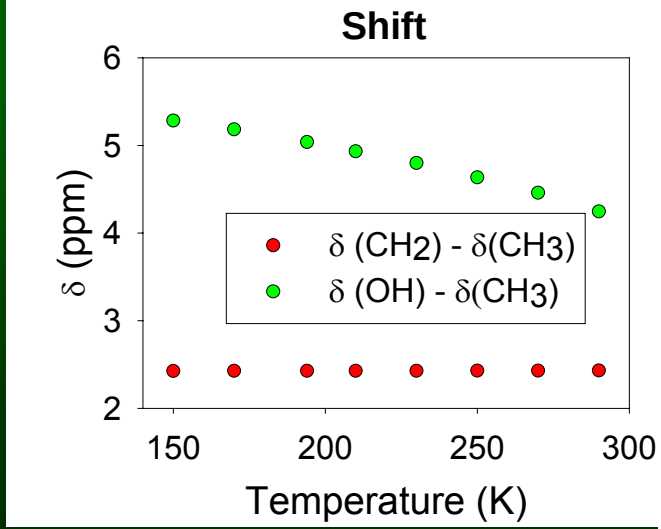



# Ethanol + TEMPO, high resolution NMR in solution

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

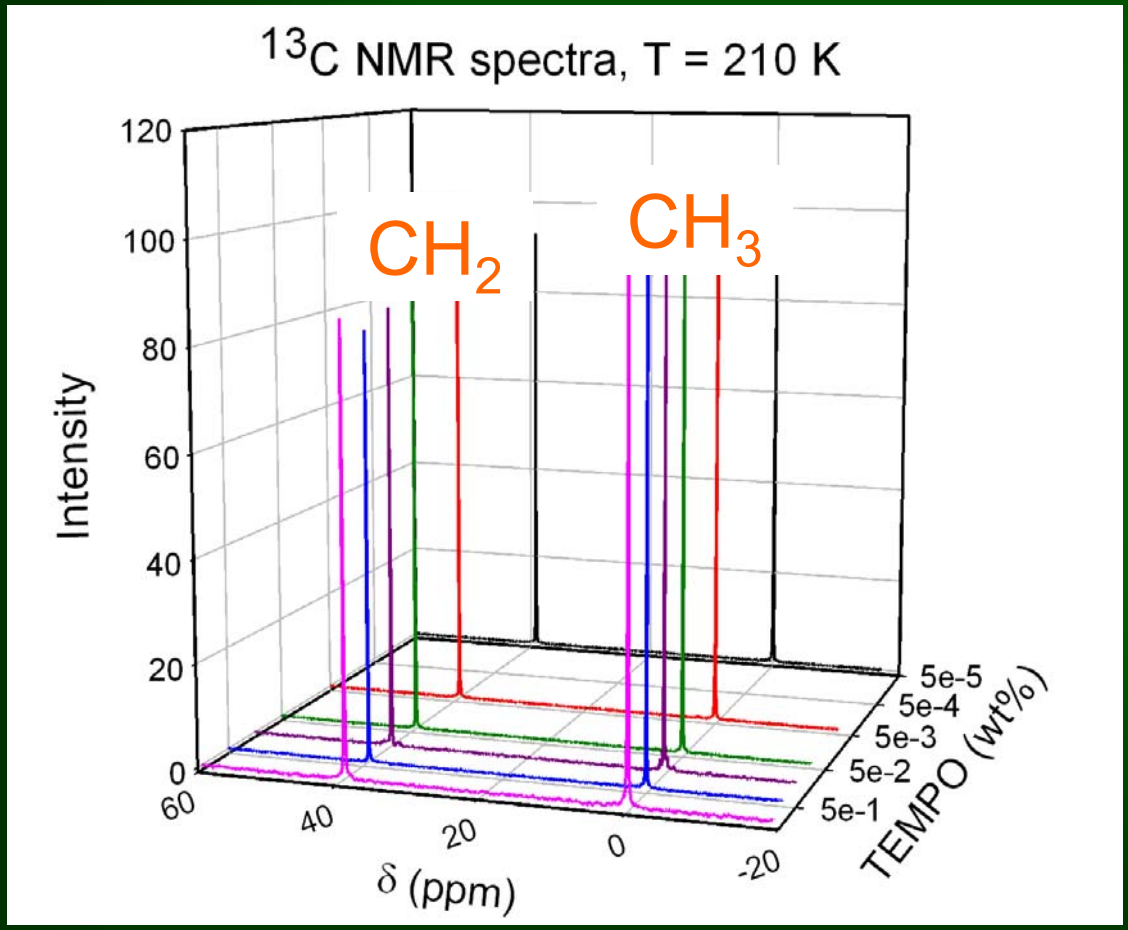


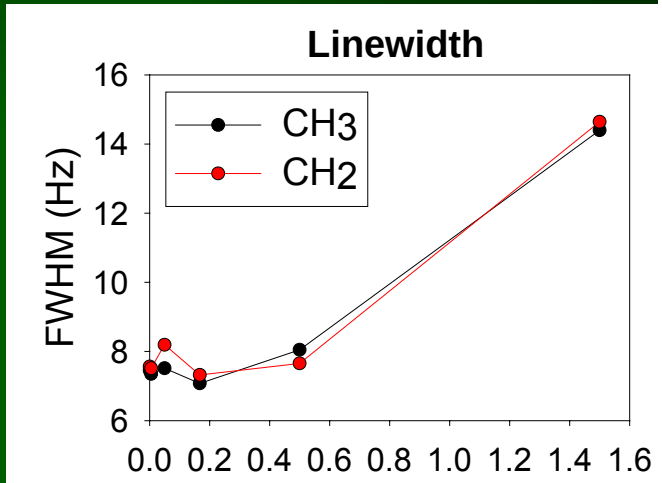



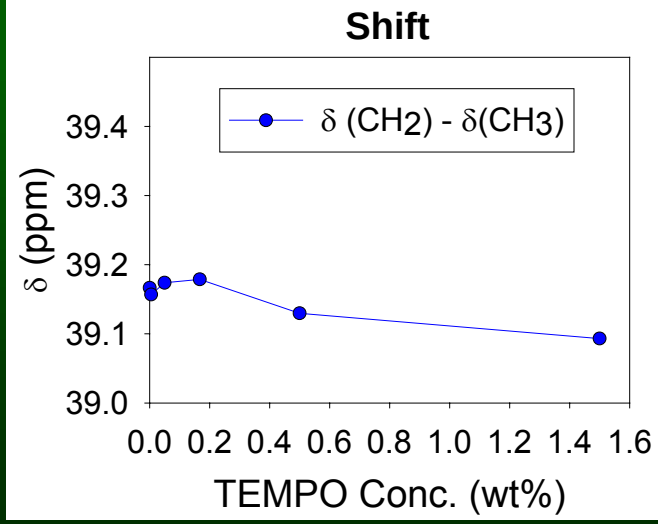



# Ethanol + TEMPO, high resolution NMR in solution

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

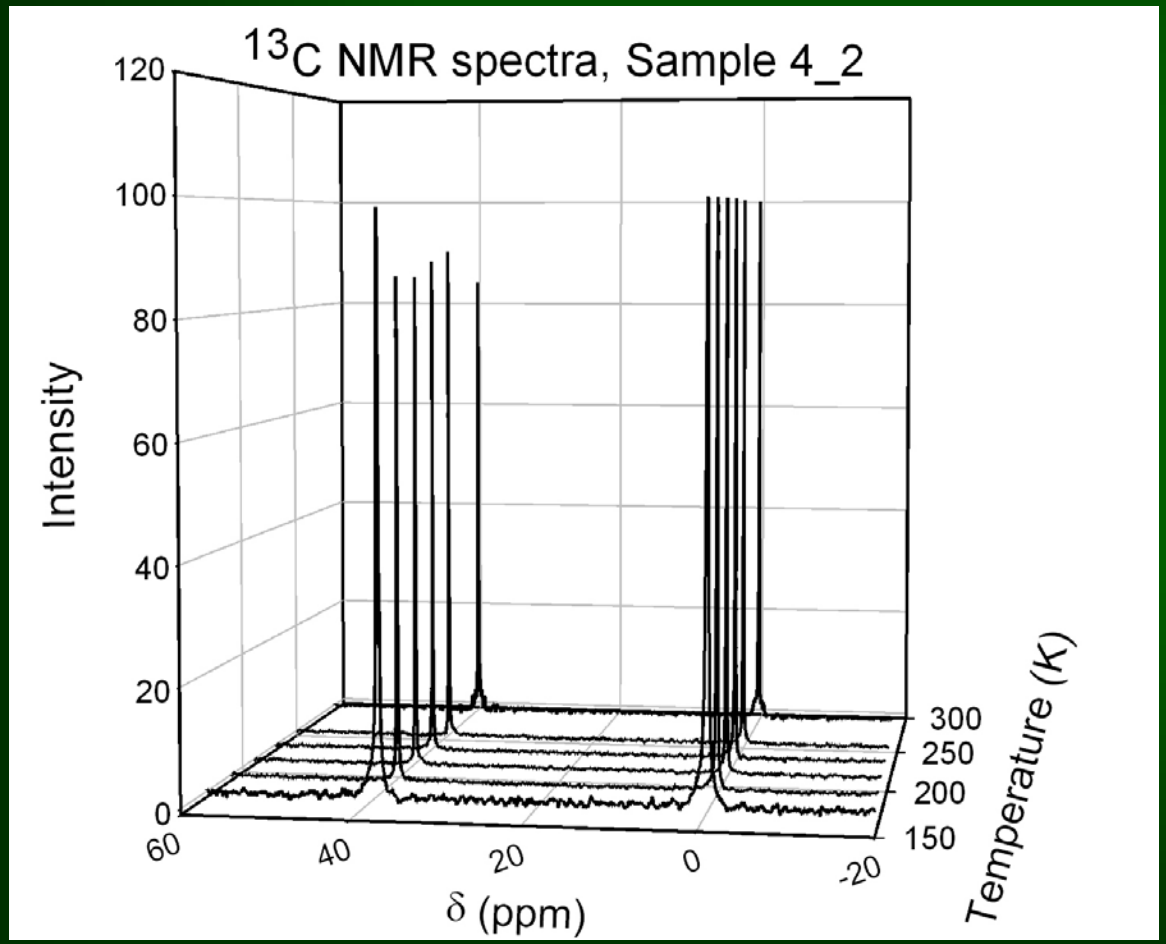


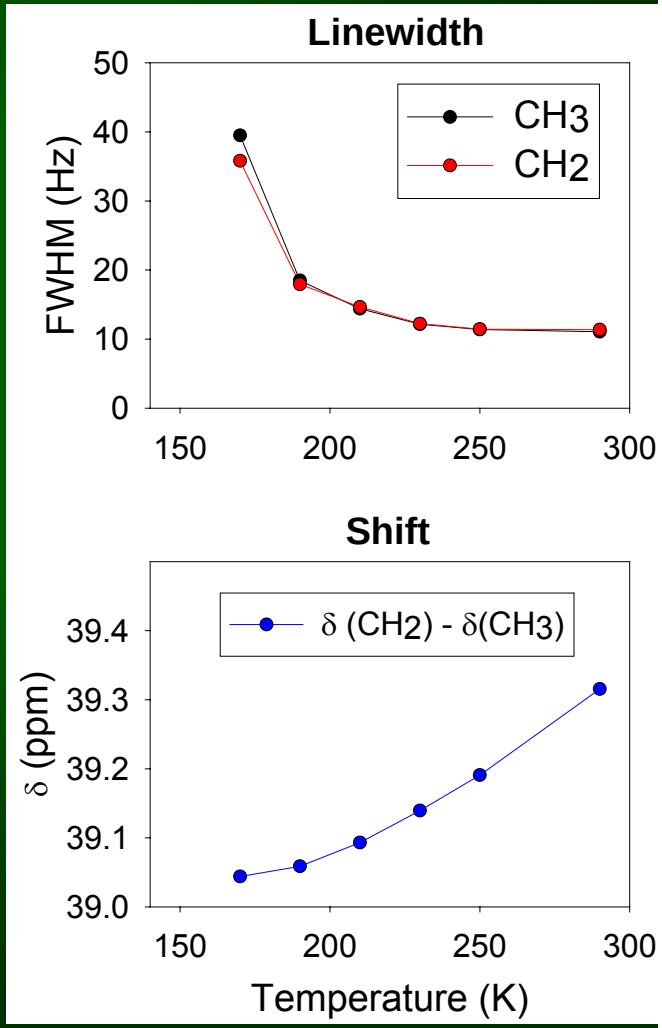



# Ethanol + TEMPO, high resolution NMR in solution

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



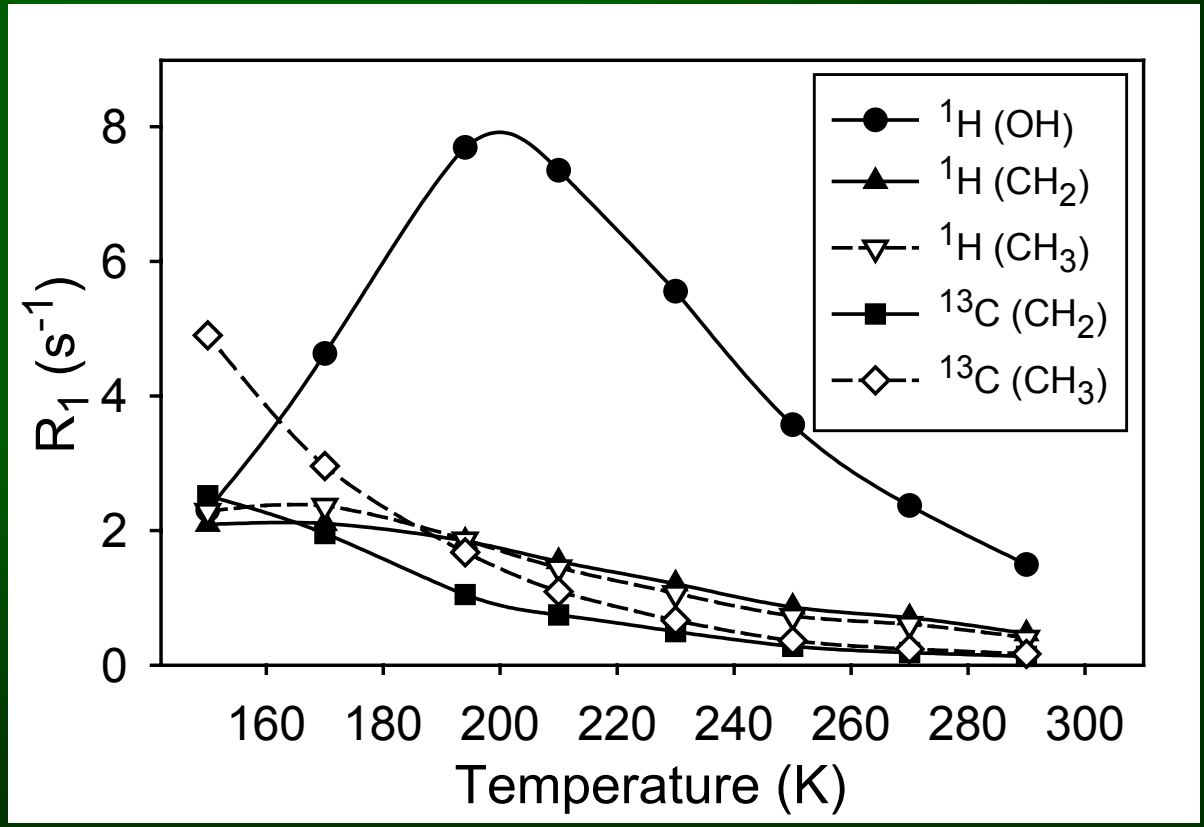



# Ethanol + TEMPO, high resolution NMR in solution

**Relaxation rate $R_1 = 1/T_1$**

Strong dependence of proton and carbon relaxation rates on temperature, maximal OH-proton relaxation rate at ~200K

0.05 wt% of TEMPO

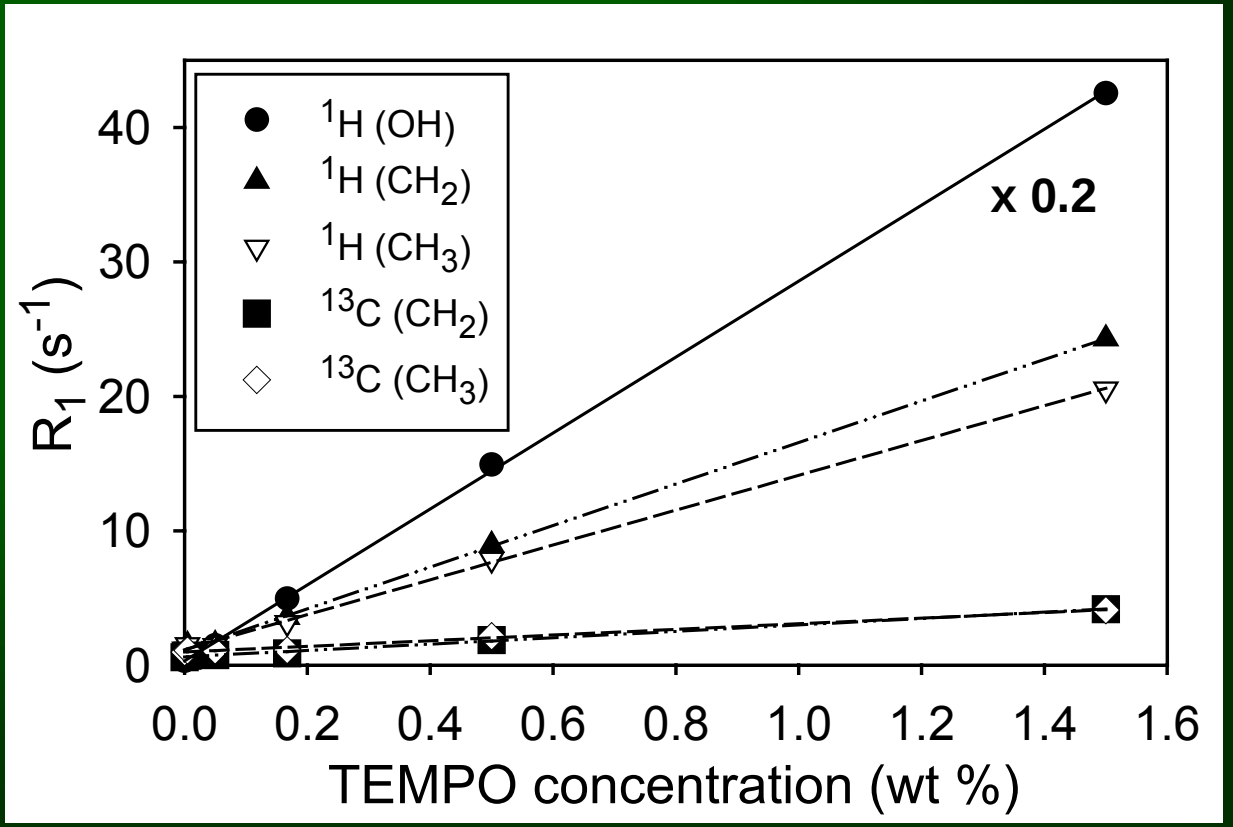


# Ethanol + TEMPO, high resolution NMR in solution

## Relaxation rate $R_1 = 1/T_1$

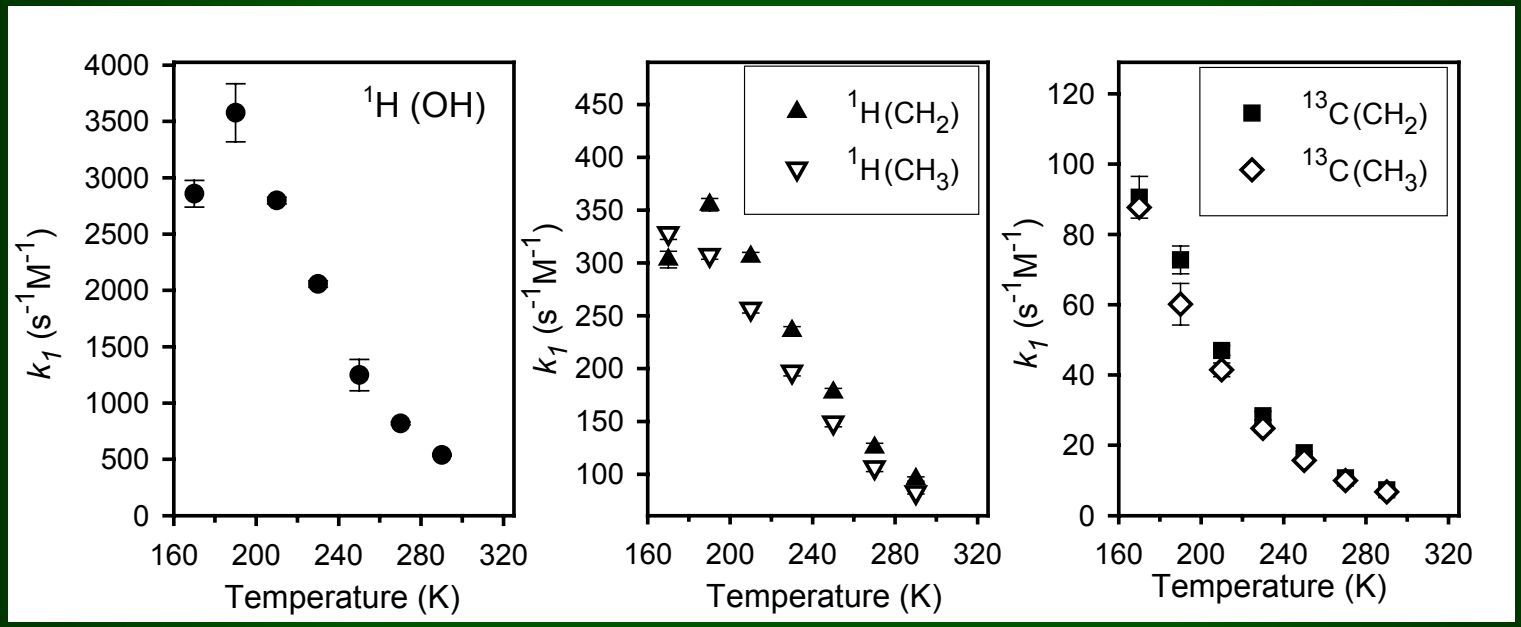
Strong and linear dependence of proton and carbon relaxation rates of ethanol on TEMPO concentration

210 K



# Ethanol + TEMPO, high resolution NMR in solution

**Relaxation enhancement** $k_1 \equiv dR_1/d(\textit{concentration})$




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

# Ethanol + TEMPO, high resolution NMR in solution

## Mechanisms of nuclear relaxation enhancement

**Fluctuating magnetic interactions between nuclear (ethanol) and electron (TEMPO) spins:**

- Dipolar interaction modified by motion
  - translational diffusion
  - rotational diffusion (of complex)

- Contact interaction

Particular models; approximations.
Concentration, temperature, field dependences.
(NMRD... dispersion of nuclear magnetic relaxation rates)

# Ethanol + TEMPO, high resolution NMR in solution

## Translational diffusion

*Force free (FF) model for motion (excluded volume).*
*Long electron spin correlation time.*

$$k_1 = \frac{32\pi}{405}\,\frac{\hbar^2\gamma_S^2\gamma_I^2 N_a S(S+1)}{1000\,d\,D}\left(7J(\omega_S)+3J(\omega_I)\right),$$

where the spectral density function is given by $J(\omega)$:

$$J(z) = \frac{1+5z/8+z^2/8}{1+z+z^2/2+z^3/6+4z^4/81+z^5/81+z^6/648}; \quad z_n = \sqrt{2\,\omega_n\,\tau_D}$$

translational diffusion correlation time $\tau_D = d^2/D$

$D = D_{ethanol} + D_{TEMPO}, \quad D_i = k_B\,T/6\,\pi\,a_i\,\eta$

$D_i$ ... translation - diffusion coefficients

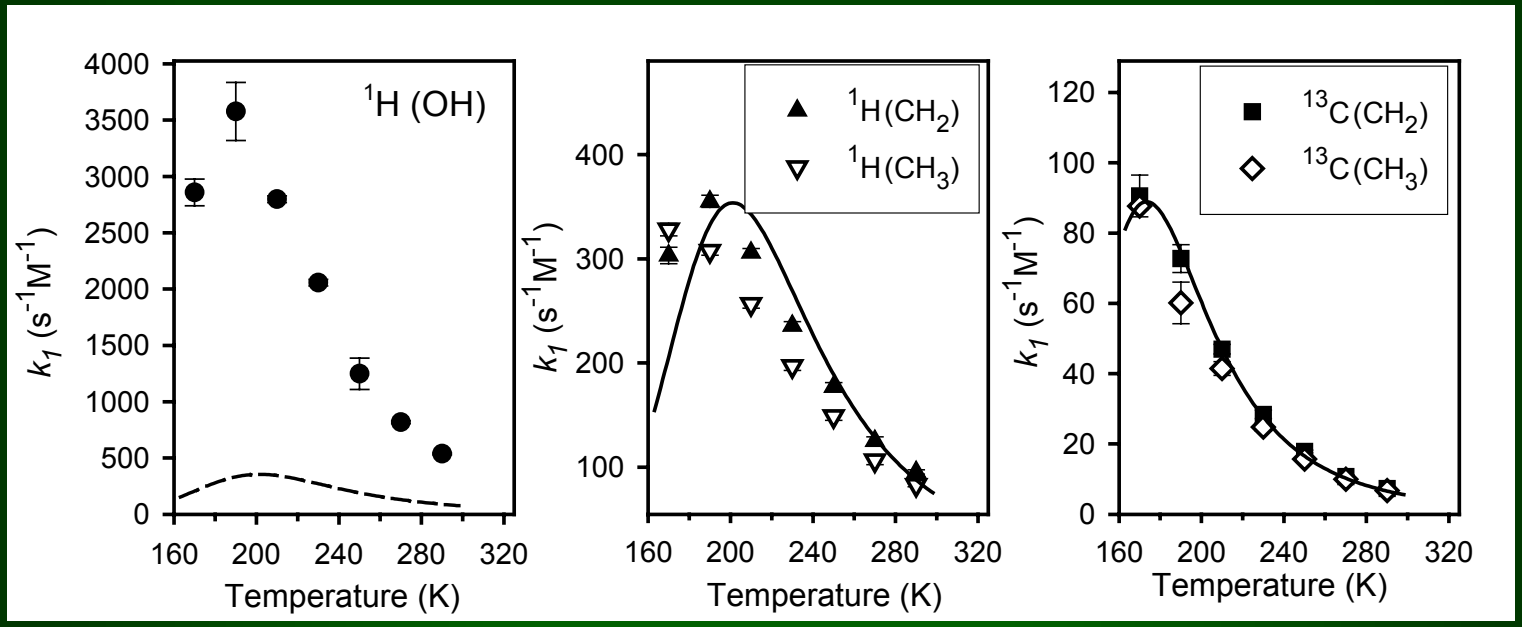
$d$ ... distance of the closest approach

$a_i$ ... size of the i - molecule (its dynamic radius)

$\eta$ ... viscosity of the liquid ($\tau_D$ is proportional to $\eta$/T)

# Ethanol + TEMPO, high resolution NMR in solution

## Relaxation enhancement $k_1 = dR_1/d(concentration)$

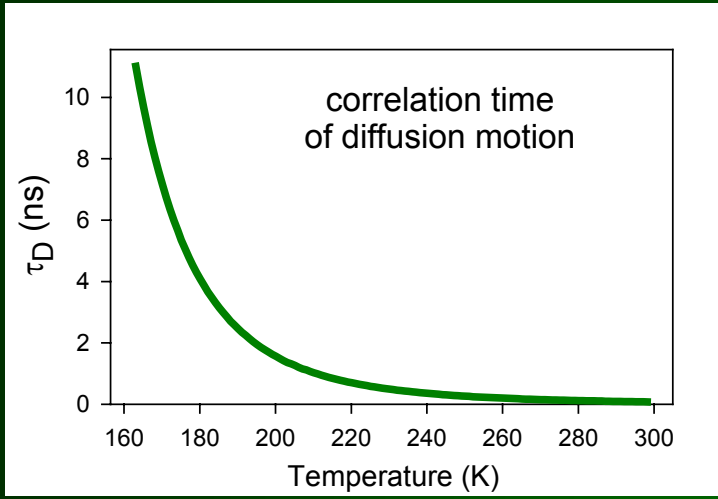


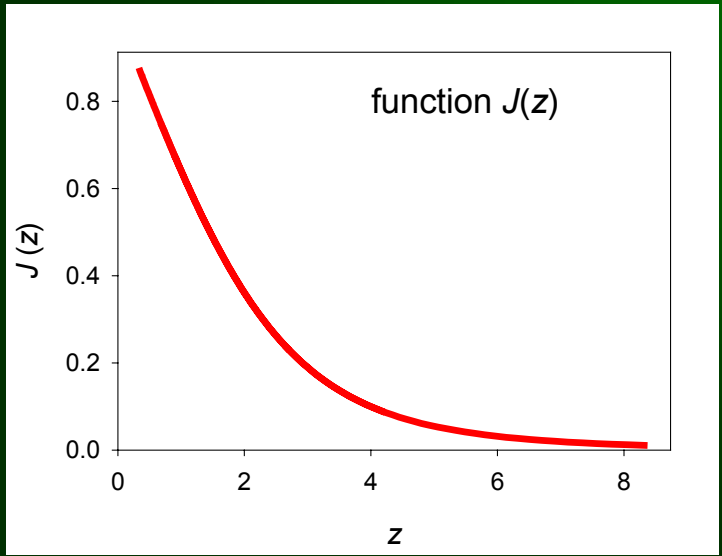

- We made a fit of $k_1$ (translation diffusion) for protons except the 1H(OH) and for carbon nuclei, using common free parameters.
- Reasonable agreement for relaxations of $^{13}$C, $^1$H(CH$_2$) and $^1$H(CH$_3$) in the region of temperatures above ~ 210K.
- The optimized values of the free parameters

  $d$ = 0.40 nm , $\zeta \equiv a_{ethanol}\, a_{TEMPO} / (a_{ethanol} + a_{TEMPO})$ = 0.12 nm.
- The diffusion-controlled regime could be dominant for the relaxation enhancement of carbon nuclei and protons in ethanol except the OH group.

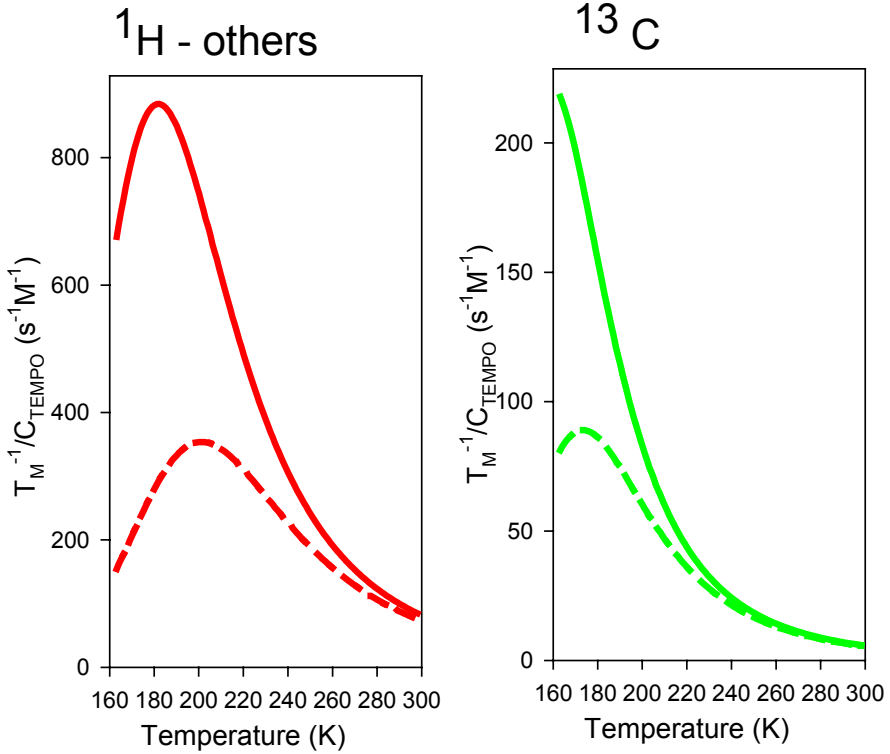
# Ethanol + TEMPO, high resolution NMR in solution

## Translational diffusion




Comparison of fitted slopes $k_1$ for 500 MHz (dashed lines) and predicted for 200 MHz (solid lines) spectrometers (FF model)



# Ethanol + TEMPO, high resolution NMR in solution

## Rotational diffusion

$$k_1 = \frac{2}{15}\frac{\hbar^2\gamma_S^2\gamma_I^2 n\, S(S+1)}{b_r^6[I]}\left(7J(\omega_S)+3J(\omega_I)\right),$$

where the spectral density function $J(\omega)$ is :

$$J(\omega) = \frac{\tau_R}{1+\omega^2\tau_R^2};$$

rotational diffusion correlation time $\tau_R = \frac{4\pi\eta a^3}{3kT}$

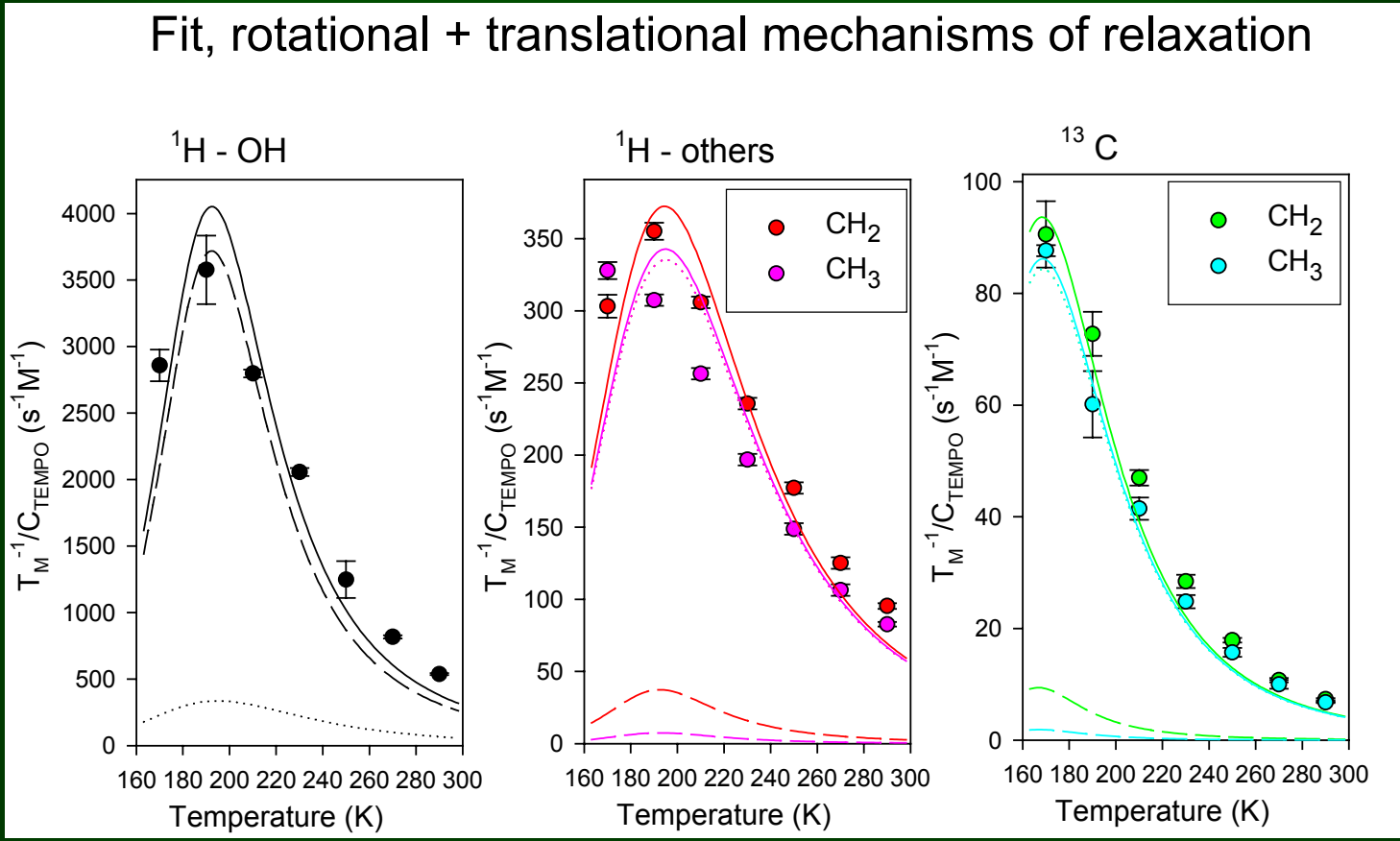
$b_r$... distance between the $I$ and $S$ spins

$[I]$... molar concentration of the $I$ spins

($\tau_R$ is proportional to $\eta$/T)

# Ethanol + TEMPO, high resolution NMR in solution

## Rotational and translation diffusion




Anisotropic motion? Internal motions?

# Ethanol + TEMPO, high resolution NMR in solution

*Outlook:*

- Relaxation models
- Dependence on frequency
- Chemical shifts interpretation
- Other alcohols/radicals
- Non polar solvents
- Adding water
- Changing viscosity
- Deuterated solvents
- Technical questions

# Laboratory views

May/June 2005
New NMR laboratories
in a new pavilion

# Lower temperatures (solid state)

- 200 MHz NMR spectrometer (homemade): new hardware components and software

# Lower temperatures (solid state)

- 5 T cryomagnet, cryoshimms (homogeneity ~$10^{-5}$) 57 mm bore

# Lower temperatures (solid state)

- 5 T cryomagnet, cryoshimms (homogeneity ~$10^{-5}$) 57 mm bore

# Lower temperatures (solid state)

- Helium gas continuous flow cryostat Janis,
  2 - 400K

# Lower temperatures (solid state)

- Nitrogen liquid cryostat (77 K) Vakuum Praha

# Lower temperatures (solid state)

- NMR tunable probe for protons designed, made and tested

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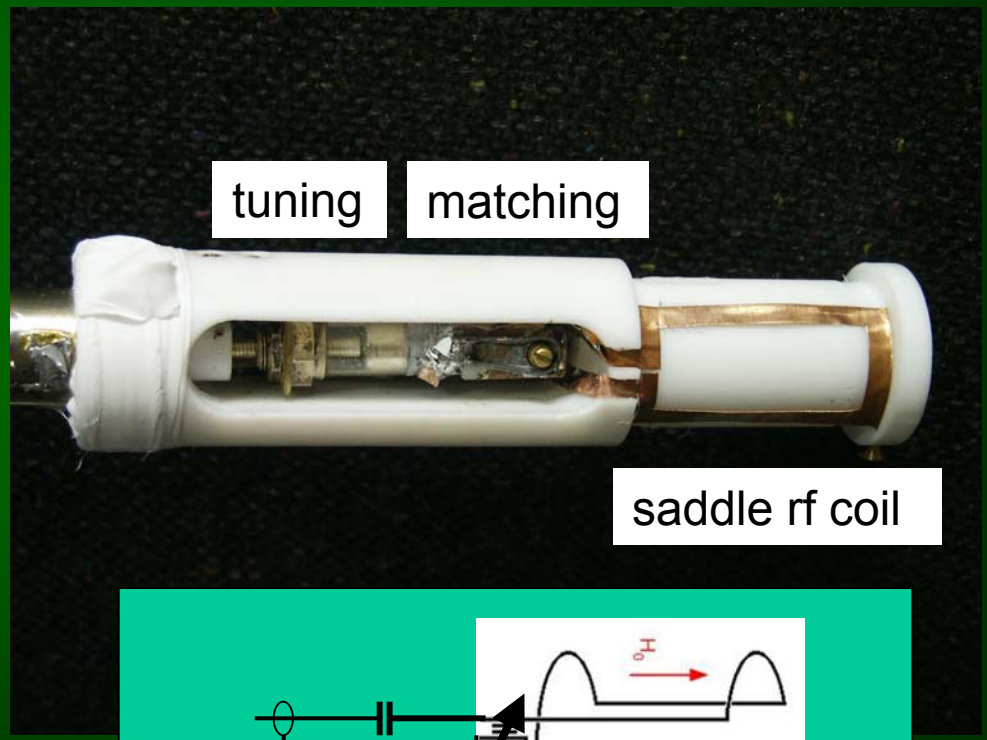
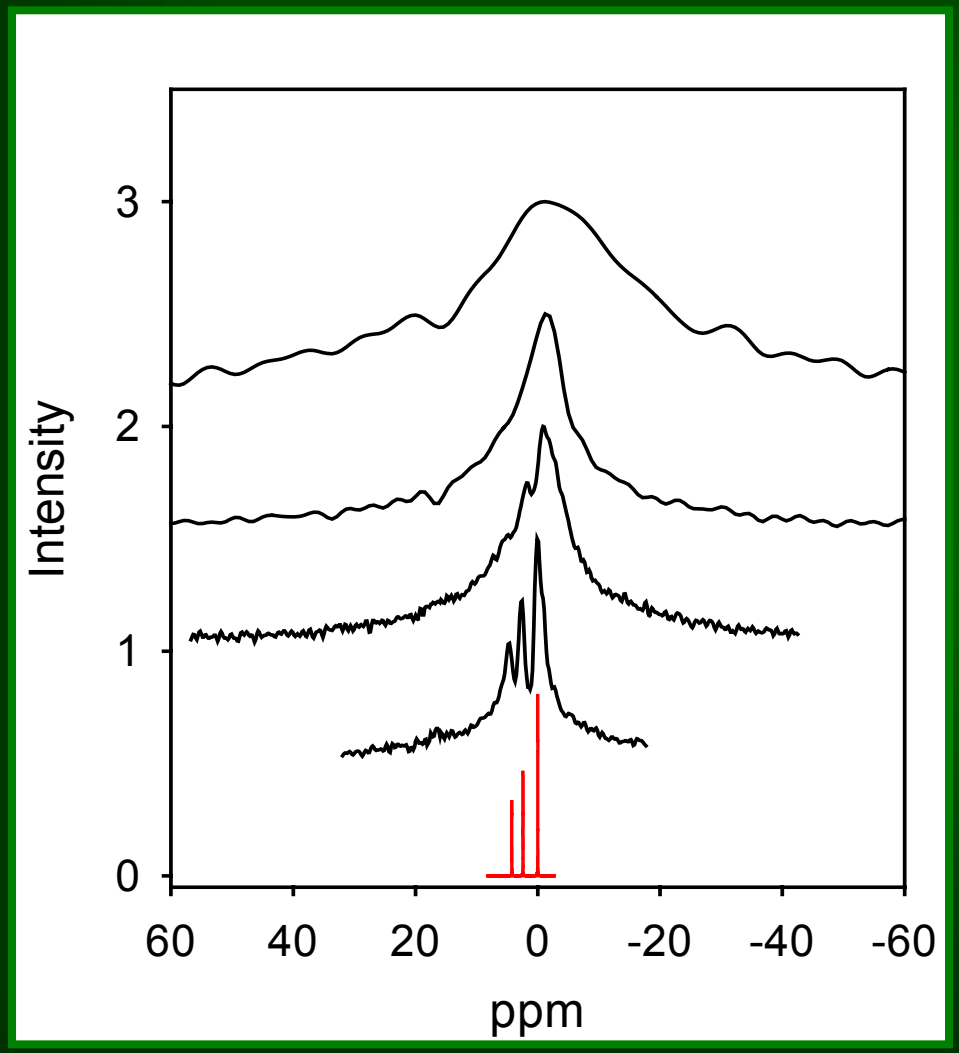


# Lower temperatures (solid state)

- Installation of a new cryomagnet 9.4 T (400 MHz)
  cryoshimms
  (homogeneity ~$10^{-5}$)
  52 mm bore

# Lower temperatures (solid state)

Test of the new facilities: $^{1}$H NMR spectra in ethanol




Decreasing temperature

300 K, 200 MHz

290 K, high resolution spectrum 500 MHz

# Lower temperatures (solid state)

*Outlook:*

- ♣ Technical questions
- ♣ Cooling regime:

*complicated thermal properties of ethanol - polymorphic forms*

- $T_{melt}$=159 K crystal I (monoclinic)
- supercooled liquid →

  → $T_g$=97 K glassy liquid (extremely rapid chilling);
- supercooled liquid →

  → $T'_{melt}$=127.5 K metastable crystal II (cubic, 'plastic',molecules rotate) →

  → $T'$g=97 K glassy crystal II (molecules frozen at random orientation)

- ♣ Relaxation models, structural and motional dependent, embedded TEMPO
- ♣ Deuterated ethanols

# Lower temperatures (solid state)

*Outlook:*

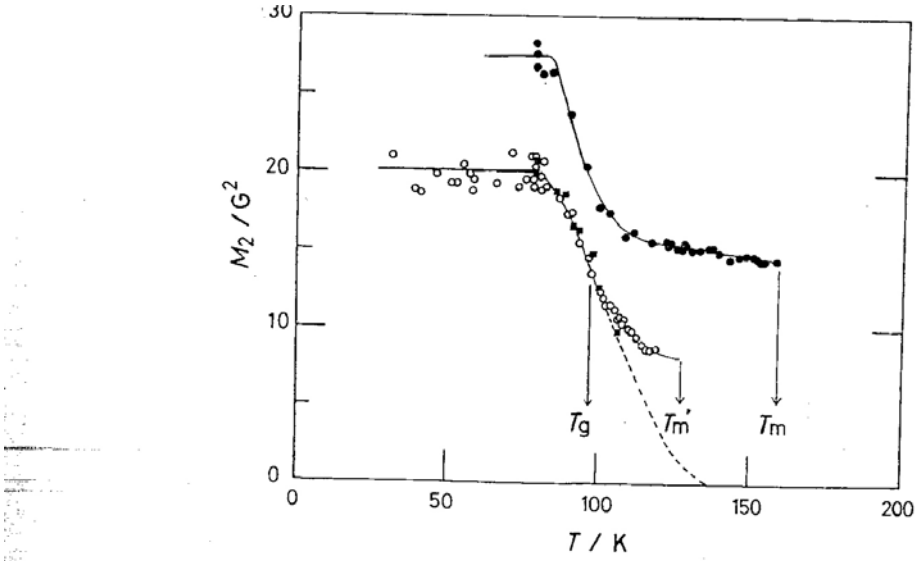



Figure 2. The temperature dependence of the second moments of the proton resonance line in ethanol. ●, Crystal I ; ○, Crystal II and glassy Crystal II ; ■, supercooled liquid and glassy liquid ; – – –, expected line in supercooled liquid.

*T. Eguchi et al.*