

# Relaxation Processes and Constraints on Distance Measurements

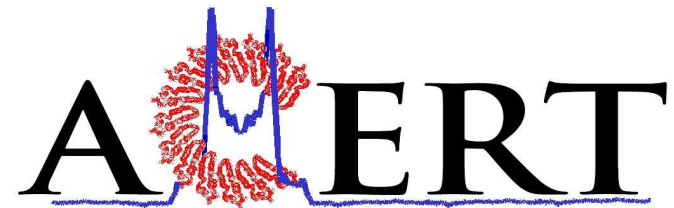
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# Scope

- Why should you care about relaxation times?
- Solids and frozen solutions
  - Spin echo decays
    - Spin diffusion
  - Spin-lattice relaxation
    - Relaxation processes and mechanisms
    - Results for metals and organic radicals
  - Summary of contributions to  $T_1$  and  $T_m$
  - Summary of relaxation mechanisms
- Fluid solutions
  - Relaxation mechanisms
  - Results for nitroxyl radicals
  - Results for triarylmethyl radicals
- Implications for distance measurements

# Why understanding of relaxation is important for distance measurements

$T_1$

- Affects the temperature range in which the study can be performed.
- Limits pulse repetition rates
- Selects for sub-populations
- Identifies optimum frequency for experiment

$T_2$

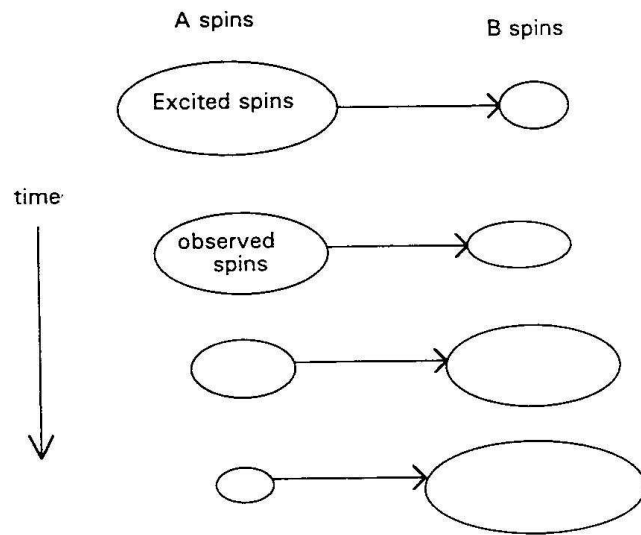
- Determines the time window during which any method based on observation of an echo or FID can be measured.

Understanding the mechanisms of relaxation guides selection of paramagnetic centers to use.

## What can you learn by measuring spin echo dephasing in solids?

- Feasibility of doing pulse experiments that depend upon echo detection
- Local spin concentration
- Librational motion
- Proton spin concentration
- Methyl group types and concentrations
- Dynamic processes that average inequivalent nuclei
- Enhancement of echo dephasing by neighboring fast relaxing spin

# A Spins and B Spins



The spins that are excited in an experiment are called the A spins. All other spins are designated as B spins. As a function of time A spins become B spins due to spectral diffusion, which decreases the number of A spins that can be observed.

# Analysis of Spin Echo Decays

## 1. Fit to a stretched exponential

$$E(2\tau) = \exp\left[-\left(\frac{2\tau}{T_m}\right)^x\right] \quad \text{Eq. (1)}$$

$\tau$  is the time between pulses

$T_m$  is the dephasing time constant

$x$  is a phenomenological parameter that depends on dephasing mechanism

Values of  $x$  are between 0.5 and about 2.5

For nuclear spin diffusion,  $x > 2$

For a process that averages inequivalent environments,  $x$  varies from  $\sim 2$  to 0.5 to 1 as the rate of the process increases.

For instantaneous diffusion  $x = 1$

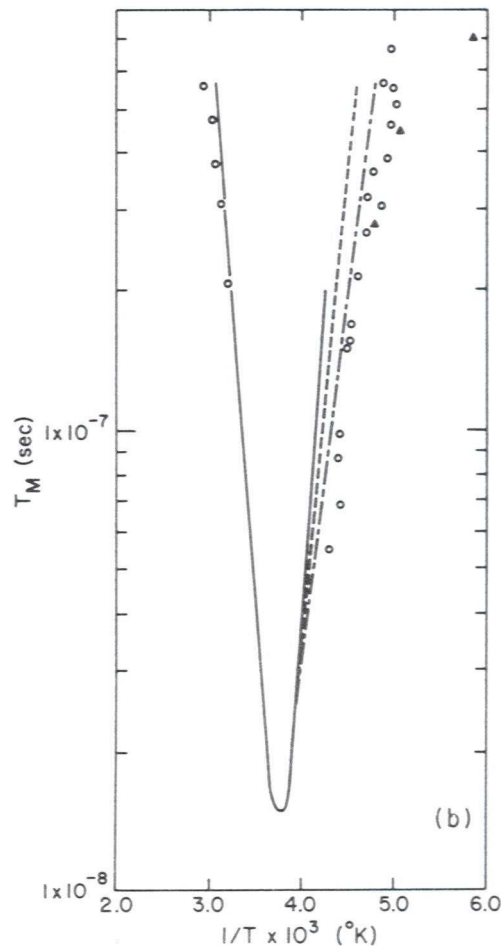
If dephasing is  $T_1$  driven,  $x = 1$

# Analysis of Spin Echo Decays

2. Fit to a model appropriate for a particular dephasing mechanism
  - a. Nuclear spin diffusion
  - b. Dynamic averaging of inequivalent nuclei
  - c. Dipolar interaction with rapidly relaxing metal

# Nitroxyl Radicals – $T_m$

~ 330 K



← Temperature

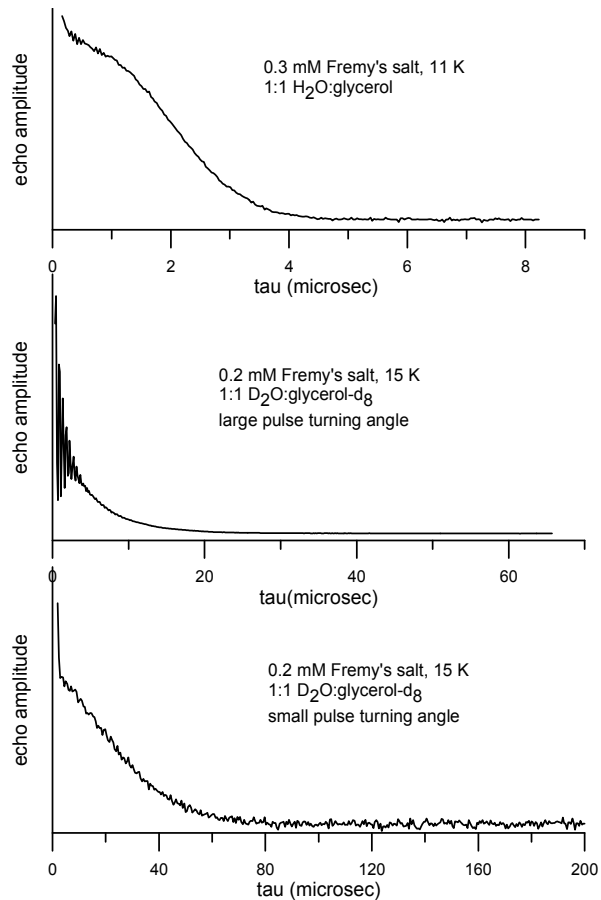
Values of  $T_m$  for tempone in 85% glycerol:15% water obtained by (O) two-pulse spin echo data ( $\Delta$ ) 2D- ESE contour plots. The three lines show the calculated values based on jump diffusion (—), free diffusion (---) and Brownian diffusion (-.-.).

In the intermediate tumbling regime  $T_m$  for a nitroxyl radical is too short to measure by current spin echo techniques.

G. L. Millhauser and J. H. Freed, *J. Chem. Phys.* **81**, 37 (1984).



# Nuclear Spin Diffusion and Instantaneous Diffusion



Protons in the solvent  
dominate dephasing

When protons are replaced  
by deuterons, instantaneous  
diffusion makes a larger  
contribution.

Instantaneous diffusion is  
decreased by making the turning  
angle smaller.

Note the difference in x-axis scales  
for the 3 plots and the much longer  
 $T_m$  in deuterated solvent.

S. S. Eaton and G. R. Eaton, *Biol. Magn. Reson.* **19**, 29 (2000).

# Nuclear Spin Diffusion

Frequently, an unpaired electron is dipolar coupled to many surrounding nuclear spins.

If one of these nuclear spins flips, the dipolar coupling to the unpaired electron is changed, which changes the precession frequency for the unpaired electron.

Although the spin flip rate for an individual nuclear spin is relatively slow, the probability of some nuclear spin flipping is large, because of the large number of nuclear spins in typical biological and organic materials, and water.

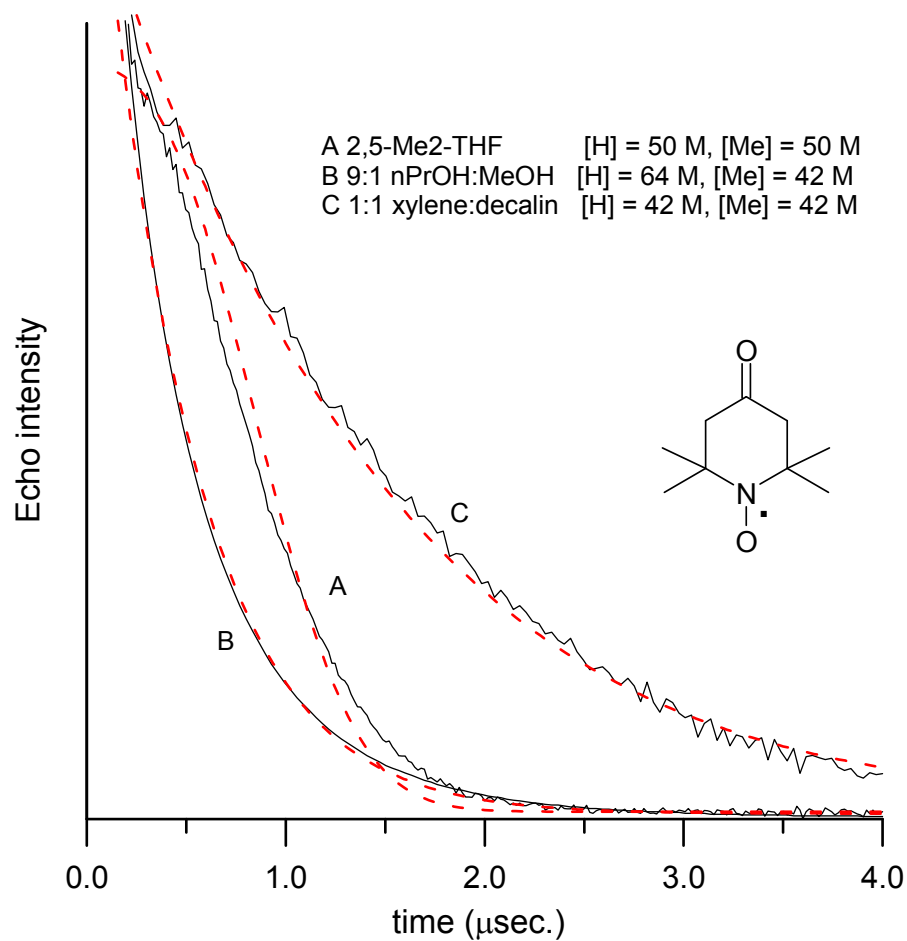
The most common nuclear spin flip process is a flip-flop,  $I_{1+}I_{2-}$ .

The rate of this process increases proportional to the nuclear spin concentration.

Dipolar coupling is proportional to  $\gamma$  so proton spin diffusion is a more effective dephasing process than is deuteron spin diffusion.

A. Zecevic, G. R. Eaton, S. S. Eaton, and M. Lindgren, *Mol. Phys.* **95**, 1255 (1988).

# Effects of Methyl Groups

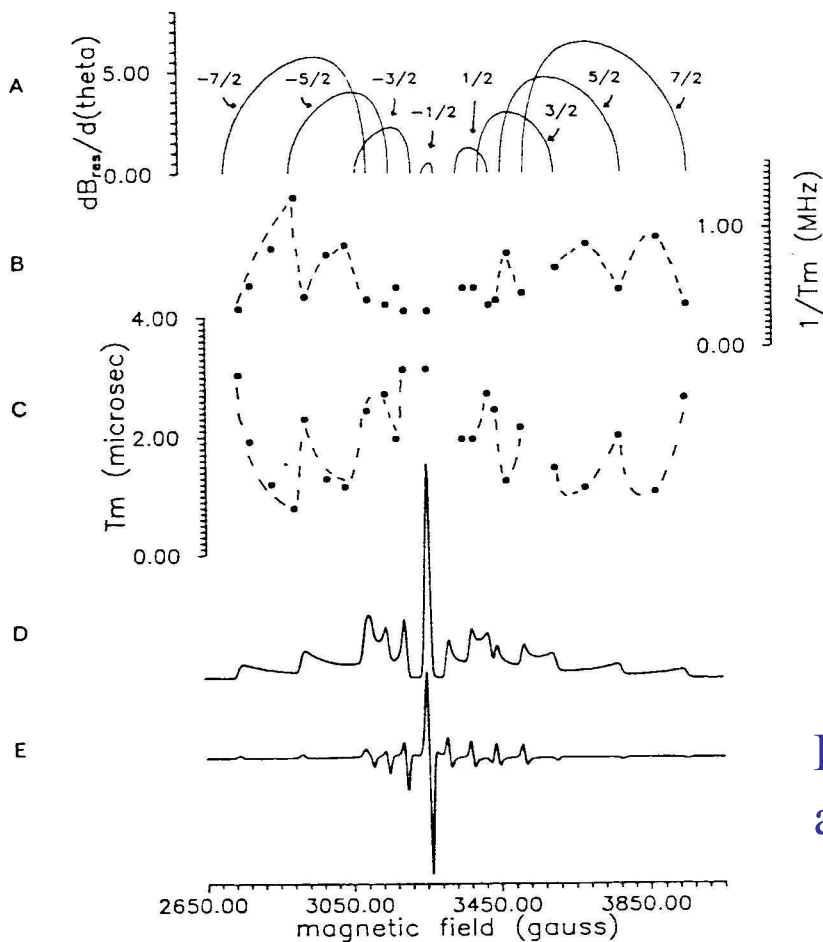


Echo decay curves are substantially different for tempone in these 3 solvents with approximately the same concentration of methyl protons. Because the barrier to rotation is lower, the aromatic methyl groups in xylene are less effective in echo dephasing than the methyls in n-propanol or 2,5-Me<sub>2</sub>-THF.



# Librations and Anisotropy in $T_m$

Vanadyl porphyrin in 9:1 toluene:THF



The change in resonance field per degree of rotational reorientation is largest at intermediate orientations of the molecule.

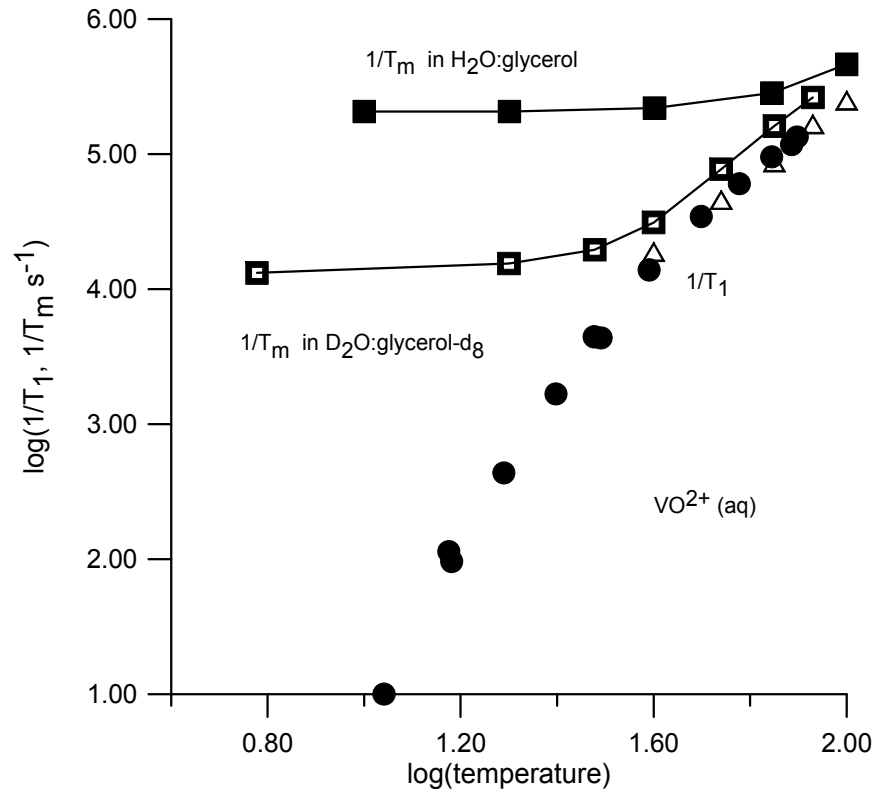
$1/T_m$  is largest at intermediate orientations and smallest along the principal axes.

Field-swept echo detected spectrum at 50 K

First-derivative CW spectrum at 20 K

J.-L. Du, K. M. More, S. S. Eaton, G. R. Eaton, *Isr. J. Chem.* 32, 351 (1992).

# Spin Lattice Relaxation



As temperature increases,  $1/T_1$  increases and eventually becomes the dominant contribution to  $1/T_m$ . The contribution from nuclear spin diffusion is smaller in deuterated solvent so  $1/T_1$  dominates echo dephasing at lower temperature in deuterated solvent than in natural abundance solvent.

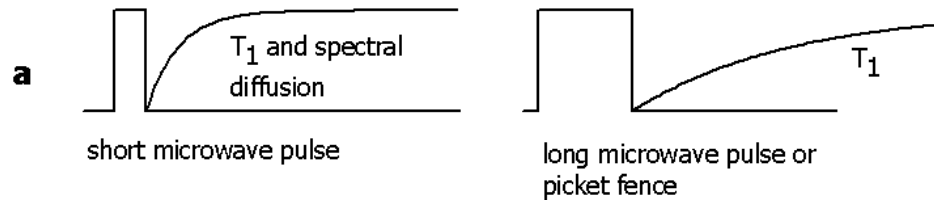
- Saturation recovery
- △ Inversion recovery

## Vanadyl ion in 1:1 water:glycerol

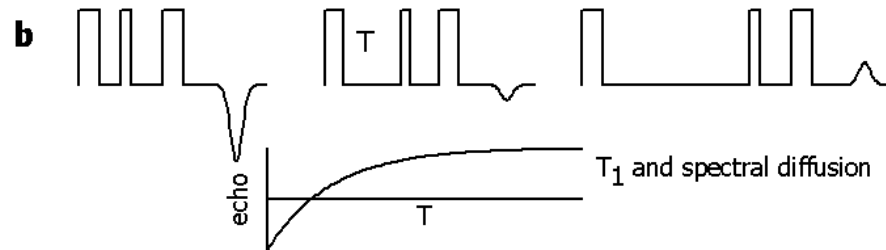
G. R. Eaton and S. S. Eaton, *J. Magn. Reson.* **136**, 63 (1999).

## Methods to Measure Electron Spin Relaxation Times

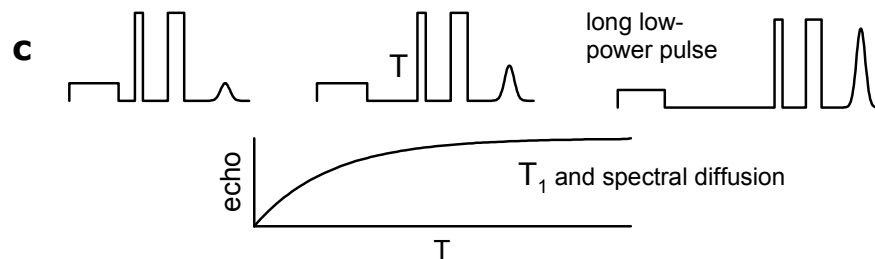
### Saturation Recovery



### Inversion Recovery



### Echo-Detected Saturation Recovery



Any process that takes spins off resonance can contribute to a recovery curve. The key to measuring  $T_{1e}$  is to separate its contribution from those of spectral diffusion processes. Most EPR spectra are so broad that only a small fraction of the spins are saturated or inverted in a pulse experiment.

# Spin-Lattice Relaxation Processes

**Direct Process** - There is an exact match of the spin transition energy with a phonon energy so there can be direct transfer of energy from the spin system to the lattice phonon bath. A phonon mode involves collective motion of lattice atoms.

**Orbach Process** is a two-phonon process in which the energy to be transferred to the lattice is the difference between the energies absorbed and emitted for a specific low-lying excited state.

**Raman Process** is a two-phonon process in which the energy to be transferred to the lattice is the difference between the energies absorbed and emitted for a virtual excited state at any energy less than the Debye temperature.

**Local Vibrational Modes** also can contribute to relaxation.

**Thermally-activated process** is characterized by a correlation time and an activation energy.

**Each process has a characteristic temperature dependence.**



# Temperature Dependence

$$\frac{1}{T_1} = A_{\text{dir}} T + A_{\text{Ram}} \left(\frac{T}{\theta_D}\right)^9 J_8\left(\frac{\theta_D}{T}\right) + A_{\text{loc}} \left[ \frac{e^{\Delta_{\text{loc}}/T}}{(e^{\Delta_{\text{loc}}/T} - 1)^2} \right] +$$
$$+ A_{\text{orb}} \frac{\Delta_{\text{Orb}}^3}{e^{\Delta_{\text{Orb}}/T} - 1} + A_{\text{therm}} \left[ \frac{2\tau_c}{1 + \omega^2 \tau_c^2} \right] \quad [1]$$

T is temperature in Kelvin

$A_{\text{dir}}$  is the coefficient for the contribution from the direct process

$A_{\text{Ram}}$  is the coefficient for the contribution from the Raman process

$\theta_D$  is the Debye temperature

$J_8$  is the transport integral,

$$J_8\left(\frac{\theta_D}{T}\right) = \int_0^{\theta_D/T} x^8 \frac{e^x}{(e^x - 1)^2} dx$$

# Temperature Dependence

$A_{\text{loc}}$  is the coefficient for the contribution from a local vibrational mode

$\Delta_{\text{loc}}$  is the energy for the local mode in units of Kelvin

$A_{\text{orb}}$  is the coefficient for the contribution from the Orbach process

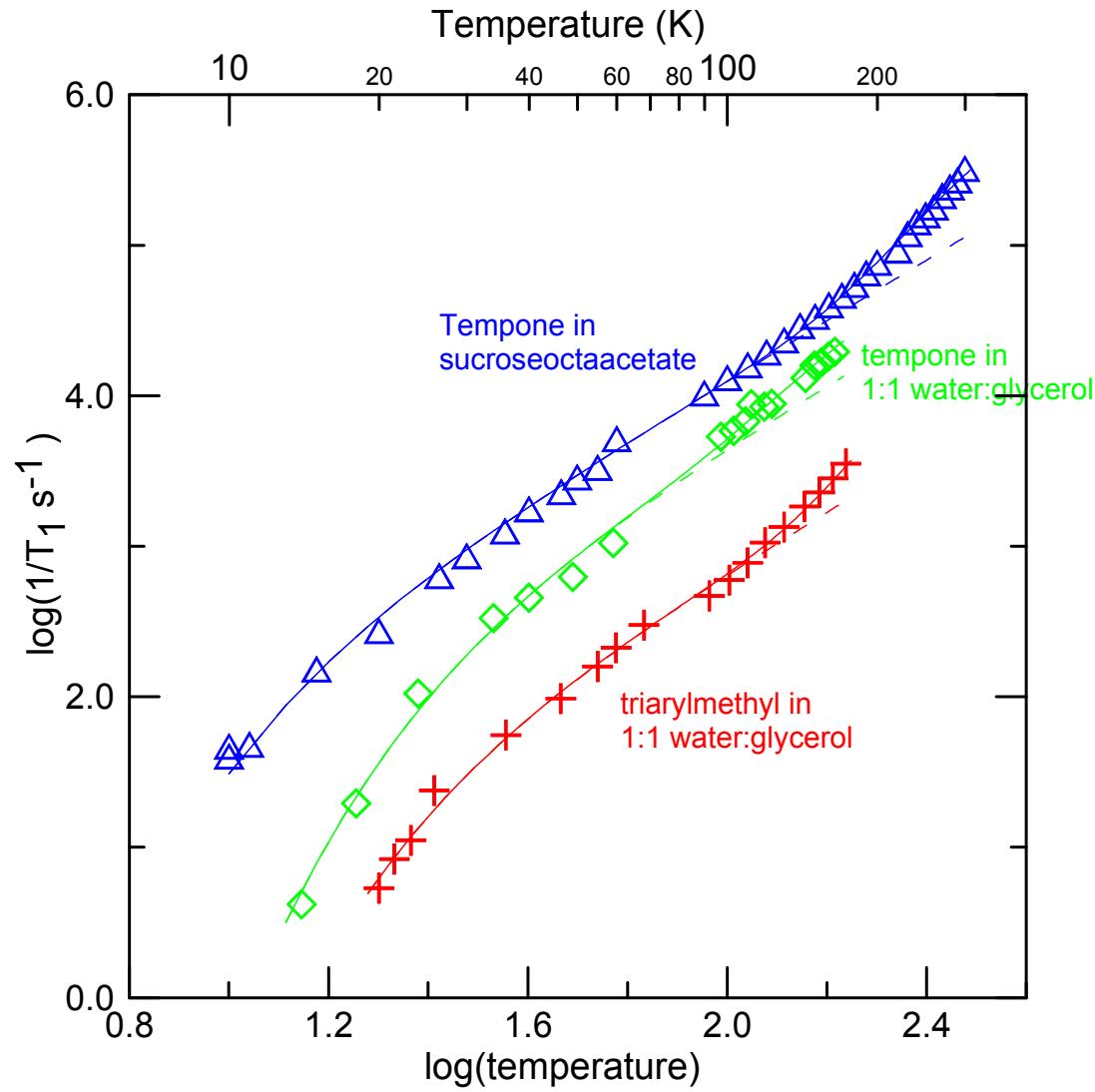
$\Delta_{\text{orb}}$  is the energy separation between the ground state and the excited state for the Orbach process

$A_{\text{therm}}$  is the coefficient for the contribution from the thermally-activated process

$\tau_c$  is the correlation time for the thermally-activated process =  $\tau_c^0 e^{E_a/T}$

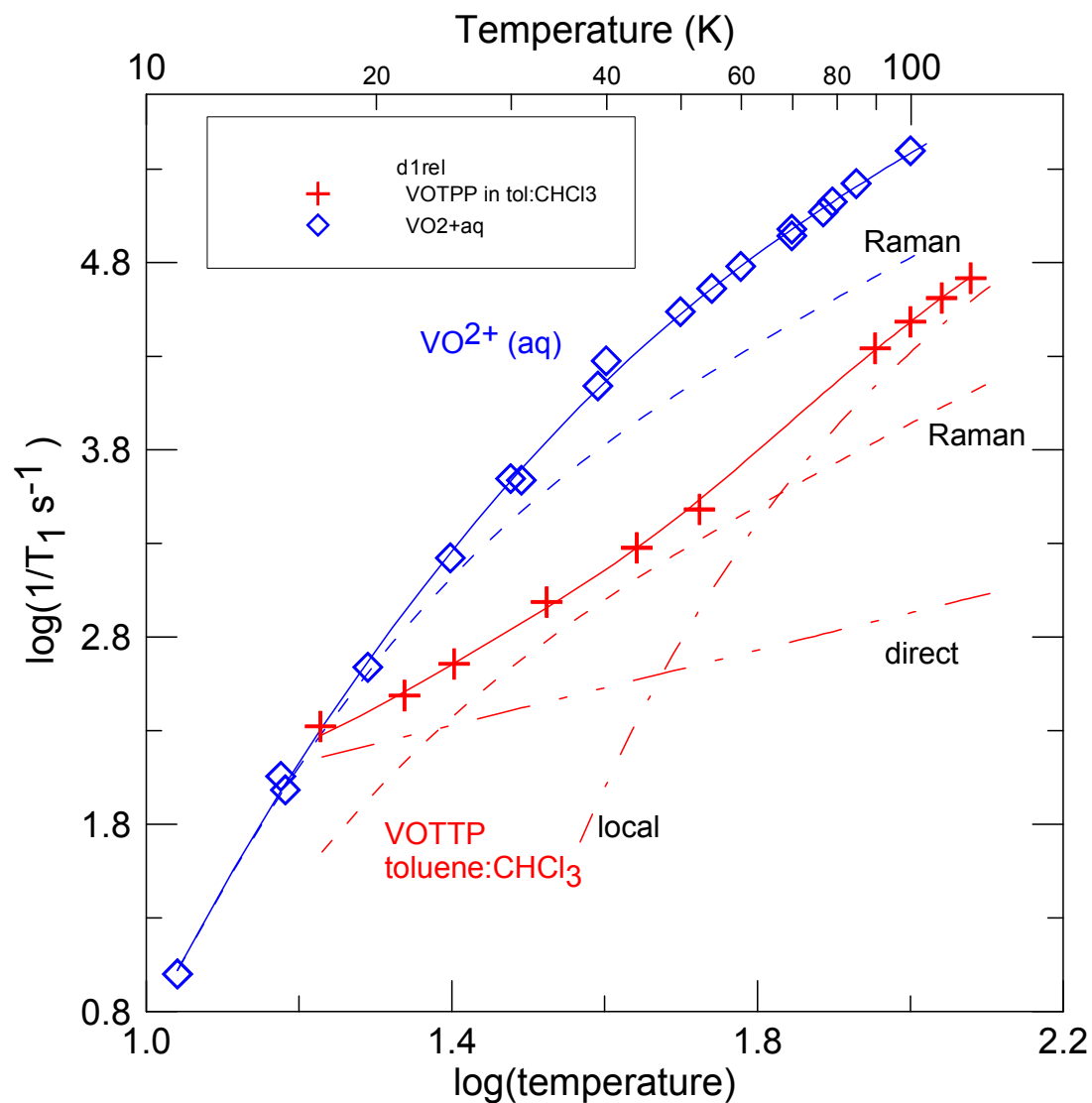
$E_a$  is the activation energy for the thermally-activated process

# Raman Process



The dashed lines are the contributions from the Raman process. An additional process contributes at higher temperatures. The faster relaxation for tempone is attributed to its greater spin-orbit coupling. The faster relaxation in sucrose octaacetate is attributed to a lower Debye temperature.

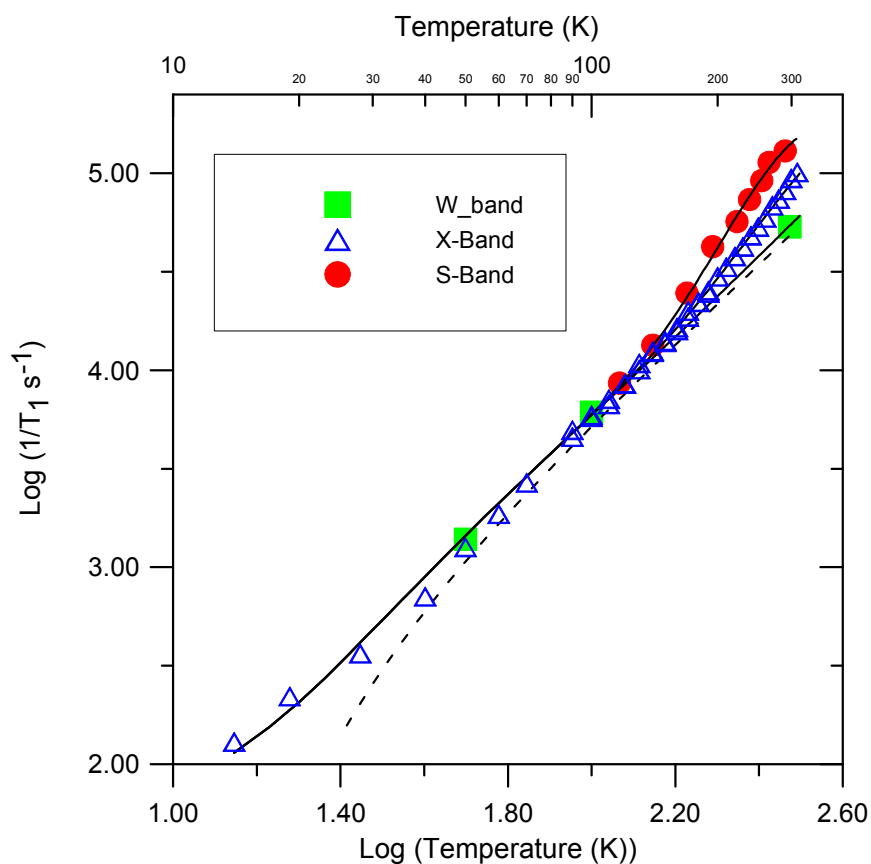
# Local modes: vanadyl ion – d<sup>1</sup>



Relaxation is faster for the more flexible aquo vanadyl ion than for the more rigid vanadyl porphyrin. The lines were calculated to fit the data.

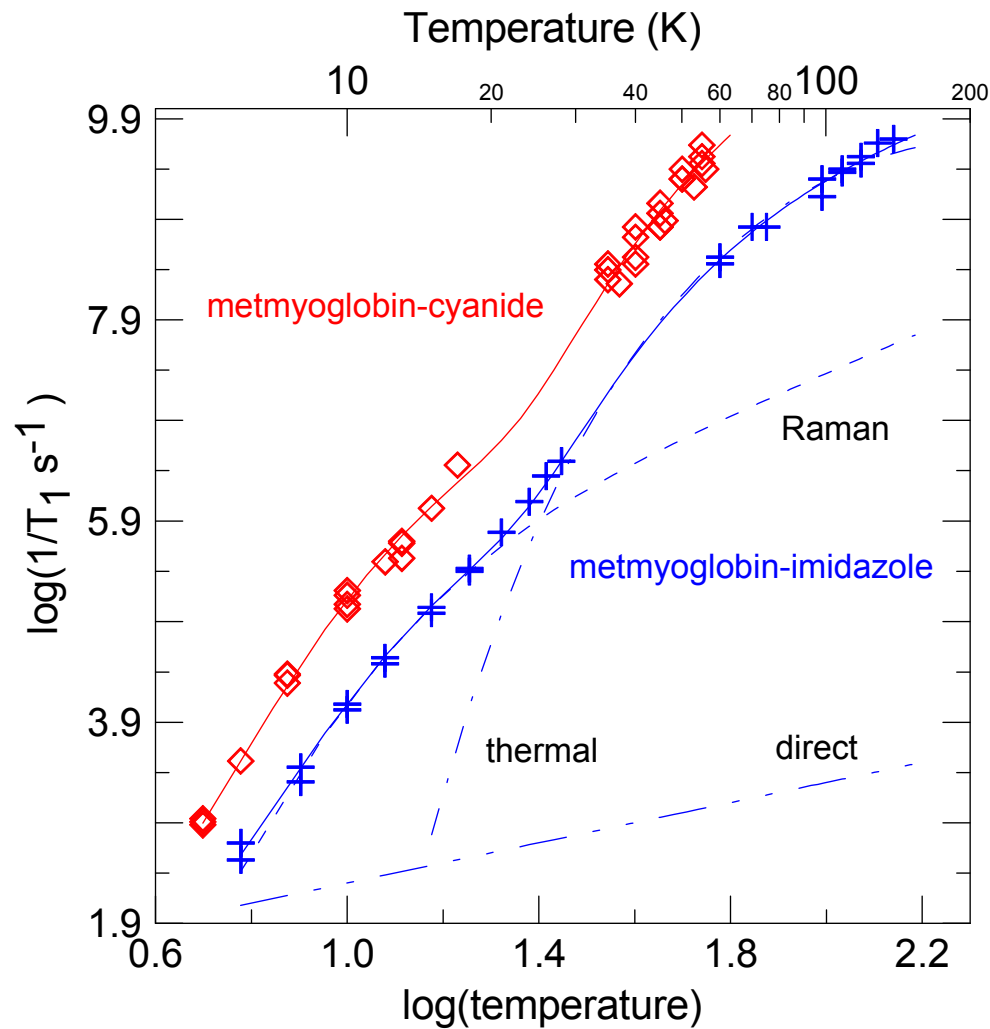
# Frequency Dependence - Thermally activated process

$T_{1e}$  for tempol doped into 4-hydroxy-tetramethyl-piperidinol



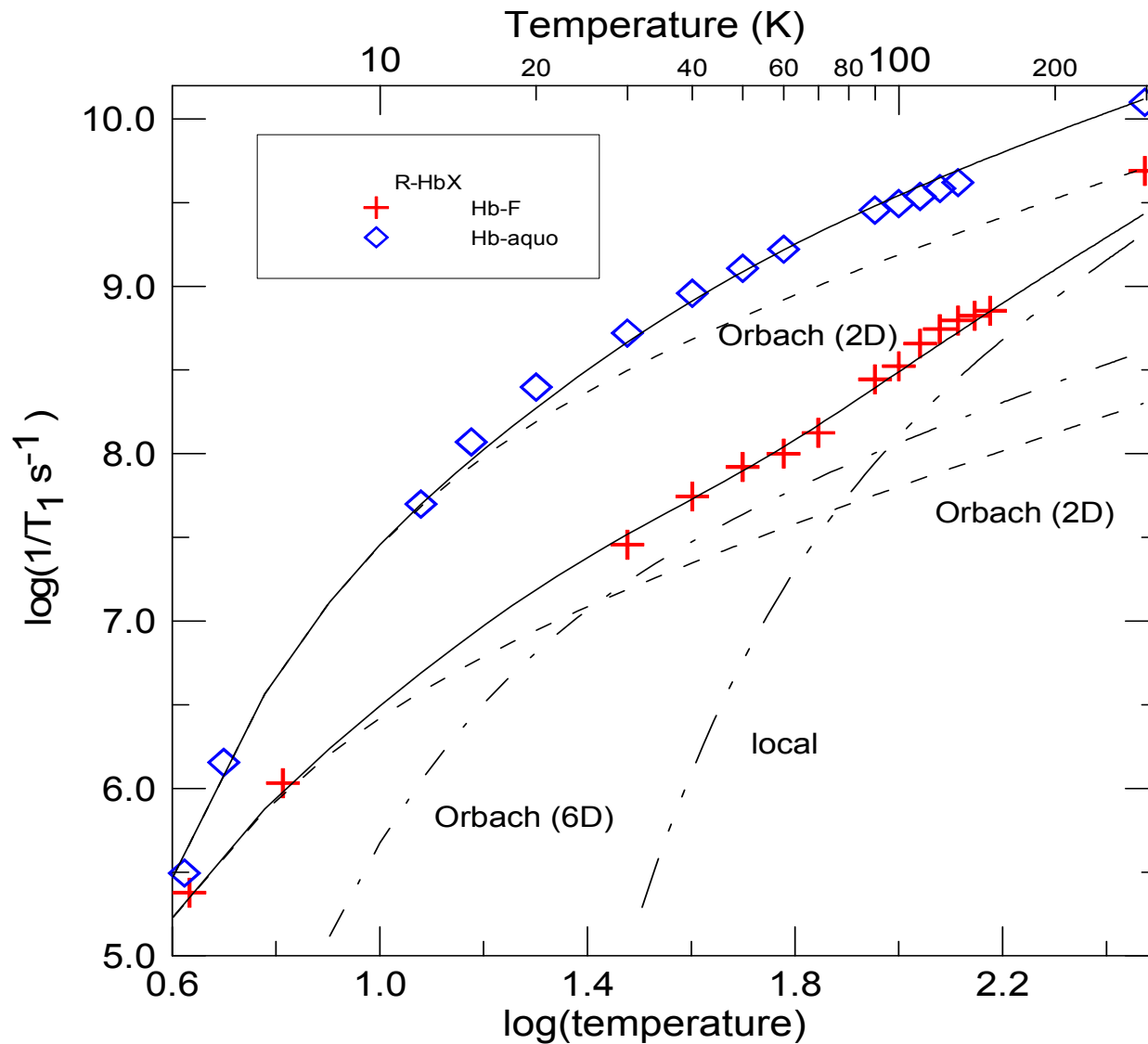
The relaxation rate is frequency dependent. This indicates a contribution from a thermally-activated process, which may be rotation of the nitroxyl ring methyl groups.

# Thermal Process – low spin Fe(III), S=1/2



The solid lines were calculated to fit the data.

# Orbach Process – high-spin Fe(III), $S=5/2$



The zero-field splitting of the high-spin iron results in low-lying excited states at 2D and 6D. The value of D can be determined by analyzing the temperature dependence of  $T_{1e}$  in the range where the Orbach process dominates.

Hb-F, 2D = 17 K

Hb-aquo, 2D = 30 K

Cu<sup>2+</sup> - d<sup>9</sup>

