

Spin Lattice Relaxation – Part 1, Solids

Gareth R. Eaton and Sandra S. Eaton
Department of Chemistry and Biochemistry
University of Denver



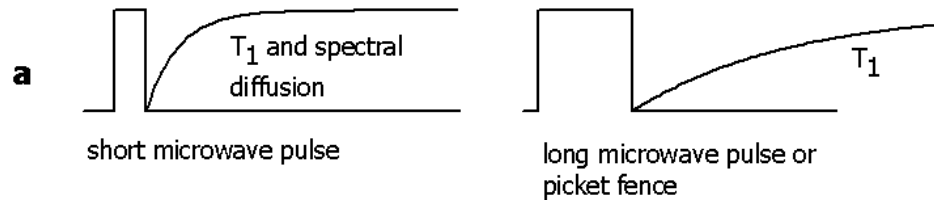
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What can you learn by measuring T_1 in solids?

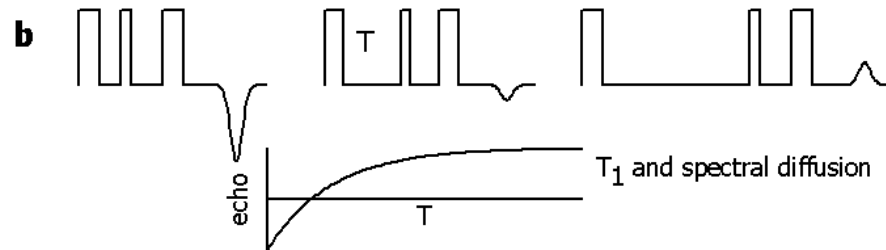
- Select parameters for CW spectra – understand power dependence
- Select temperature and conditions for an ENDOR spectrum
- Interpret orientation dependence of relaxation
- Characterize spectral diffusion processes that contribute to recovery curves
- Relaxation processes reveal the following information
 - Orbach process – energy of low-lying excited states
 - Raman process – Debye temperature of a solid
 - Local vibrational modes
 - Thermally-activated processes that impact T_1

Methods to Measure Electron Spin Relaxation Times

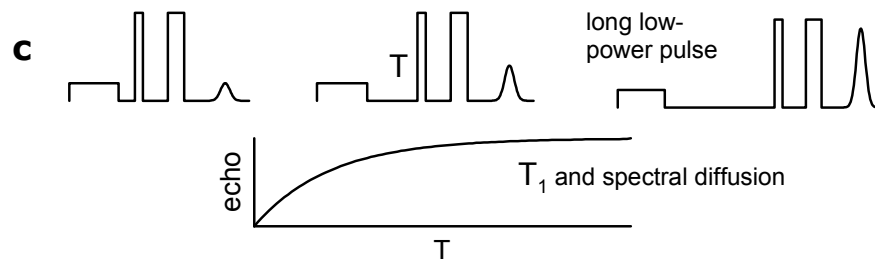
Saturation Recovery



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 an experiment.

Saturation Recovery

In a CW EPR experiment the microwave observe power is kept low so that the saturation factor, S , is close to 1.

$$S = \frac{1}{1 + \gamma^2 B_1^2 T_{1e} T_{2e}}$$

In a saturation recovery experiment, pump pulse power is selected to make S small. The goal is to equalize the populations of the spin energy levels. After the pump pulse, a low B_1 is used to observe the CW EPR signal.

When the pump pulse is short, relative to the time scale of spectral processes, the observed recovery curve contains contributions from **spectral diffusion in addition to T_{1e}** .

As the pump time is increased, the populations of spin energy levels that are interconverted by spectral diffusion become saturated and the contributions of spectral diffusion to the recovery curve are minimized.

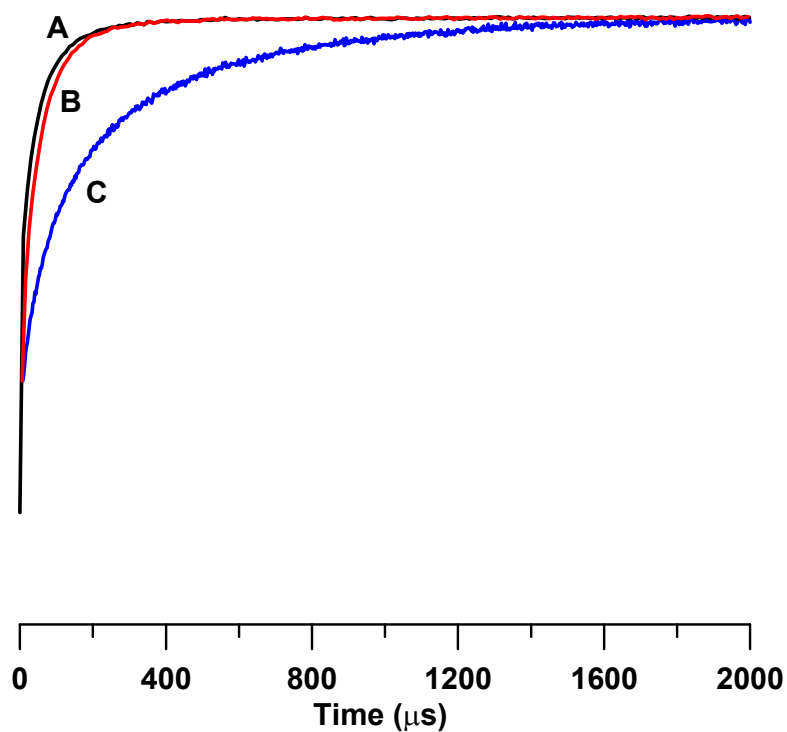
Inversion Recovery

In an inversion recovery experiment a 180° pulse is used to invert the spin populations. A 2-pulse spin echo sequence is used to monitor the magnetization along the z axis as a function of time between the inverting pulse and the 2-pulse observe sequence.

Advantage: The hard pulses of the inversion recovery sequence excite essentially all of the spins within a several gauss window. By contrast, the low observe power in a CW-SR experiment excites only a small fraction of the spins, over a narrow field range. Consequently signal-to-noise frequently is better for inversion recovery than for CW-SR.

Disadvantage: The short inverting pulse does not saturate spin levels that are accessible by spectral diffusion so the observed recovery curve is strongly impacted by spectral diffusion.

Comparison of inversion recovery and CW-SR for irradiated methyl malonic acid



Recovery curves at 77 K
obtained by
(A) inversion recovery
with $B_1 = 1.5$ G,
(B) ED-SR with $6 \mu\text{s}$
pump pulse, and
(C) CW-SR with pump
pulse $\gg T_{1e}$.

Other Saturating Pulse Sequences

Picket Fence. The single inverting pulse of the inversion recovery sequence can be replaced with a series of pulses that is called a picket fence. In order for the picket fence to effectively saturate the spectral diffusion processes, the time between the pulses must be short compared with the time constant for the spectral diffusion processes. The duty cycle of the TWT may limit the spacing of the picket pulses or the total length of the pulse train.

Echo-detected SR. A long low-power pulse can be used, analogous to CW-SR, combined with 2-pulse spin echo detection. The primary requirement for this experiment is a microwave amplifier with output of several watts and a duty cycle that permits long saturating pulses. If the saturating pulse is not long enough, spectral diffusion again contributes to the recovery curve.

Data Analysis - Exponentials

1. Fit a single exponential to the data. If the experimental recovery curve at a particular temperature can be fit well with a single exponential, a single process dominates the relaxation. However, in many cases the recovery curves do not fit well to a single exponential, which can arise from orientation dependence of T_{1e} in polycrystalline samples, a distribution in T_{1e} , and/or contributions from spectral diffusion processes.
2. Fit a sum of exponentials to the data. In some cases the recovery curve fits better to the sum of exponentials, which may indicate contributions from spectral diffusion in addition to T_{1e} . Careful statistical tests are required to distinguish a sum of exponentials from a distribution of exponentials or a sum of distributions of exponentials.

Data Analysis – Models

When a rapidly relaxing spin enhances the relaxation rate for a neighboring spin, the recovery curve is a distribution of exponentials. The distribution arises from the fact that each orientation of the spin-coupled pair with respect to the external magnetic field produces a different magnitude of relaxation enhancement. For these samples, it is wiser to analyze the data based on a model of the spin-spin interaction than to simply fit a sum of exponentials to the data.

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_{dir} is the coefficient for the contribution from the direct process

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

θ_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_{loc} is the coefficient for the contribution from a local vibrational mode

Δ_{loc} is the energy for the local mode in units of Kelvin

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

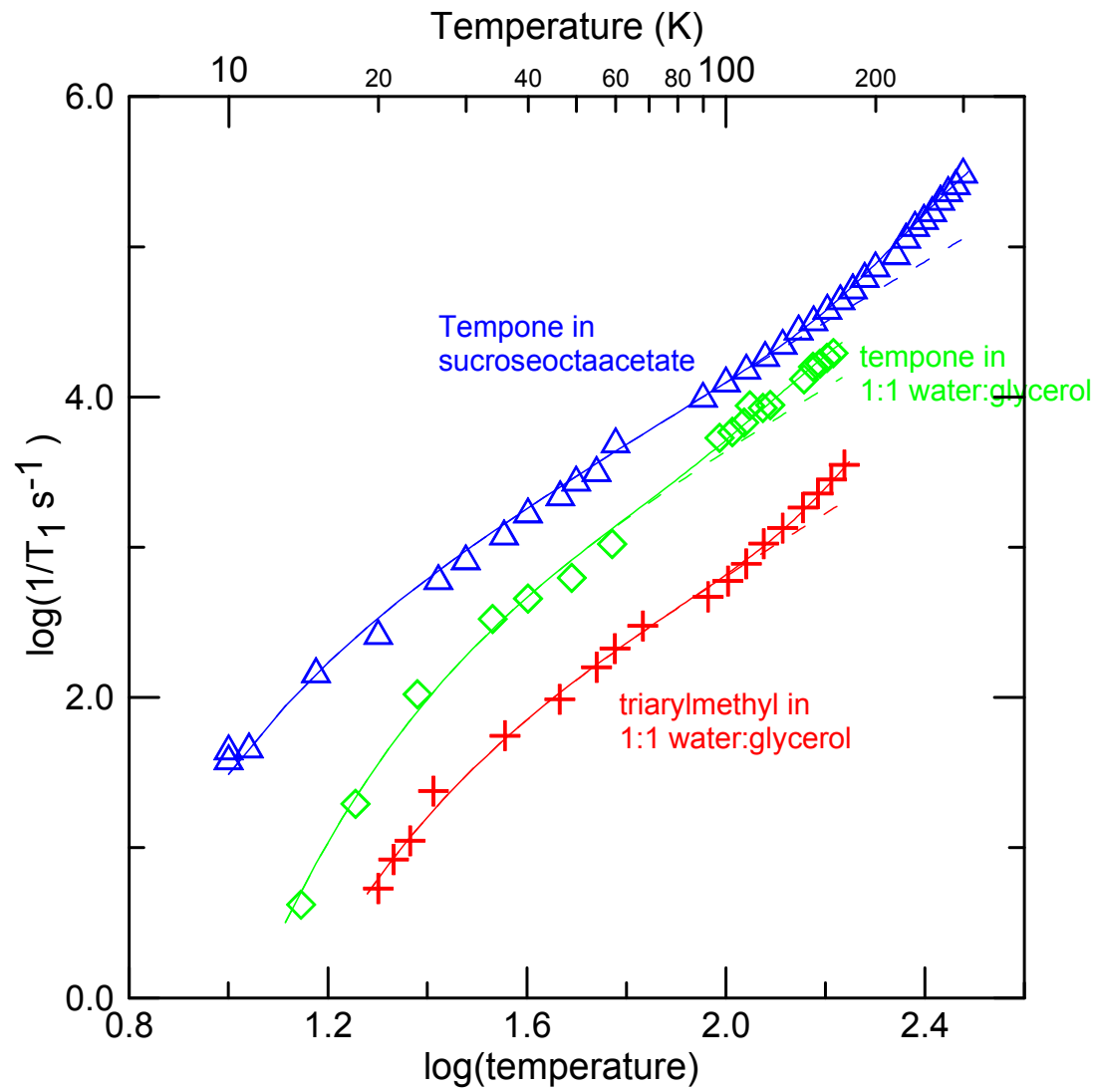
Δ_{orb} is the energy separation between the ground state and the excited state for the Orbach process

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

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

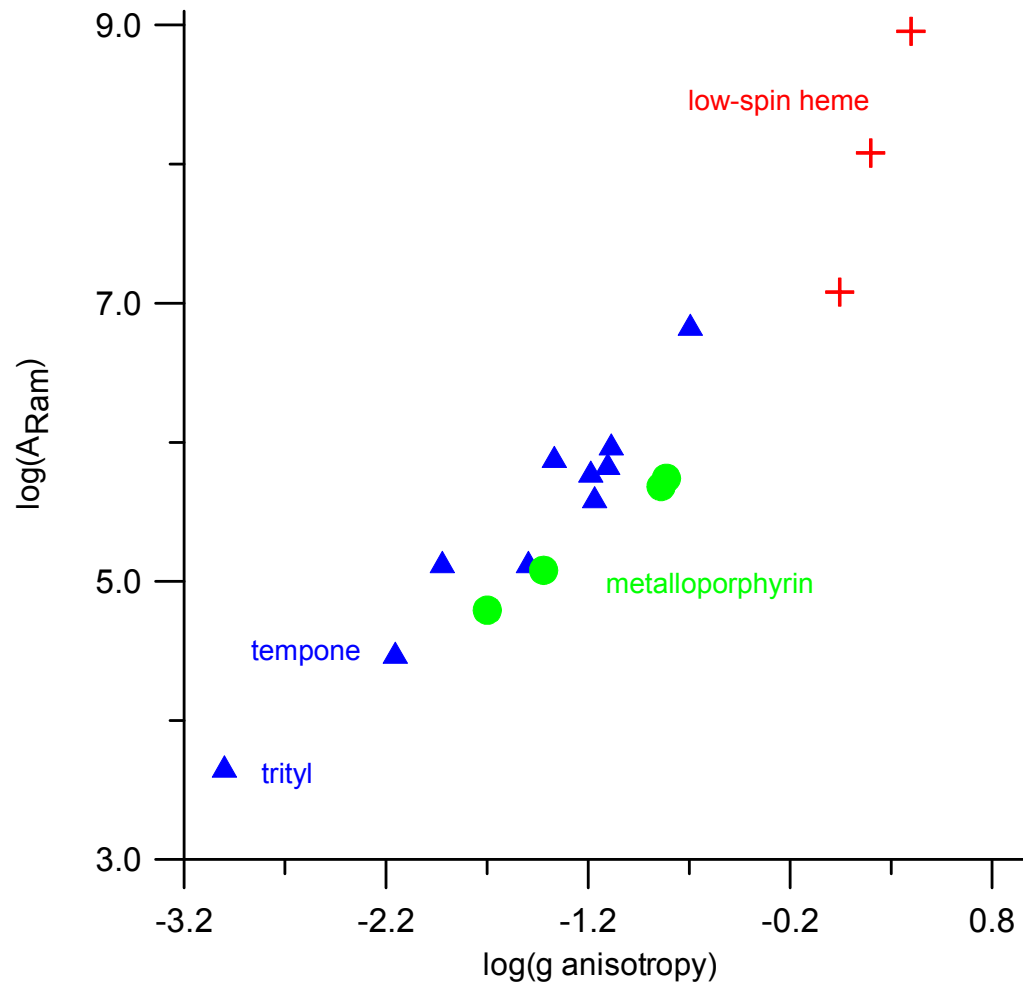
E_a is the activation energy for the thermally-activated process

Raman Process



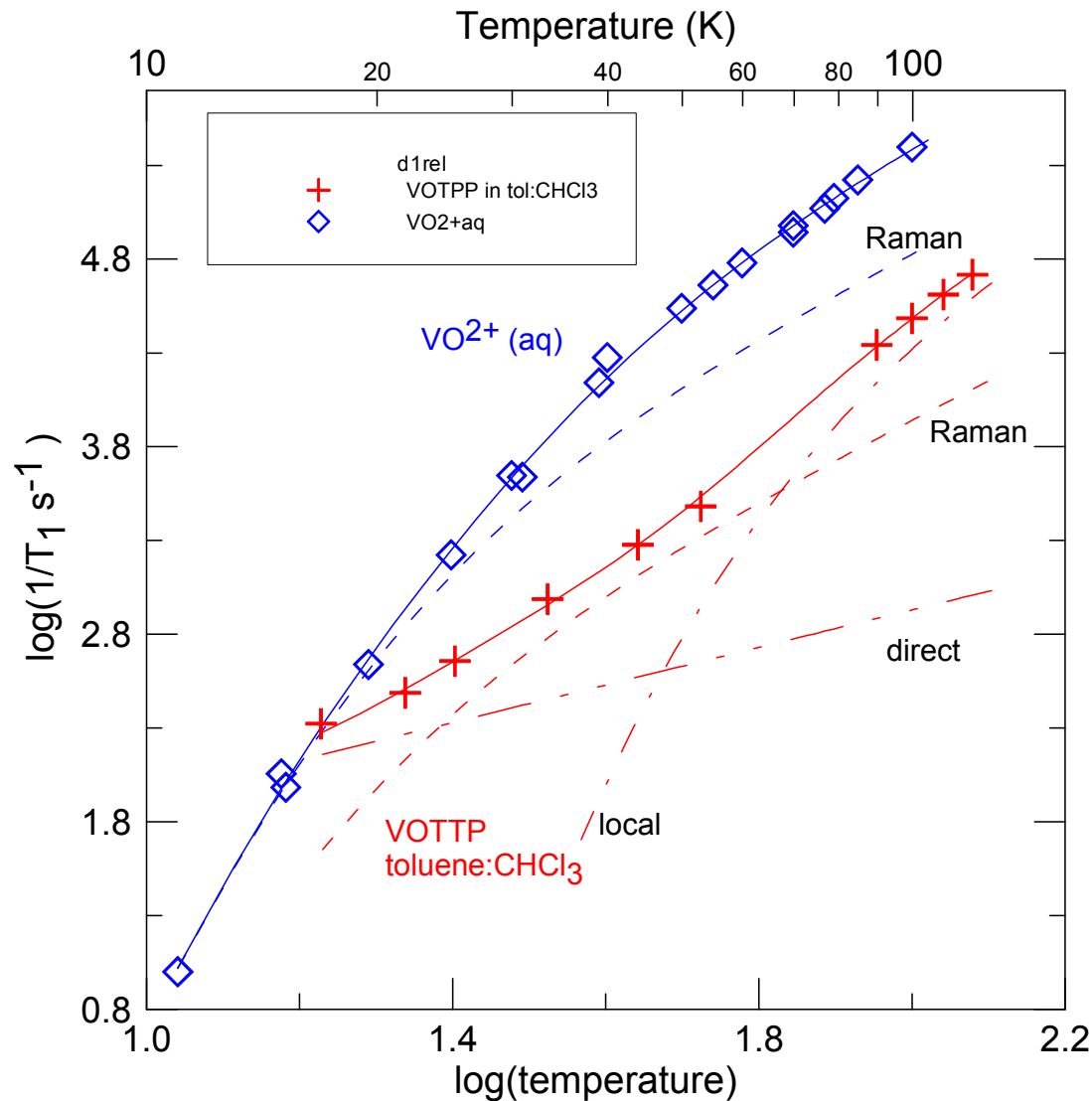
The dashed lines are the contributions from the Raman process. An additional process contributes at higher temperatures. The faster relaxation for tempone is attributed to its greater spin-orbit coupling. The faster relaxation in sucrose octaacetate is attributed to a lower Debye temperature.

Coefficients of Raman Process



For organic radicals and first-row transition metals, the coefficient of the Raman process increases with increasing g anisotropy ($g_{\text{max}} - g_{\text{min}}$), which is a measure of spin-orbit coupling.

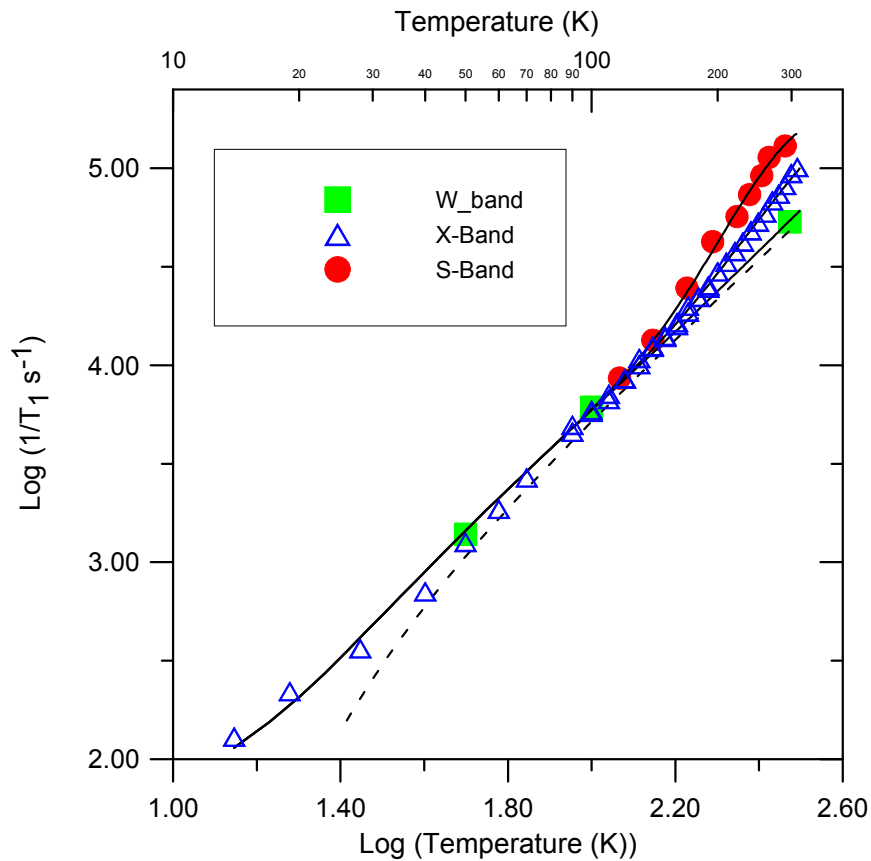
Local modes: vanadyl ion – d¹



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, using Eq. [1].

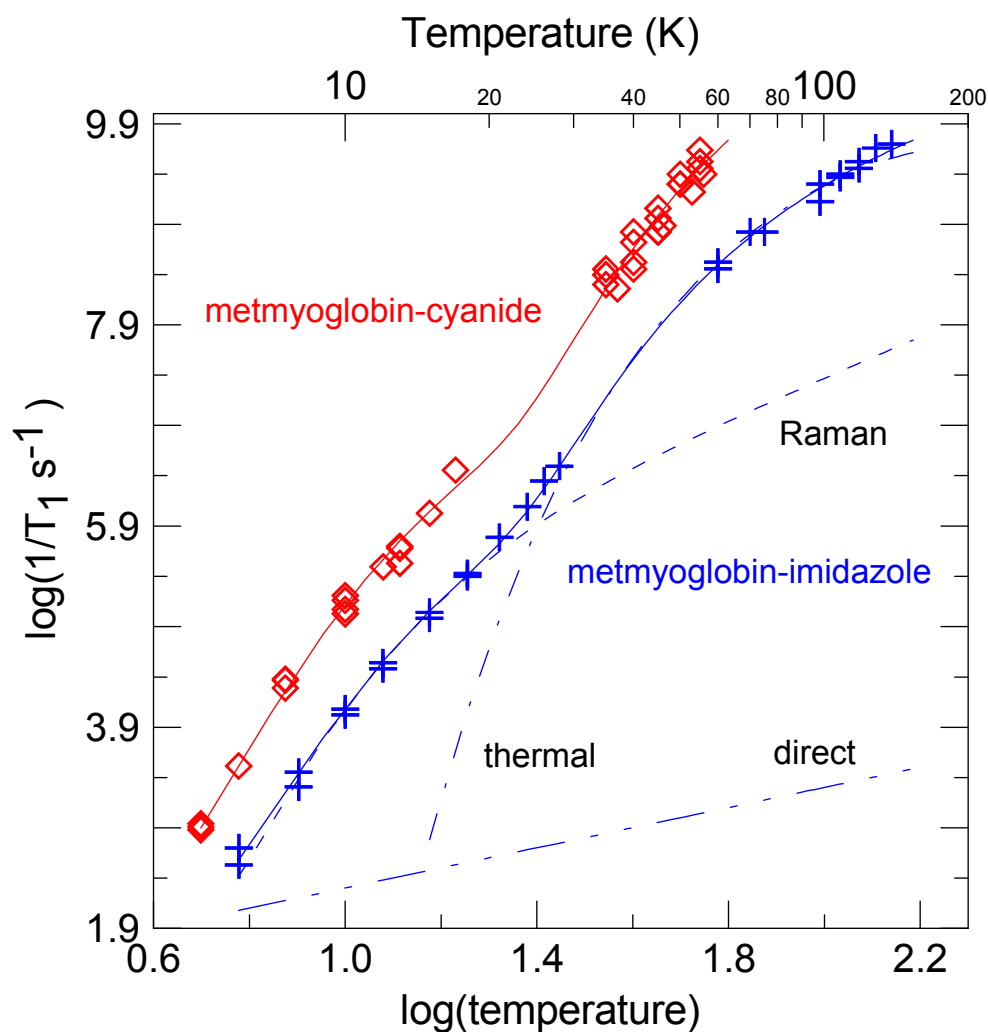
Frequency Dependence - Thermally activated process

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



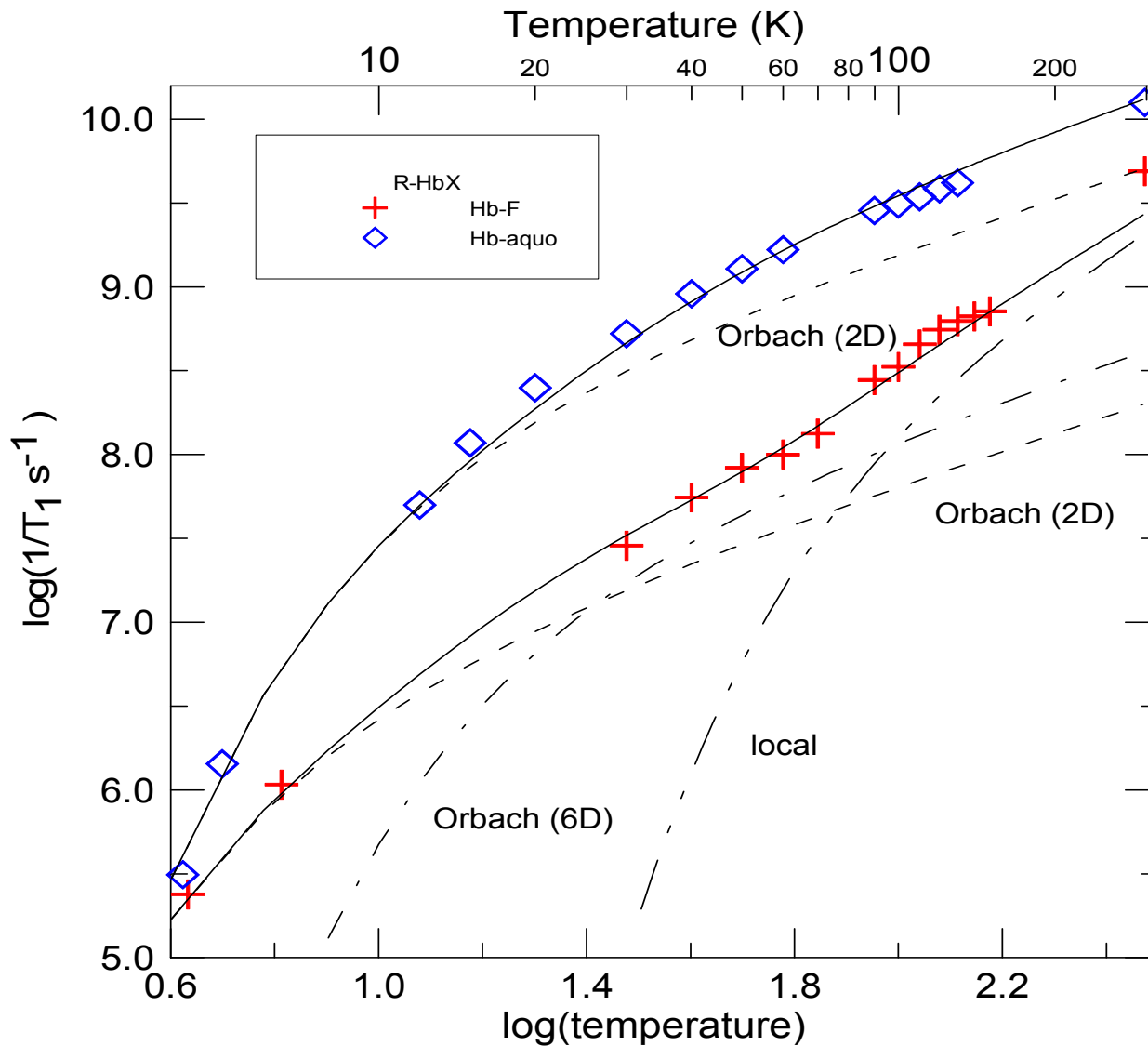
The relaxation rate is frequency dependent. This indicates a contribution from a thermally-activated process, which is attributed to rotation of the nitroxyl ring methyl groups.

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



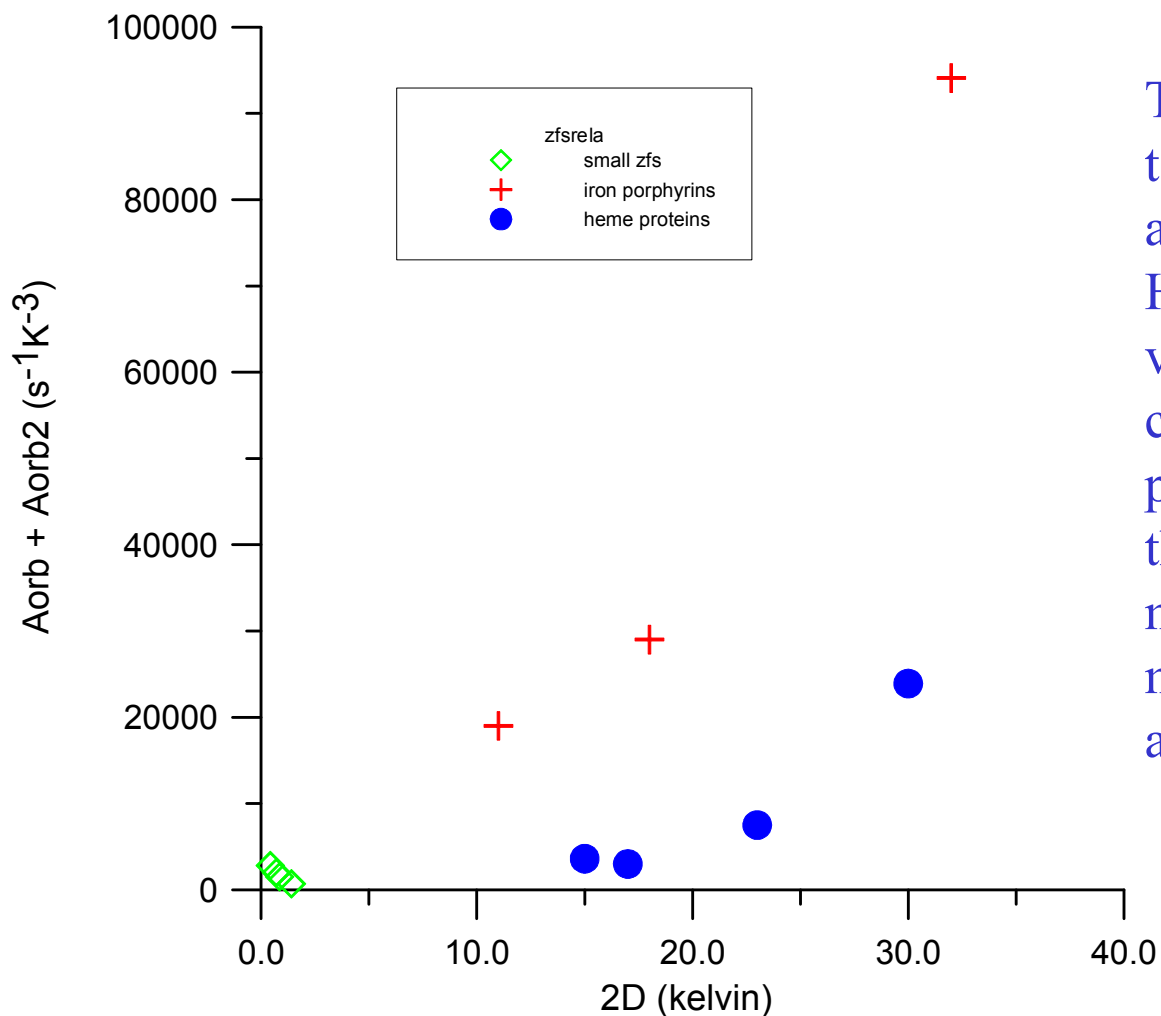
The solid lines were calculated to fit the data, using Eq. [1].

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



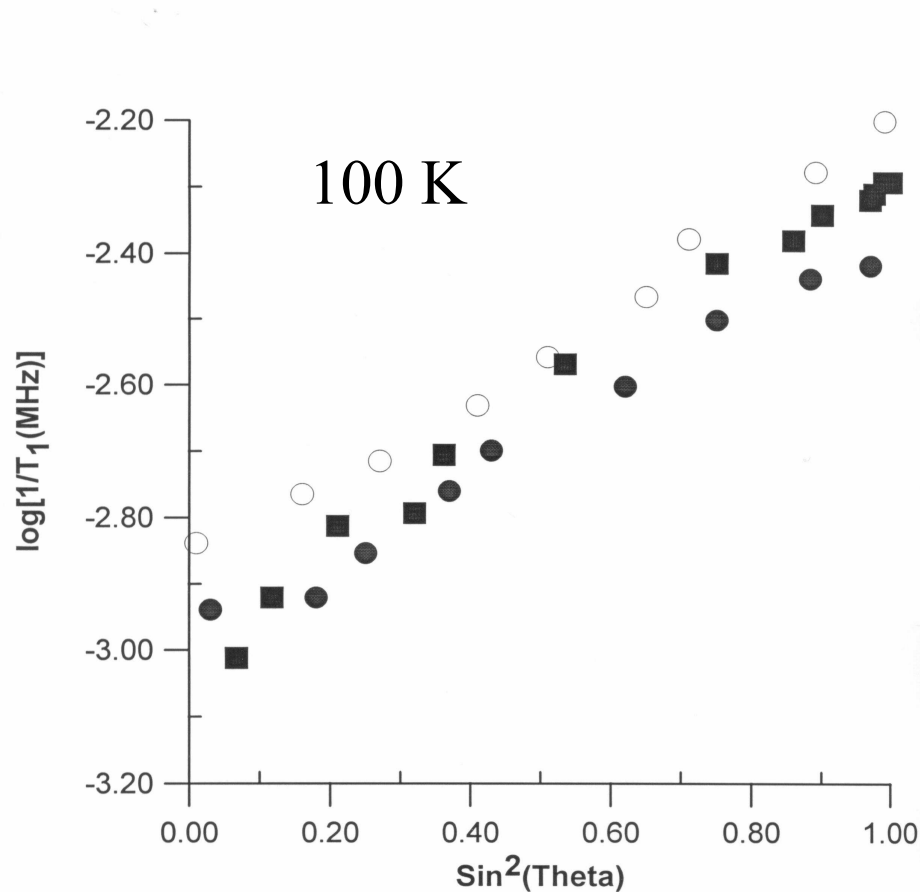
The zero-field splitting of the high-spin iron results in low-lying excited states at 2D and 6D. The value of D can be determined by analyzing the temperature dependence of T_{1e} in the range where the Orbach process dominates.

Coefficients of Orbach process for h.s. Fe(III)



There is a general trend toward larger coefficients as the ZFS increases. However, for comparable values of 2D the coefficients for the heme proteins are smaller than for the iron porphyrins, which may be due to decreased motional flexibility of the axial ligands in the proteins.

Orientation Dependence of T_{1e}



- Tempone in 1:1 water:glycerol
- ^{15}N – tempone in 1:1 water:glycerol
- 4-OH-tempo doped into single crystal

For molecules with axial symmetry, in temperature regions where Raman or local mode processes dominate, T_{1e} often is longer along the molecular z axis than in the perpendicular plane. This orientation dependence is attributed to the symmetry of the vibrational modes.

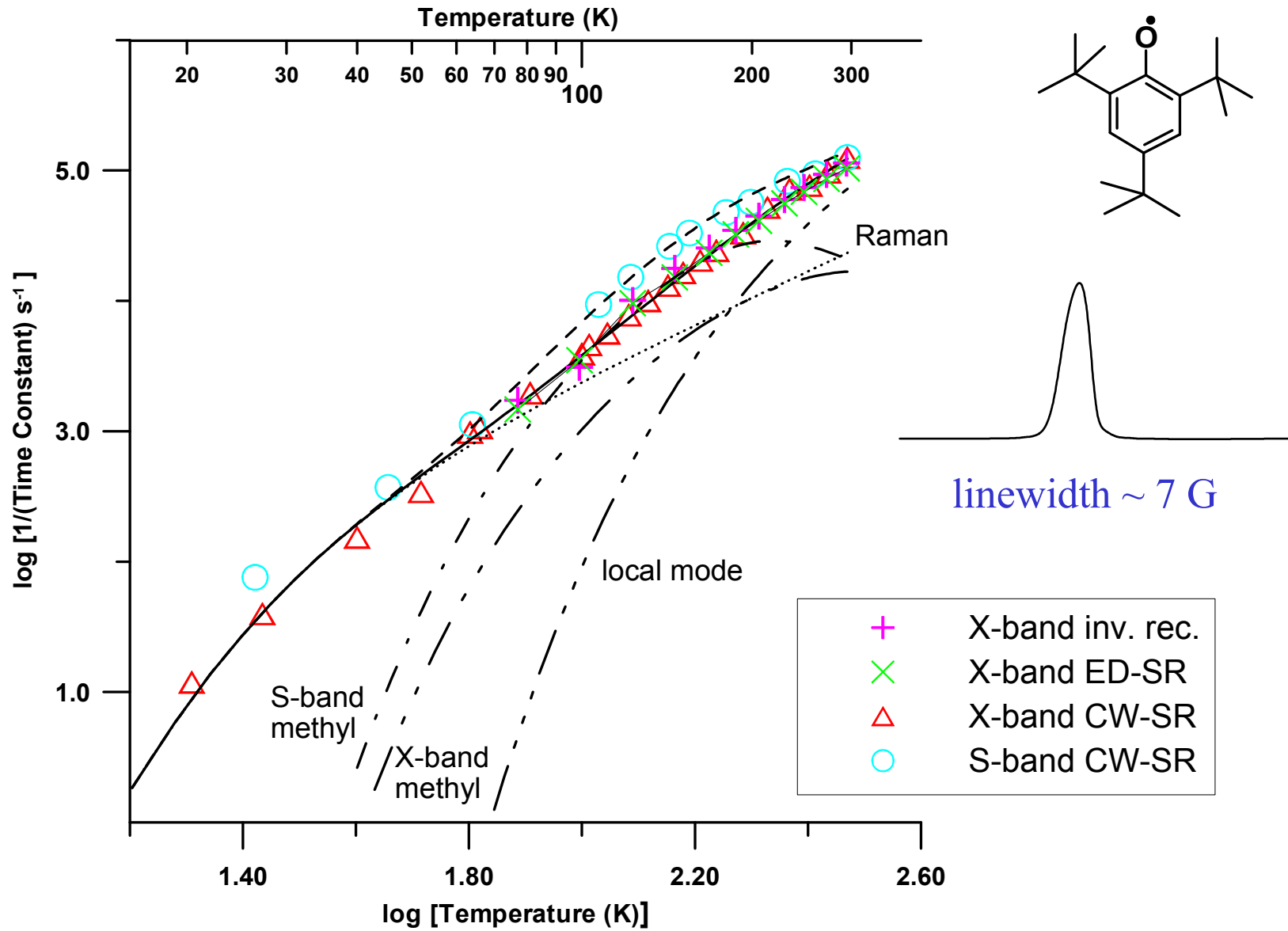
Theta is the angle between the molecular z axis and the external magnetic field.

Competing Processes – Spectral Diffusion

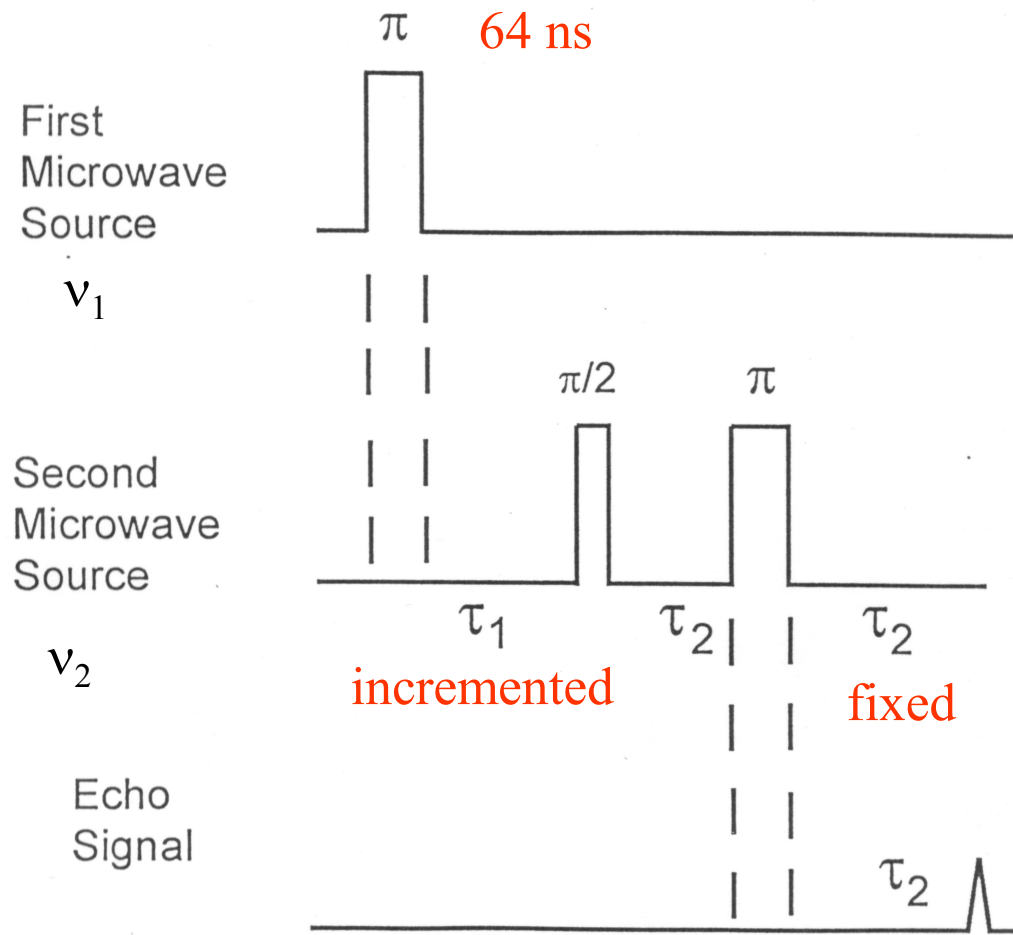
- **Nuclear spin relaxation** ($\Delta M_s = 0, \Delta M_l = 1$) transfers spin polarization from one nuclear spin state to another
- **Cross-relaxation** transfers spin polarization between Zeeman frequencies. Here, cross relaxation is used to designate spectral diffusion processes in which $\Delta M_s = \pm 1, \Delta M_l = \mp 1$.
- **Spin diffusion** moves magnetization between unresolved hyperfine components within an inhomogeneously broadened line.

ELDOR (electron-electron double resonance) can be used to characterize spectral diffusion processes. In an ELDOR experiment the pump pulse is applied at one microwave frequency and a 2-pulse spin echo sequence is performed at a second microwave frequency to observe the magnetization.

γ -irradiated 2,4,6-tri(t-butyl)-phenol

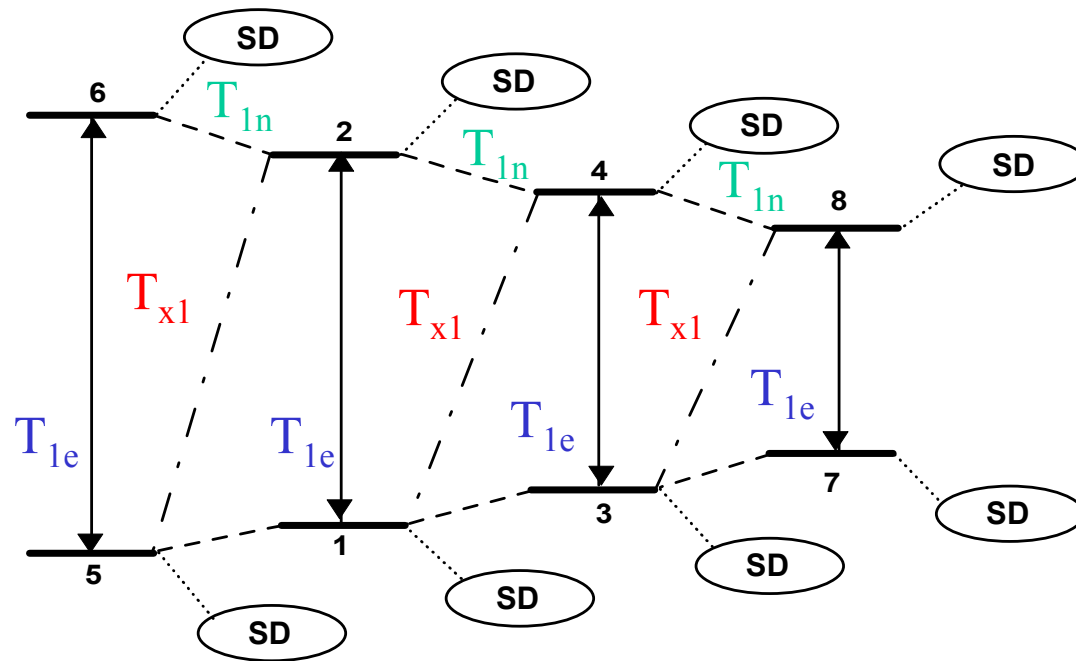


Inversion ELDOR



The ELDOR signal is the ratio of the echo amplitudes in the presence and absence of a pulse at ν_1 .

Relaxation and spectral diffusion processes

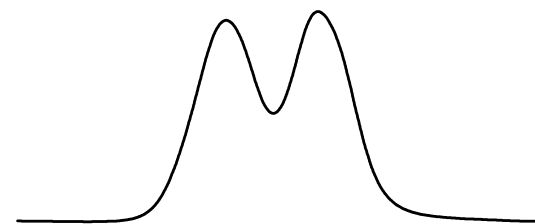
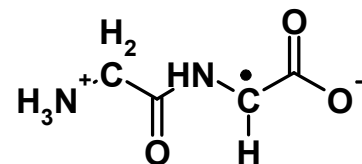
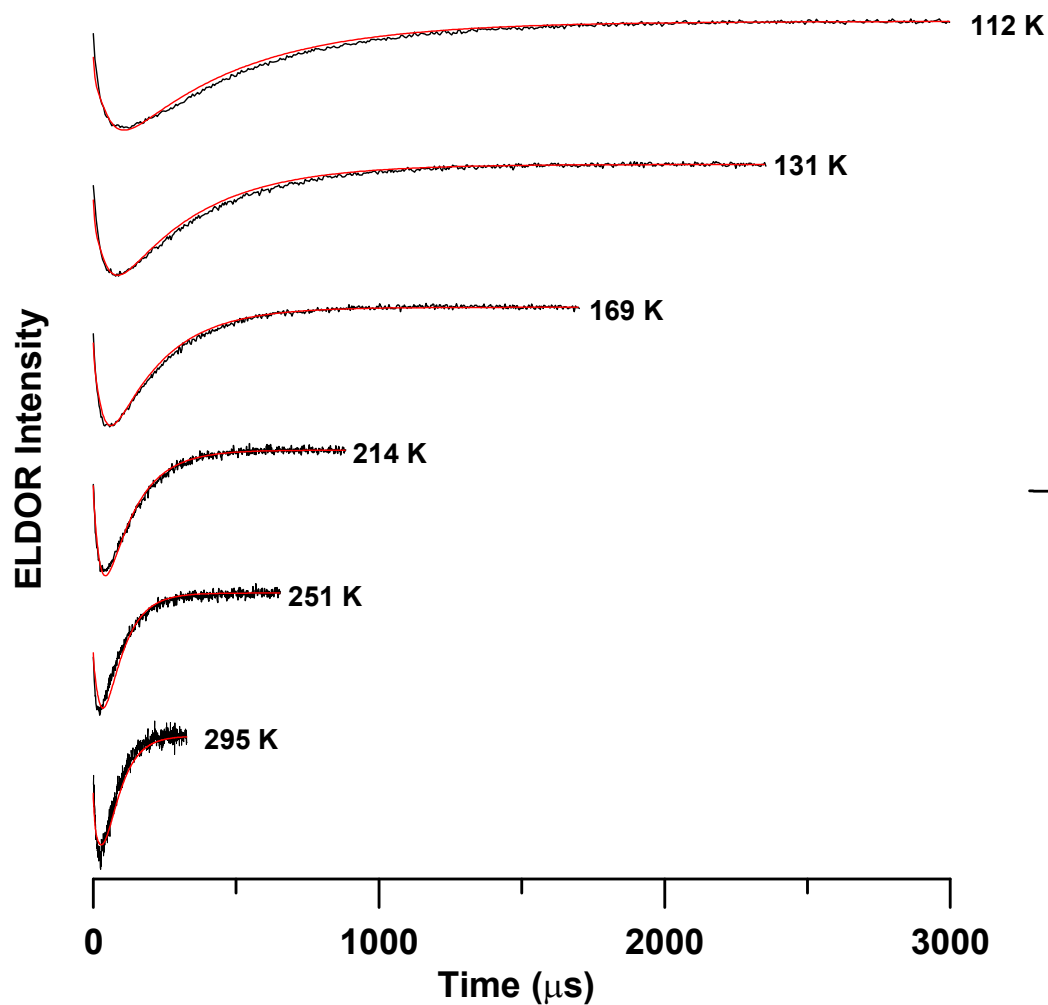


When $T_{1n} < T_{1e}$, an ELDOR reduction is observed.

When $T_{x1} < T_{1e}$ an ELDOR enhancement is observed.

Recovery curves can be simulated to determine time constants.

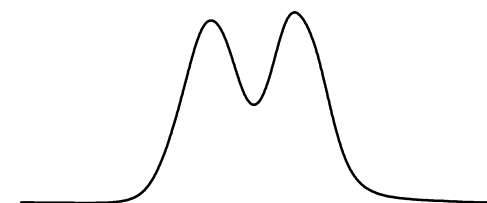
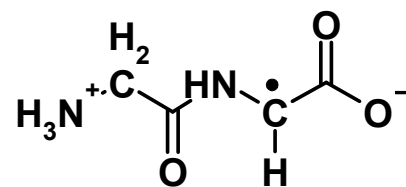
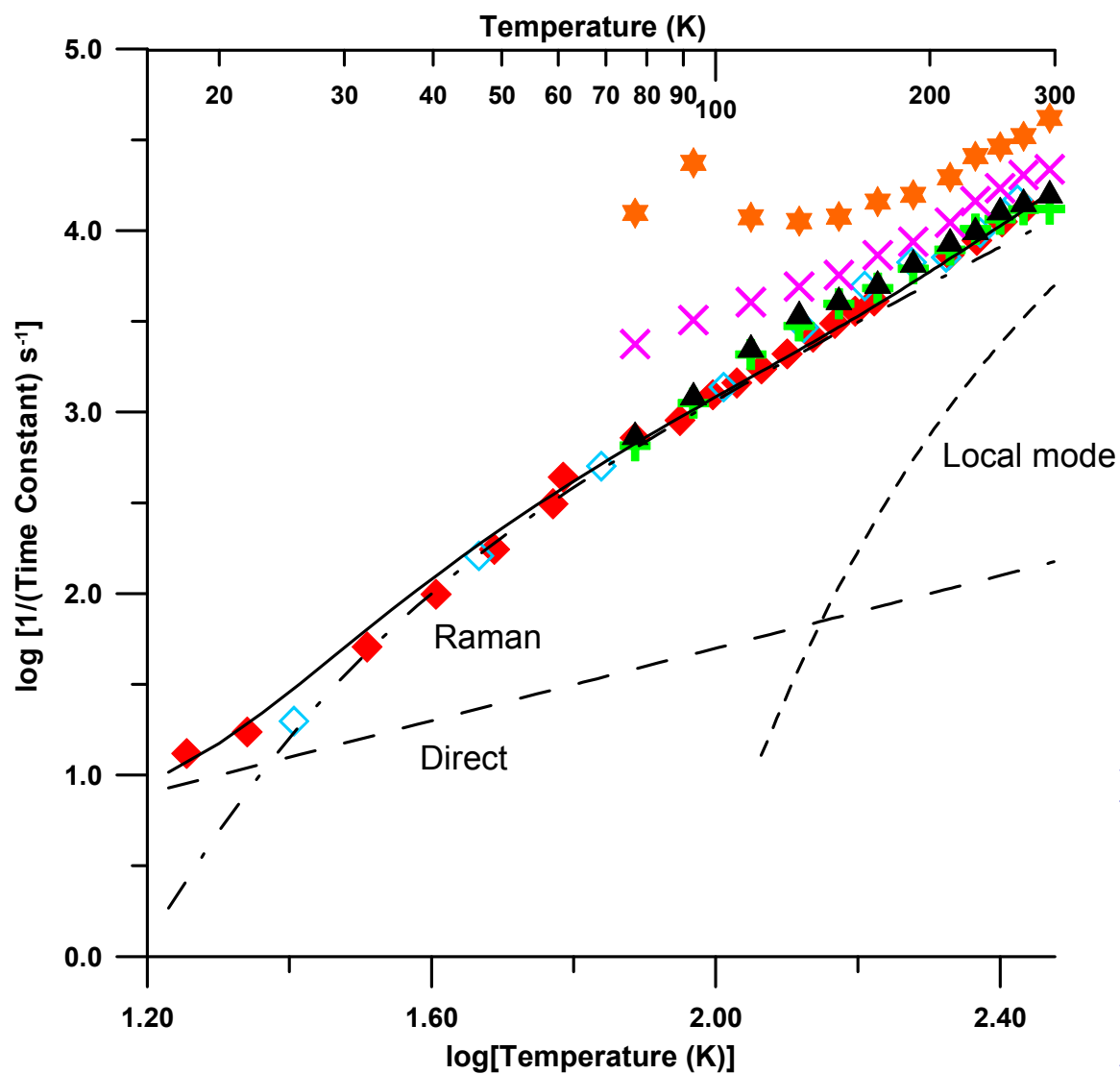
ELDOR for glycyglycine radical



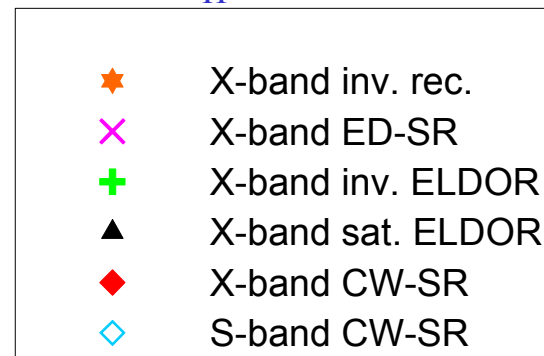
$$a_{\text{H}} \sim 19 \text{ G}$$

The ELDOR reduction indicates $T_{1n} < T_{1e}$.
The maximum reduction was about 10%.

T_{1e} for γ -irradiated glycylglycine

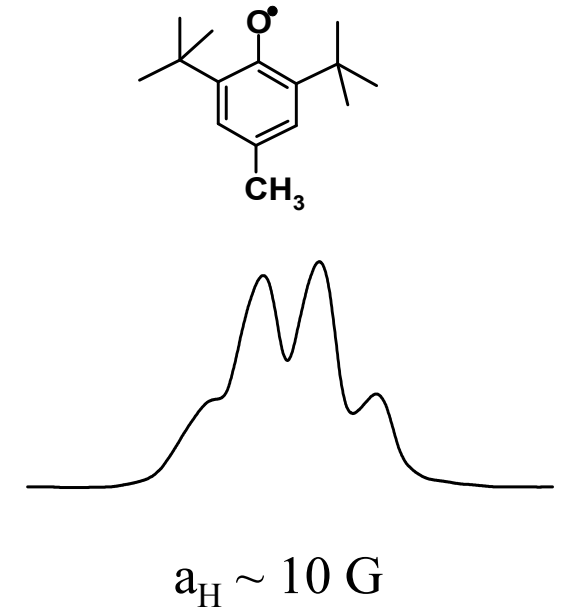
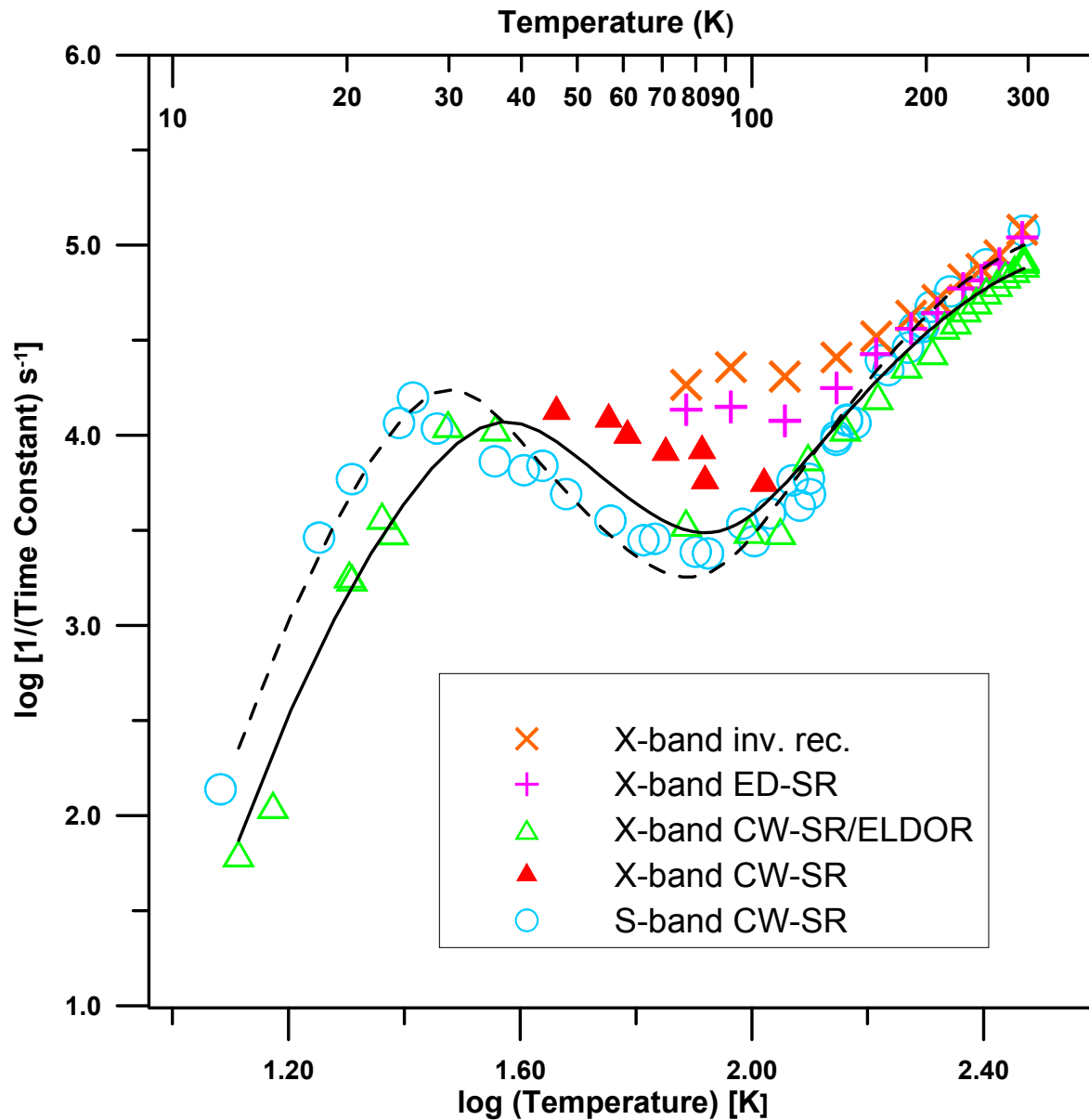


$a_H \sim 19$ G



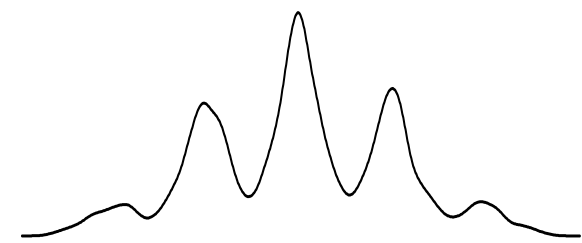
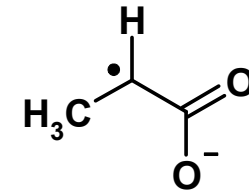
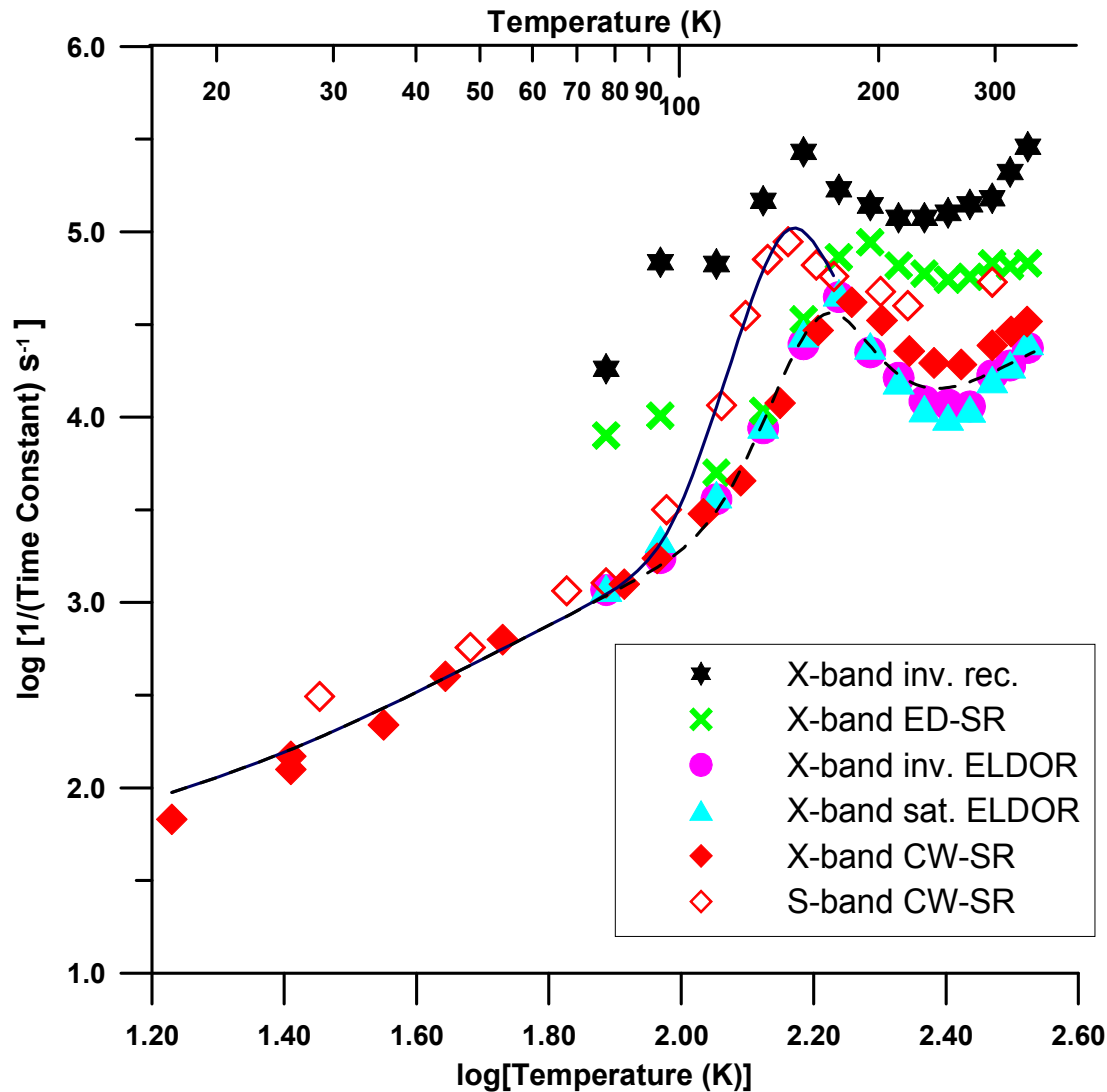
The spectral diffusion processes that increased the rate constants for the inversion recovery curves can be suppressed by CW-SR or taken into account by ELDOR.

T_{1e} for γ -irradiated 4-Me-2,6-t-Bu-phenol



Rotation of methyl group at rate comparable to the electron Larmor frequency has dramatic impact on T_{1e} between about 20 and 60 K. The lines were calculated to fit the data, using Eq. [1].

T_{1e} for γ -irradiated L-alanine

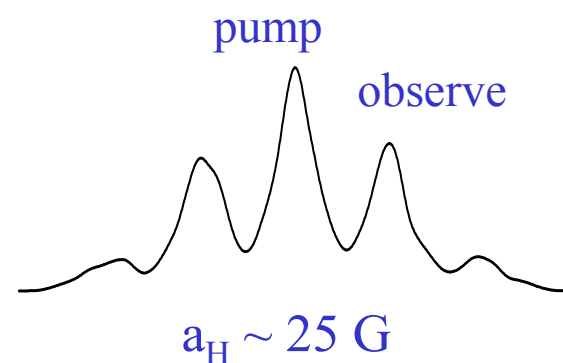
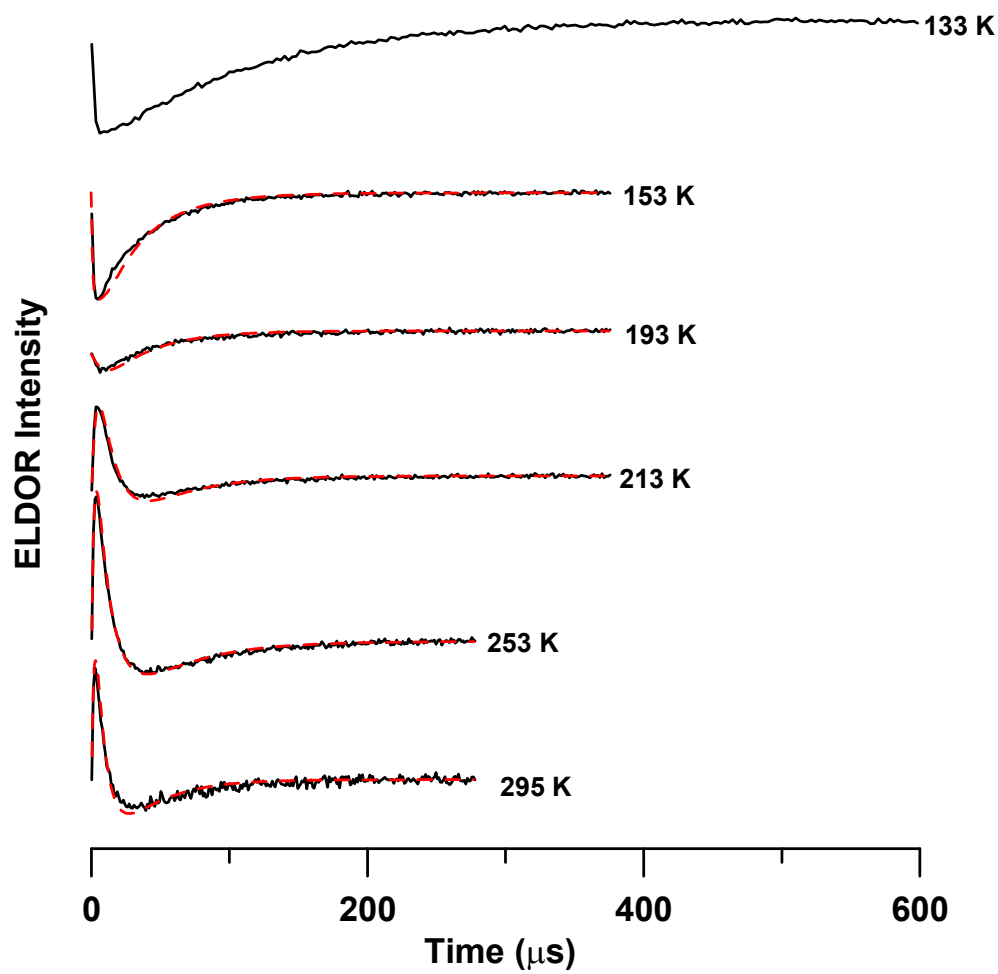
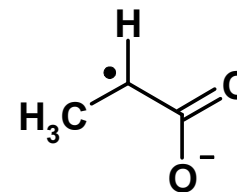


$a_H \sim 25$ G

The barrier to rotation of methyl group in irradiated L-alanine is much higher than for 4-Me-phenol, so the impact of methyl rotation on T_{1e} occurs at higher temperature.

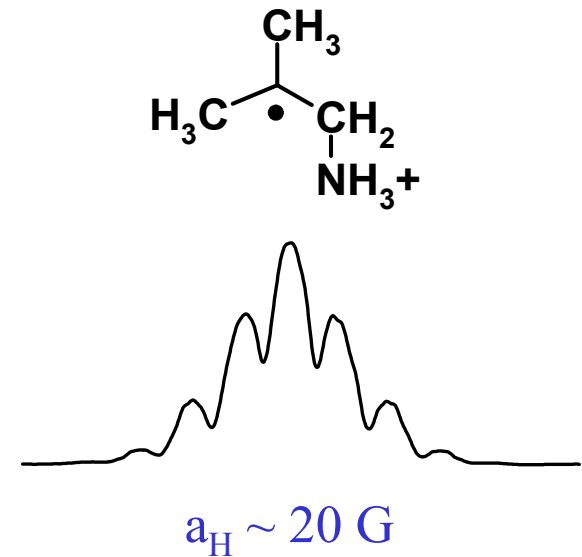
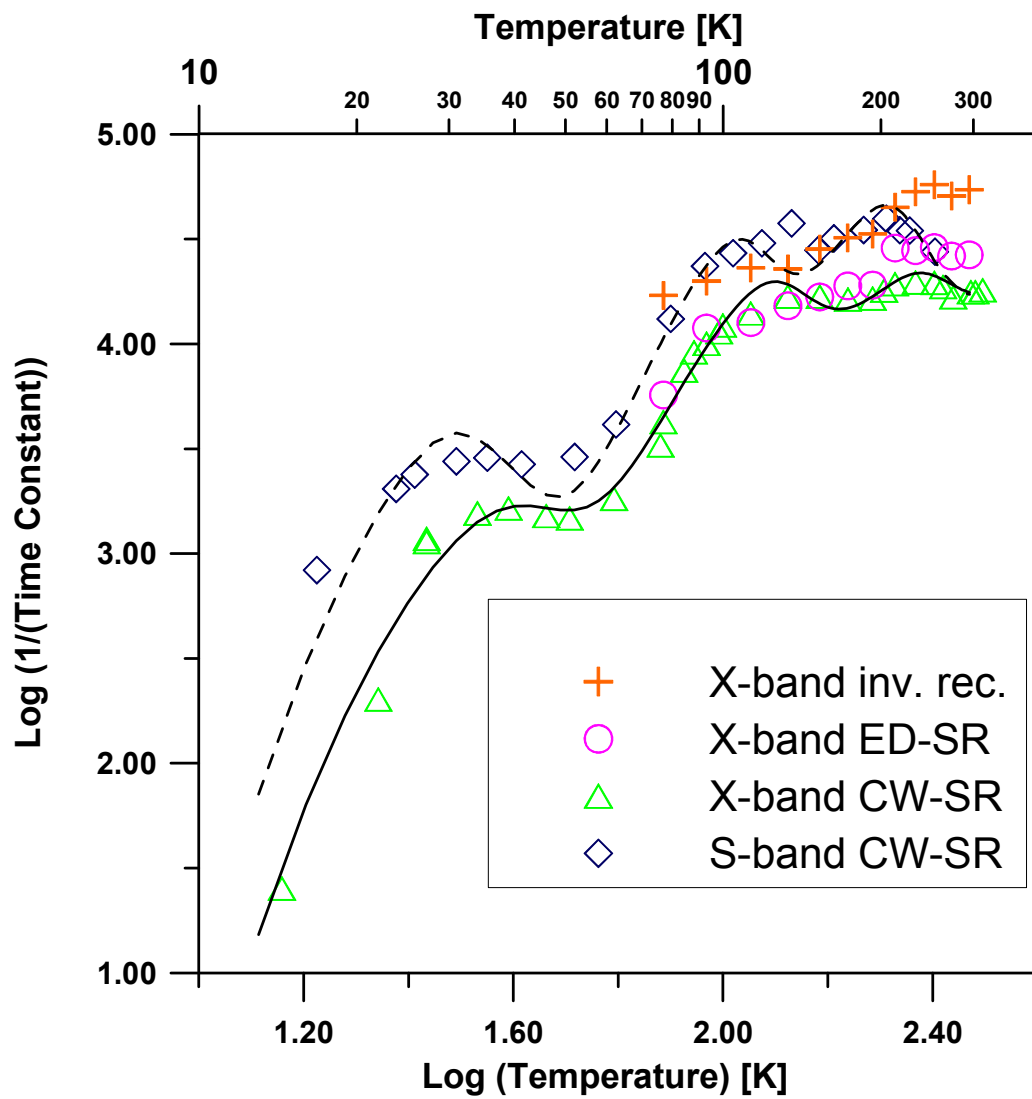
The lines were calculated to fit the data, using Eq. [1].

ELDOR: γ -irradiated L-alanine

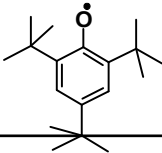
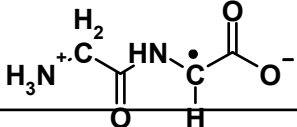
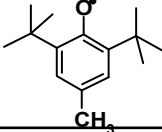
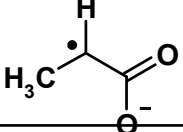
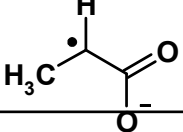
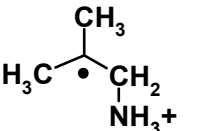


The y-scale for each curve is 0.88 to 1.12. The ELDOR enhancement indicates $T_{x1} < T_{1e}$, which is observed for this sample when the rate of methyl rotation is comparable to the electron Larmor frequency.

T_{1e} for γ -irradiated L-valine



The rotational barrier is different for the two methyl groups, so rotation at the electron Larmor frequency occurs at different temperatures. The lines were calculated to fit the data, using Eq. [1]

radical	host	ELDOR	E_a (kJ)
	2,4,6-tri- <i>t</i> -butyl phenol		6.7 10
	glycyglycine	R: 77 to 295 K	
	4-Me-2,6-di- <i>t</i> -butyl phenol	E: 77 to 293 K	1.4 10
	methyl-malonic acid	E: 77 to 253 K	2.1 4
	L-alanine	R: 77 to 193 K E: 200 to 295 K	12
	L-valine	E: 77 to 295 K	1.4 7.5

E = enhancement, R = reduction

Summary

When measuring T_{1e} it is crucial to check the experimental data for effects of spectral diffusion. The "right" technique to measure T_{1e} for a particular sample is strongly dependent on the nature of competing spectral diffusion processes.

The temperature and microwave frequency dependence of T_{1e} provides insight into the dominant relaxation process.

Relaxation processes shed light on electronic structure and molecular motion.