Electron Paramagnetic Resonance of the Methyl Radical

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- The methyl radical CH3 has 1 unpaired electron. This electron has a spin, S=1/2. Under the influence of an external magnetic field, the electron spin along the axis of the magnetic field an take a value of m_s=+/- ½ .This splits the energy into two levels. The effect is called the electronic Zeeman effect.
- The nuclei of the molecule can also possess a spin. In the case of the methyl radical the carbon nucleus has 0 spin, while the hydrogen nuclei have a nuclear spin of I=1/2.
- These spins couple to the electron spin to produce the hyperfine spectrum of the molecule.
- After using ORCA to calculate the g coupling tensor for the electron spin-Magnetic field interaction and the A coupling tensor for the nuclear spin-electron spin interactions, the program Easy Spin can be used to simulate the spectra under various experimental conditions. The theory is as follows:

The Spin Hamiltonian*

EasySpin supports spin systems with any number of electron spins and nuclear spins. The total spin Hamiltonian is

$$\hat{H} = \sum_i \left[\hat{H}_{\mathrm{EZ}}(i) + \hat{H}_{\mathrm{ZF}}(i)\right] + \sum_k \left[\hat{H}_{\mathrm{NZ}}(i) + \hat{H}_{\mathrm{NQ}}(i)\right] + \sum_i \sum_{j>i} \hat{H}_{\mathrm{EE}}(i,j) + \sum_i \sum_k \hat{H}_{\mathrm{HF}}(i,k)$$

with the following terms

- $H_{EZ}(i)$: Electron Zeeman Interaction of electron spin i
- $H_{ZF}(i)$: Zero-Field Interaction of electron spin i
- $H_{NZ}(k)$: Nuclear Zeeman Interaction of nuclear spin k
- $H_{NQ}(k)$: Nuclear Quadrupole Interaction of nuclear spin k
- $H_{EE}(i,j)$: Electron-Electron Interaction between electron spins i and j
- $H_{HF}(i,k)$: Hyperfine Interaction between electron spin i and nuclear spin k

This spin Hamiltonian is a linear function of the magnetic field

with the operators $\hat{H}(\boldsymbol{B}) = \hat{F} + \boldsymbol{B}^{\mathrm{T}}\hat{\boldsymbol{G}} = \hat{F} + B_{\mathrm{x}}\hat{G}_{\mathrm{x}} + B_{\mathrm{y}}\hat{G}_{\mathrm{y}} + B_{\mathrm{z}}\hat{G}_{\mathrm{z}}$

$$\hat{F} = \hat{H}_{\mathrm{NQ}} + \hat{H}_{\mathrm{ZF}} + \hat{H}_{\mathrm{EE}} + \hat{H}_{\mathrm{HF}} \qquad \boldsymbol{B}^{\mathrm{T}}\hat{\boldsymbol{G}} = \hat{H}_{\mathrm{EZ}} + \hat{H}_{\mathrm{NZ}}$$

* From EasySpin Documentation

Electron Zeeman Interaction*

$$\hat{H}_{\mathrm{EZ}} = \mu \boldsymbol{g} \boldsymbol{B}^{\mathrm{T}} \boldsymbol{g} \hat{\boldsymbol{S}} = \mu_{\mathrm{B}} \begin{pmatrix} B_{\mathrm{x}} & B_{\mathrm{y}} & B_{\mathrm{z}} \end{pmatrix} \begin{pmatrix} g_{\mathrm{xx}} & g_{\mathrm{xy}} & g_{\mathrm{xz}} \\ g_{\mathrm{yx}} & g_{\mathrm{yy}} & g_{\mathrm{yz}} \\ g_{\mathrm{zx}} & g_{\mathrm{zy}} & g_{\mathrm{zz}} \end{pmatrix} \begin{pmatrix} \hat{S}_{\mathrm{x}} \\ \hat{S}_{\mathrm{y}} \\ \hat{S}_{\mathrm{z}} \end{pmatrix} = \mu_{\mathrm{B}} \sum_{k=\mathrm{xyz}} \sum_{q=\mathrm{xyz}} g_{kq} B_k \hat{S}_q$$

T

The matrix $\boldsymbol{g}$ is usually symmetric, in which case it can be transformed into its diagonal form $\boldsymbol{g}_{\mathrm{diag}} = \begin{pmatrix} g_1 & 0 & 0 \\ 0 & g_2 & 0 \\ 0 & 0 & g_3 \end{pmatrix}$

via a rotation $\boldsymbol{R}$ parametrized by three Euler angles.

, $\boldsymbol{g}_{\mathrm{diag}} = \boldsymbol{R}(\alpha,\beta,\gamma)^{\mathrm{T}} \boldsymbol{g} \boldsymbol{R}(\alpha,\beta,\gamma) \qquad \boldsymbol{g} = \boldsymbol{R}(\alpha,\beta,\gamma) \boldsymbol{g}_{\mathrm{diag}} \boldsymbol{R}(\alpha,\beta,\gamma)^{\mathrm{T}}$

where g_1, g_2, and g_3 are the three principal values of the $\boldsymbol{g}$ matrix. If $\boldsymbol{g}$ is asymmetric, the diagonalization gives complex principal values.
In its diagonal form, the matrix is the sum of an isotropic component $g_{\mathrm{e}} = 2.002319\ldots$ and a "g shift" contribution $\boldsymbol{\Delta g}$.

$$\boldsymbol{g}_{\mathrm{diag}} = g_{\mathrm{e}} \boldsymbol{I} + \boldsymbol{\Delta g} = \begin{pmatrix} g_{\mathrm{e}} & 0 & 0 \\ 0 & g_{\mathrm{e}} & 0 \\ 0 & 0 & g_{\mathrm{e}} \end{pmatrix} + \begin{pmatrix} \Delta g_1 & 0 & 0 \\ 0 & \Delta g_2 & 0 \\ 0 & 0 & \Delta g_3 \end{pmatrix}$$

* From EasySpin Documentation

Nuclear Zeeman Interaction*

The spin Hamiltonian term describing the interaction of a nuclear spin with the external magnetic field is

$$\hat{H}_{\mathrm{NZ}} = -\mu_{\mathrm{n}} g_{\mathrm{n}} \boldsymbol{B}^{\mathrm{T}} \hat{\boldsymbol{I}} = -\mu_{\mathrm{n}} g_{\mathrm{n}} \sum_{k=\mathrm{xyz}} B_k \hat{I}_k$$

In EPR, chemical shifts and the chemical shift anisotropy are neglected.

* From EasySpin Documentation

Zero Field Interaction*

For a spin S > 1/2, the energy term describing the zero-field interaction (ZF) is

$$\hat{H}_{\mathrm{ZF}}/h = \hat{\boldsymbol{S}}^{\mathrm{T}}\boldsymbol{D}\hat{\boldsymbol{S}} = \begin{pmatrix}\hat{S}_{\mathrm{x}} & \hat{S}_{\mathrm{y}} & \hat{S}_{\mathrm{z}}\end{pmatrix}\begin{pmatrix}D_{\mathrm{xx}} & D_{\mathrm{xy}} & D_{\mathrm{xz}}\\ D_{\mathrm{yx}} & D_{\mathrm{yy}} & D_{\mathrm{yz}}\\ D_{\mathrm{zx}} & D_{\mathrm{zy}} & D_{\mathrm{zz}}\end{pmatrix}\begin{pmatrix}\hat{S}_{\mathrm{x}}\\ \hat{S}_{\mathrm{y}}\\ \hat{S}_{\mathrm{z}}\end{pmatrix} = \sum_{i,j=\mathrm{xyz}} D_{ij}\hat{S}_i\hat{S}_j$$

where x, y and z are the axes of an arbitrary molecule-fixed frame and the 3x3 matrix $\boldsymbol{D}$ is the D tensor. Systems with S = 1/2 do not have a zero-field interaction term.

In its form commonly used in the spin Hamiltonian, the D tensor is set to be traceless (sum of diagonal elements is zero) and symmetric ($D_{ij} = D_{ji}$). D tensors calculated using quantum-chemistry programs in general might not be traceless and exactly symmetric.

In its eigenframe, the D tensor is diagonal

$$\boldsymbol{D} = \begin{pmatrix}D_X & 0 & 0\\ 0 & D_Y & 0\\ 0 & 0 & D_Z\end{pmatrix}$$

where X, Y and Z are now the (molecule-fixed) principal axes of the D tensor. In this frame, the Hamiltonian is

$$\hat{H}_{\mathrm{ZF}}/h = D_X\hat{S}_X^2 + D_Y\hat{S}_Y^2 + D_Z\hat{S}_Z^2$$

Note: For the methyl radical or the Cu qubit candidate we will examine later, since S=1/2, there will be no Zero Field effect

* From EasySpin Documentation

Hyperfine Interaction

The hyperfine interaction term is

$$\hat{H}_{\mathrm{HF}}/h = \hat{\boldsymbol{S}}^{\mathrm{T}}\boldsymbol{A}\hat{\boldsymbol{I}} = \begin{pmatrix}\hat{S}_{\mathrm{x}} & \hat{S}_{\mathrm{y}} & \hat{S}_{\mathrm{z}}\end{pmatrix}\begin{pmatrix}A_{\mathrm{xx}} & A_{\mathrm{xy}} & A_{\mathrm{xz}}\\ A_{\mathrm{yx}} & A_{\mathrm{yy}} & A_{\mathrm{yz}}\\ A_{\mathrm{zx}} & A_{\mathrm{zy}} & A_{\mathrm{zz}}\end{pmatrix}\begin{pmatrix}\hat{I}_{\mathrm{x}}\\ \hat{I}_{\mathrm{y}}\\ \hat{I}_{\mathrm{z}}\end{pmatrix} = \sum_{i=\mathrm{xyz}}\sum_{j=\mathrm{xyz}} A_{ij}\hat{S}_i\hat{I}_j$$

Though it can be asymmetric, the matrix $\boldsymbol{A}$ is often symmetric and can be transformed to its diagonal form

$$\boldsymbol{A}_{\mathrm{diag}} = \begin{pmatrix}A_1 & 0 & 0\\ 0 & A_2 & 0\\ 0 & 0 & A_3\end{pmatrix}$$

via a similarity transformation with a orthogonal rotation matrix $\boldsymbol{R}$

$$\boldsymbol{A} = \boldsymbol{R}(\alpha,\beta,\gamma)\boldsymbol{A}_{\mathrm{diag}}\boldsymbol{R}(\alpha,\beta,\gamma)^{\mathrm{T}} \qquad \boldsymbol{A}_{\mathrm{diag}} = \boldsymbol{R}(\alpha,\beta,\gamma)^{\mathrm{T}}\boldsymbol{A}\boldsymbol{R}(\alpha,\beta,\gamma)$$

The symmetric $\boldsymbol{A}$ can be separated into three components, an isotropic, an axial and a rhombic component. In the eigenframe of $\boldsymbol{A}$, they are characterized by the three parameters a_{iso}, T and rho, respectively.

$$\boldsymbol{A}_{\mathrm{diag}} = a_{\mathrm{iso}}\boldsymbol{I} + \boldsymbol{T} = \begin{pmatrix}a_{\mathrm{iso}} & 0 & 0\\ 0 & a_{\mathrm{iso}} & 0\\ 0 & 0 & a_{\mathrm{iso}}\end{pmatrix} + T\begin{pmatrix}-(1-\rho) & 0 & 0\\ 0 & -(1+\rho) & 0\\ 0 & 0 & 2\end{pmatrix}$$

For a spin system with strong anisotropic g, the $\boldsymbol{A}$ matrices can be significantly asymmetric. In this case, $\boldsymbol{A}$ has complex principal values, and 9 parameters are needed to fully specify $\boldsymbol{A}$.

Electron-electron Interaction*

The general term describing the interactions between two electrons is

$$\hat{H}_{\mathrm{EE}}/h = \hat{\boldsymbol{S}}_1^{\mathrm{T}} \boldsymbol{J} \hat{\boldsymbol{S}}_2 = \begin{pmatrix} \hat{S}_{1\mathrm{x}} & \hat{S}_{1\mathrm{y}} & \hat{S}_{1\mathrm{z}} \end{pmatrix} \begin{pmatrix} J_{\mathrm{xx}} & J_{\mathrm{xy}} & J_{\mathrm{xz}} \\ J_{\mathrm{yx}} & J_{\mathrm{yy}} & J_{\mathrm{yz}} \\ J_{\mathrm{zx}} & J_{\mathrm{zy}} & J_{\mathrm{zz}} \end{pmatrix} \begin{pmatrix} \hat{S}_{2\mathrm{x}} \\ \hat{S}_{2\mathrm{y}} \\ \hat{S}_{2\mathrm{z}} \end{pmatrix} = \sum_{i=\mathrm{xyz}} \sum_{j=\mathrm{xyz}} J_{ij} \hat{S}_{1i} \hat{S}_{2j}$$

The tensor $\boldsymbol{J}$ describes the total interaction between the two electron spins and includes the isotropic, antisymmetric and symmetric interactions.

$$+J\hat{\boldsymbol{S}}_1^{\mathrm{T}}\hat{\boldsymbol{S}}_2 \qquad -J\hat{\boldsymbol{S}}_1^{\mathrm{T}}\hat{\boldsymbol{S}}_2 \qquad +2J\hat{\boldsymbol{S}}_1^{\mathrm{T}}\hat{\boldsymbol{S}}_2 \qquad -2J\hat{\boldsymbol{S}}_1^{\mathrm{T}}\hat{\boldsymbol{S}}_2$$

For the isotropic exchange interaction, several inconsistent conventions are in use in the literature:

EasySpin uses the first one in this list. Therefore, when using values from the literature, make sure to understand which convention was used.

* From EasySpin Documentation

Nuclear Quadrupole Interaction

Nuclei with spin I>1/2 have an electric quadrupole moment that can interact with the local electric field gradient at the nucleus. The term in the spin Hamiltonian describing this nuclear quadrupole interaction is

$$\hat{H}_{\mathrm{NQ}}/h = \hat{\boldsymbol{I}}^{\mathrm{T}}\boldsymbol{Q}\hat{\boldsymbol{I}} = \begin{pmatrix}\hat{I}_{\mathrm{x}} & \hat{I}_{\mathrm{y}} & \hat{I}_{\mathrm{z}}\end{pmatrix}\begin{pmatrix}Q_{\mathrm{xx}} & Q_{\mathrm{xy}} & Q_{\mathrm{xz}}\\ Q_{\mathrm{yx}} & Q_{\mathrm{yy}} & Q_{\mathrm{yz}}\\ Q_{\mathrm{zx}} & Q_{\mathrm{zy}} & Q_{\mathrm{zz}}\end{pmatrix}\begin{pmatrix}\hat{I}_{\mathrm{x}}\\ \hat{I}_{\mathrm{y}}\\ \hat{I}_{\mathrm{z}}\end{pmatrix} = \sum_{i=\mathrm{xyz}}\sum_{j=\mathrm{xyz}} Q_{ij}\hat{I}_i\hat{I}_j$$

where Q is in frequency units. The Q matrix is symmetric ($Q_{ij} = Q_{ji}$) and can be transformed into diagonal form

$$\boldsymbol{Q} = \boldsymbol{R}(\alpha,\beta,\gamma)\begin{pmatrix}Q_1 & 0 & 0\\ 0 & Q_2 & 0\\ 0 & 0 & Q_3\end{pmatrix}\boldsymbol{R}(\alpha,\beta,\gamma)^{\mathrm{T}}$$

where Q_1 , Q_2 and Q_3 are the three principal values. One common convention is to choose the eigenframe such that the three values are ordered according to $|Q_1| \le |Q_2| \le |Q_3|$.

Nuclear Quadrupole Interaction (cont.)

$\boldsymbol{Q}$ is traceless, which means $Q_{xx} + Q_{yy} + Q_{zz} = Q_1 + Q_2 + Q_3 = 0$

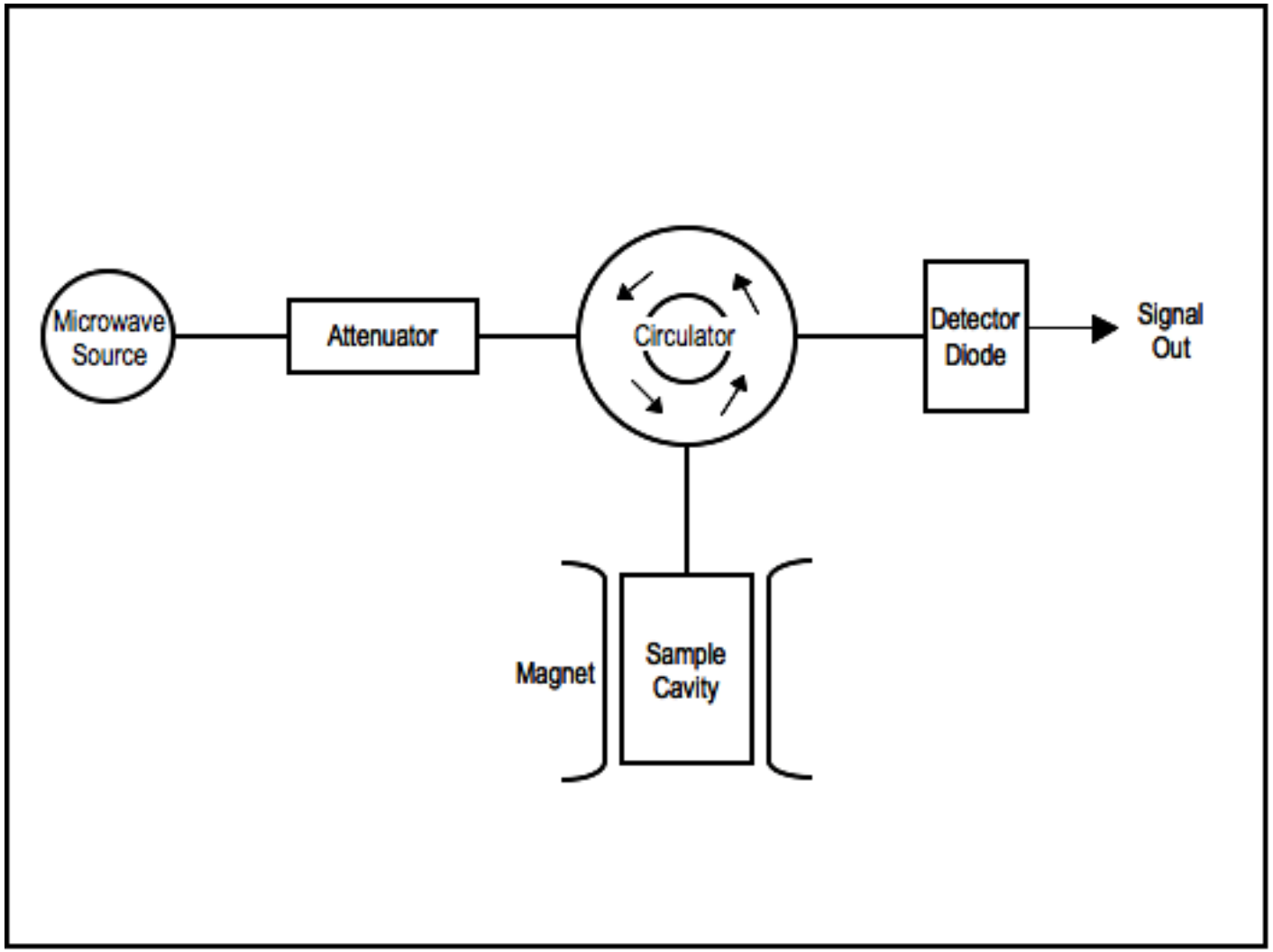
Instead of the principal values Q_1 , Q_2 , and Q_3 , it is common to encounter the conventional parameters e^2Qq/h and η , related to the principal values via

$$\boldsymbol{Q} = \begin{pmatrix} Q_1 & 0 & 0 \\ 0 & Q_2 & 0 \\ 0 & 0 & Q_3 \end{pmatrix} = \frac{e^2Qq/h}{4I(2I-1)} \begin{pmatrix} -(1-\eta) & 0 & 0 \\ 0 & -(1+\eta) & 0 \\ 0 & 0 & 2 \end{pmatrix} \qquad e^2Qq/h = 2I(2I-1)Q_3 \qquad \eta = \frac{Q_1 - Q_2}{Q_3}$$

With the ordering convention above, e^2Qq/h can be positive or negative, and η is between 0 and 1.
eq is the largest-magnitude component of the EFG (electric field gradient) tensor at the nucleus. The EFG tensor is the matrix of all second derivatives of the electrostatic potential. The atomic unit of the EFG is $E_h/e/a_0^2$, and its SI unit is V/m^2. Occasionally, $V/Å^2$ is used. Q is the electric quadrupole moment of the nucleus, its SI unit is m^2. It is usually given in barn (1 barn = 10^{-28} m^2 = 10^{-24} cm^2).
The nuclear quadrupole tensor is related to the EFG tensor $\boldsymbol{V}$ via

$$\boldsymbol{Q} = \frac{1}{h} \frac{eQ}{2I(2I-1)} \boldsymbol{V}$$

EPR Experimental Setup



The microwave source is usually a Klystron tube.

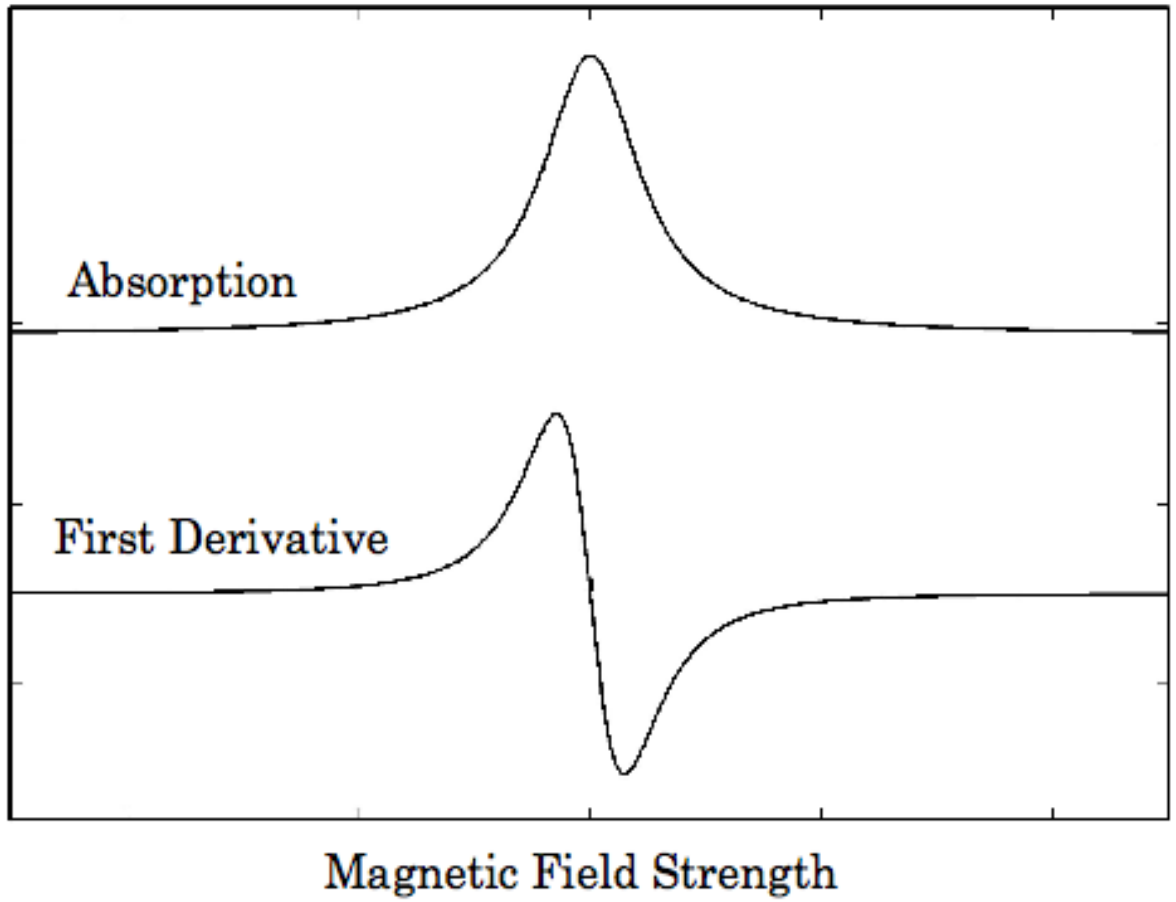
The microwave beam is then attenuated to an appropriate level to maintain linearity.

The circulator and sample cavity form a resonator, where the signal is absorbed by the sample if it is at resonance.

The resulting signal is then passed onto a detector diode where the signal is monitored.

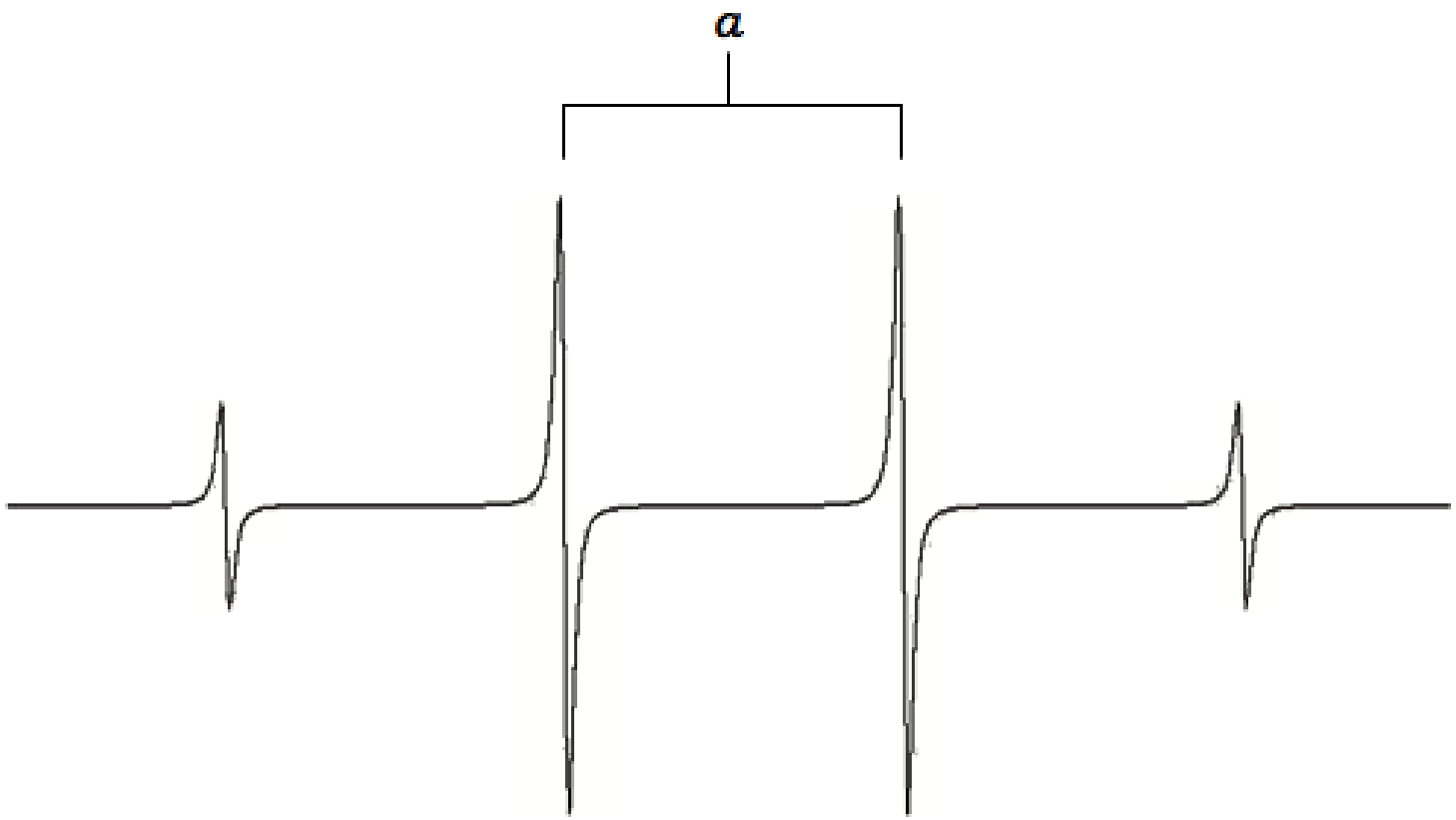
The wavelength of the microwave is generally kept constant , while the magnetic field across the sample is varied to generate the spectrum.

EPR Signal



The EPR signal is generated by an absorption of microwaves, however the signal is usually presented as the first derivative of the absorption spectrum.

Simulated methyl radical spectrum



Hyperfine coupling in EPR is analogous to spin-spin coupling in NMR. There are two kinds of hyperfine coupling: 1) coupling of the electron magnetic moment to the magnetic moment of its own nucleus; and 2) coupling of the electron to a nucleus of a different atom, called super hyperfine splitting. Both types of hyperfine coupling cause a splitting of the spectral lines with intensities following Pascal's triangle for I = 1/2 nuclei, similar to J-coupling in NMR. A simulated spectrum of the methyl radical is shown in the figure.
The line is split equally by the three hydrogens giving rise to four lines of intensity 1:3:3:1 with hyperfine coupling constant a.

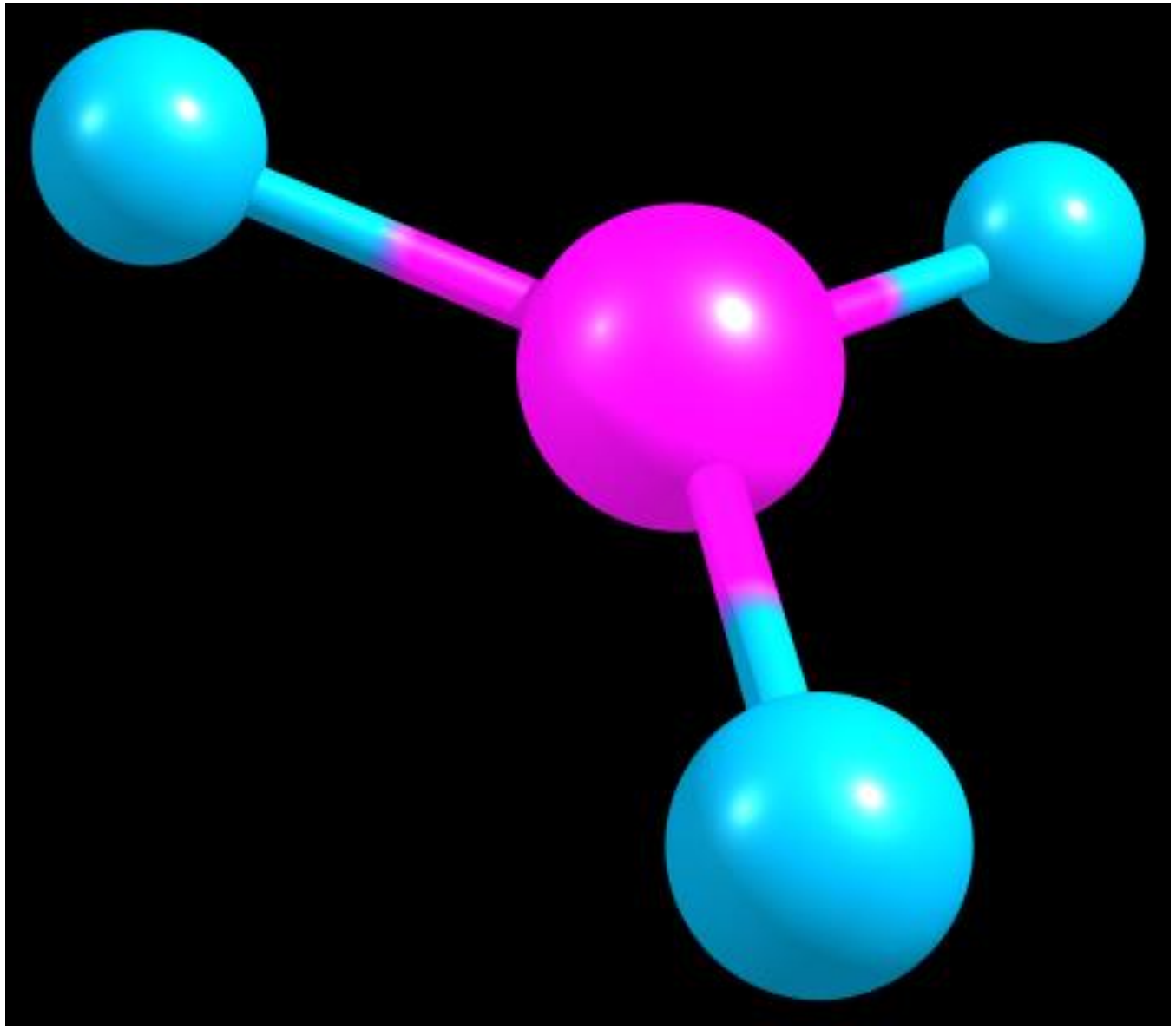
EPR of the Methyl Radical

- We start the process by doing a geometry optimization for the CH3 radical. Below is an ORCA input file.

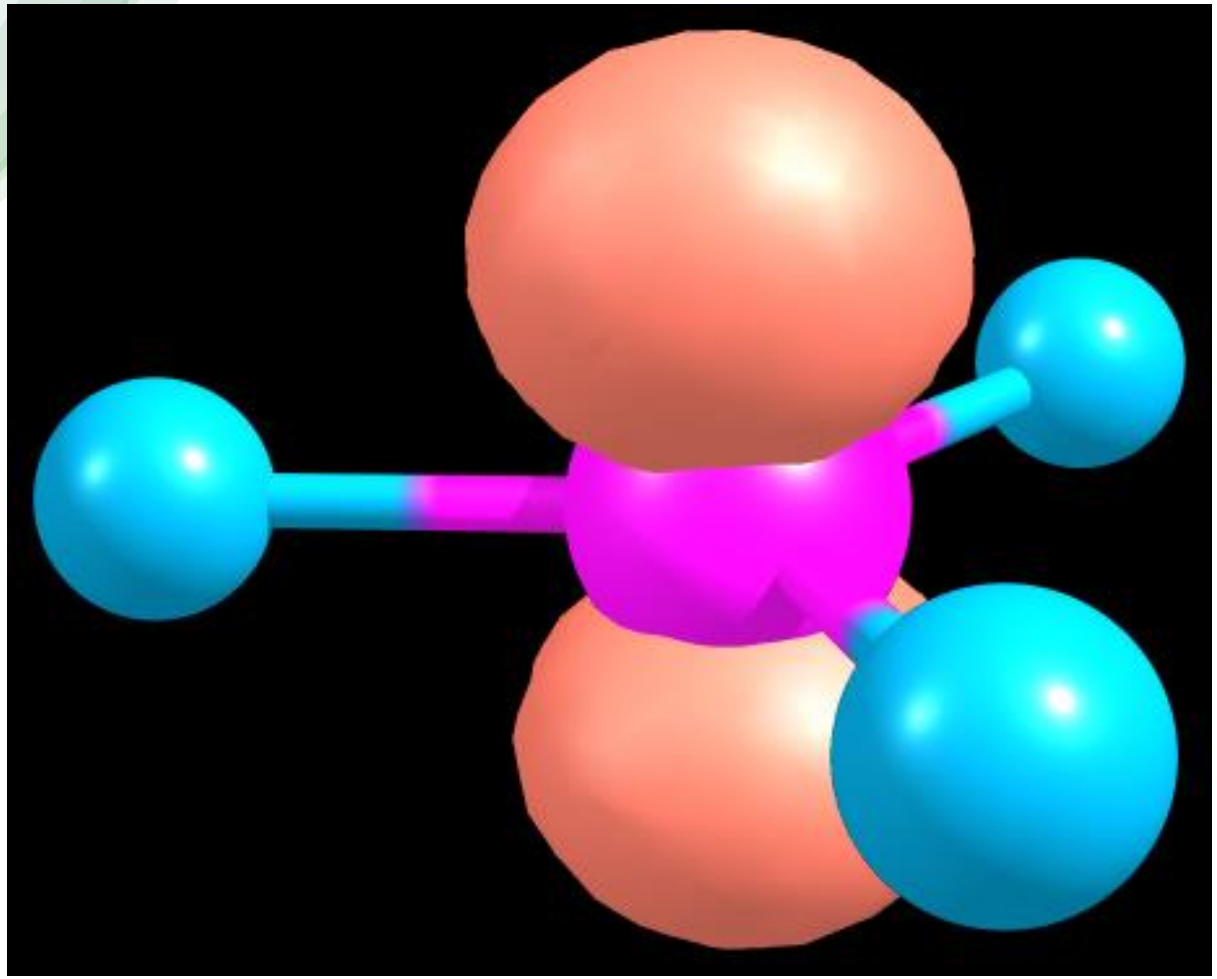
```
! B3LYP DEF2-TZVP OPT
*  xyz  0  2
   C   3.20276693914010     2.91777006829308    -1.46614904250634
   H   4.21682401439677     3.22254500904168    -1.25560882817865
   H   2.69109288861722     3.31313693290047    -2.33037576806431
   H   2.69057615784592     2.24676798976475    -0.79431636125068
*
```

Input File Explanation

- B3LYP is the DFT functional method chosen for the calculation.
- DEF2-TZVP is the basis set chosen to do the calculation.
- OPT is the calculation being executed, a Geometry Optimization.
- The xyz file attachment provides the Cartesian coordinates of the 4 atoms , the charge is 0 and the multiplicity is 2 (i.e. 2S+1 where the spin S is 1/2)



Chemcraft Rendering of the Optimized Molecule



Spin Density 3D Plot

As rendered by Chemcraft using the ORCA molecular orbital data.
Isosurface contour = 0.05

Calculation of EPR Parameters

- We will now calculate the EPR parameters for the methyl radical using ORCA. Below is the input file for the EPR calculations.

! B3LYP EPR-II AUTOAUX	B3LYP is the DFT functional.EPR-II is the basis set
! PAL8 Printbasis Largeprint PrintMOs	PAL8 sets 8 parallel cores. Other provide data for Chemcraft visualizations
* xyz 0 2	xyz file of zero charge and a multiplicity of 2
C 3.200224000 2.924869000 -1.461612000	Cartesian coordinate file of the 4 atoms in the radical
H 4.217879000 3.220147000 -1.256945000	
H 2.691704000 3.310628000 -2.331828000	
H 2.691453000 2.244576000 -0.796064000	
*	
%EPRNMR	Calls ORCA subroutine for EPR or NMR
GTENSOR TRUE	Tells ORCA to calculate the electronic g tensor.
NUCLEI = ALL H {AISO, ADIP, AORB}	Tells ORCA to calculate the nuclear hyperfine splitting
END	tensors (in this case for the hydrogen spin ½ nuclei coupled to the spin ½ electron

Electronic g-Matrix

- The ORCA calculation result for the electronic g-matrix is as follows:
- The g-matrix:
- 2.0027591 0.0001540 0.0001068
- 0.0001540 2.0024668 -0.0002488
- 0.0001069 -0.0002488 2.0026526

- gEL 2.0023193 2.0023193 2.0023193
- gRMC -0.0001271 -0.0001271 -0.0001271
- gDSO(tot) 0.0000339 0.0000705 0.0000705
- gPSO(tot) 0.0000019 0.0005626 0.0005626
- ---------- ---------- ----------
- g(tot) 2.0022280 2.0028252 2.0028253 iso= 2.0026262
- Delta-g -0.0000913 0.0005059 0.0005060 iso= 0.0003069

Orientation:

X	-0.3327910	-0.8411462	-0.4262901
Y	0.7747200	0.0138626	-0.6321525
Z	0.5376422	-0.5406301	0.6470394

Notes: (1) The g-matrix conforms to the "BgS" spin Hamiltonian convention.

(2) The principal values are square roots of the eigenvalues of g*gT.

(3) Orientations are eigenvectors of g*gT written as column vectors.

(4) Individual contributions are projections of the full matrices onto the eigenvectors of g*gT.

(5) Tensor is right-handed.

HFC matrix (all values in MHz)

- -84.3282 14.0220 -30.6819
- 14.0220 -50.8232 -15.2181
- -30.6819 -15.2181 -64.4605

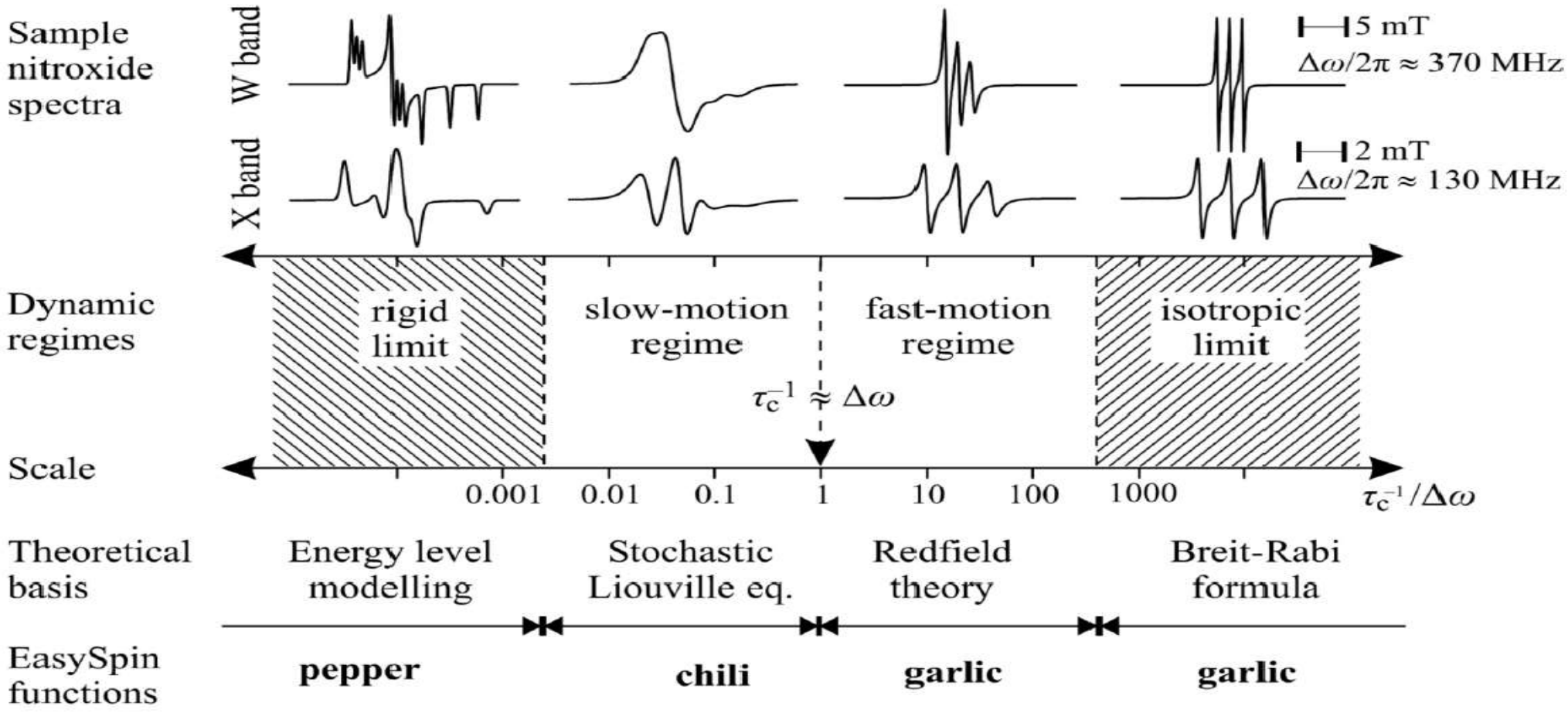
- A(FC) -66.5500 -66.5500 -66.5500
- A(SD) 41.0906 -0.8536 -40.2370
- A(ORB+DIA) 0.0114 -0.0006 0.0271 A(PC) = 0.0126
- A(ORB) 0.0064 0.0006 0.0258 A(PC) = 0.0109
- A(DIA) 0.0050 -0.0012 0.0013 A(PC) = 0.0017
- ---------- ---------- ----------
- A(Tot) -25.4480 -67.4042 -106.7598 A(iso)= -66.5373

HFC Calculation (cont.)

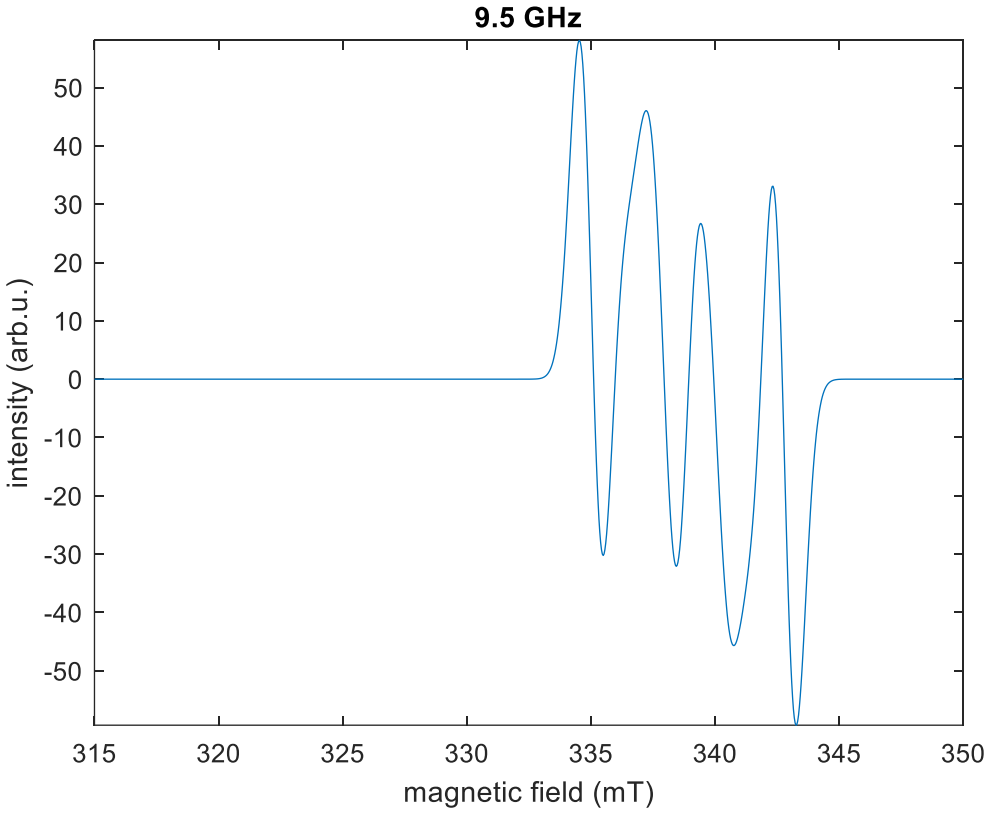
- Orientation:
- X 0.4714799 0.3327101 -0.8167072
- Y 0.6303839 -0.7747803 0.0482868
- Z -0.6167032 -0.5376053 -0.5750284

- Notes: (1) The A matrix conforms to the "SAI" spin Hamiltonian convention.
- (2) Tensor is right-handed.

EPR Regimes


Sample nitroxide spectra
W band
X band
5 mT
Δω/2π ≈ 370 MHz
2 mT
Δω/2π ≈ 130 MHz
Dynamic regimes
rigid limit
slow-motion regime
fast-motion regime
isotropic limit
τc⁻¹ ≈ Δω
Scale
0.001
0.01
0.1
1
10
100
1000
τc⁻¹/Δω
Theoretical basis
Energy level modelling
Stochastic Liouville eq.
Redfield theory
Breit-Rabi formula
EasySpin functions
pepper
chili
garlic
garlic

“Pepper” EPR Spectrum of Methyl Radical

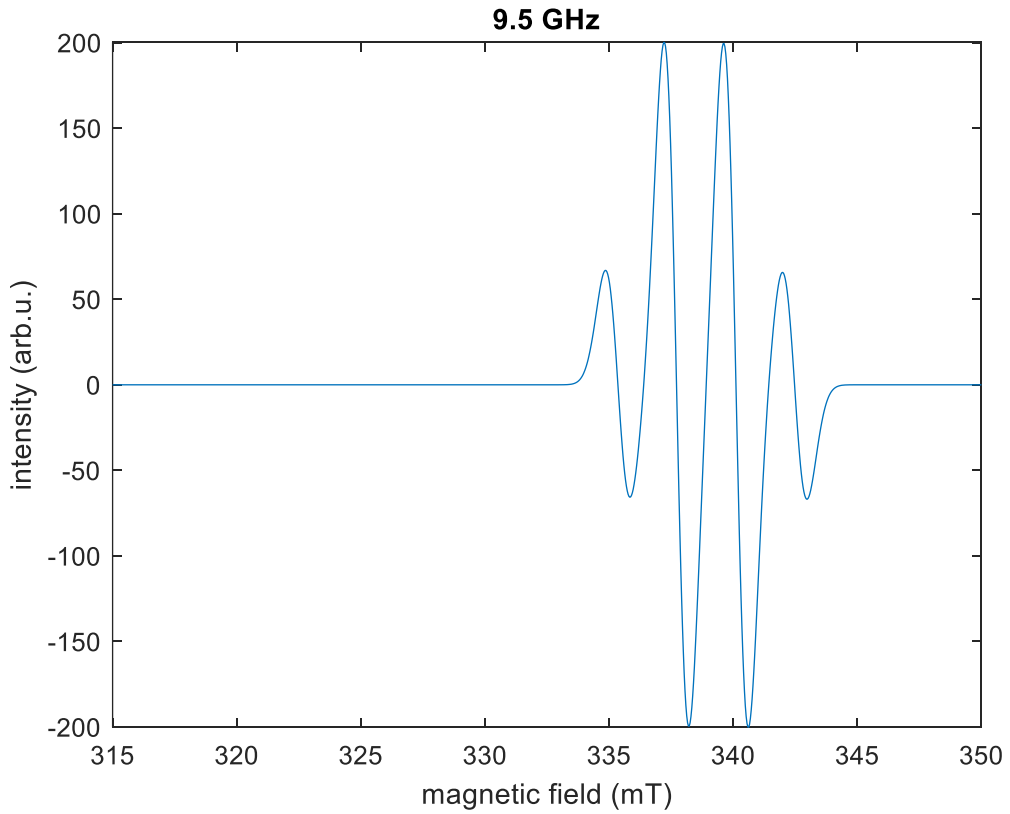


“Pepper” is the EasySpin simulated EPR spectrum in the rigid limit regime. Energy level modelling is used as the theoretical basis in this regime

MATLAB Code:

```
Sys = orca2easyspin('CH3_EPR.out');
Sys.lwpp = 1; % mT
Exp.mwFreq = 9.5; % GHz
Exp.Range = [315 350]; % mT
pepper(Sys,Exp);
```

“Garlic” EPR Spectrum of Methyl Radical

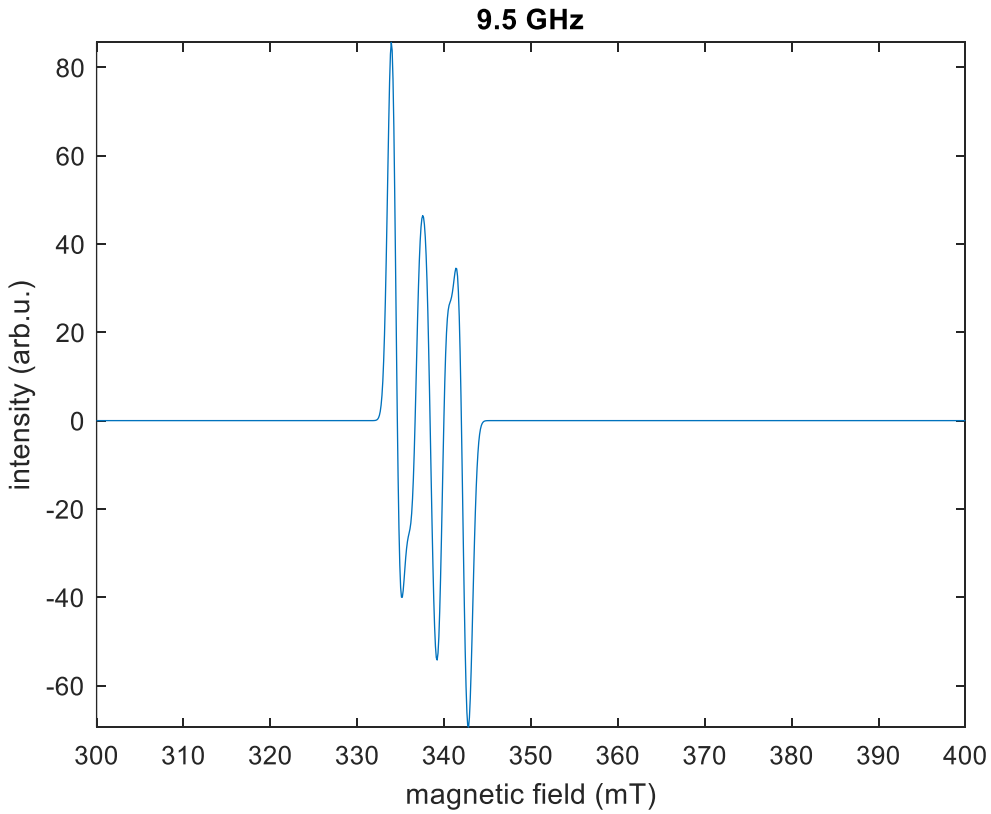


“Garlic” is the EasySpin simulated EPR spectrum in the isotopic limit regime. The Breit-Rabi formula is used as the theoretical basis in this regime

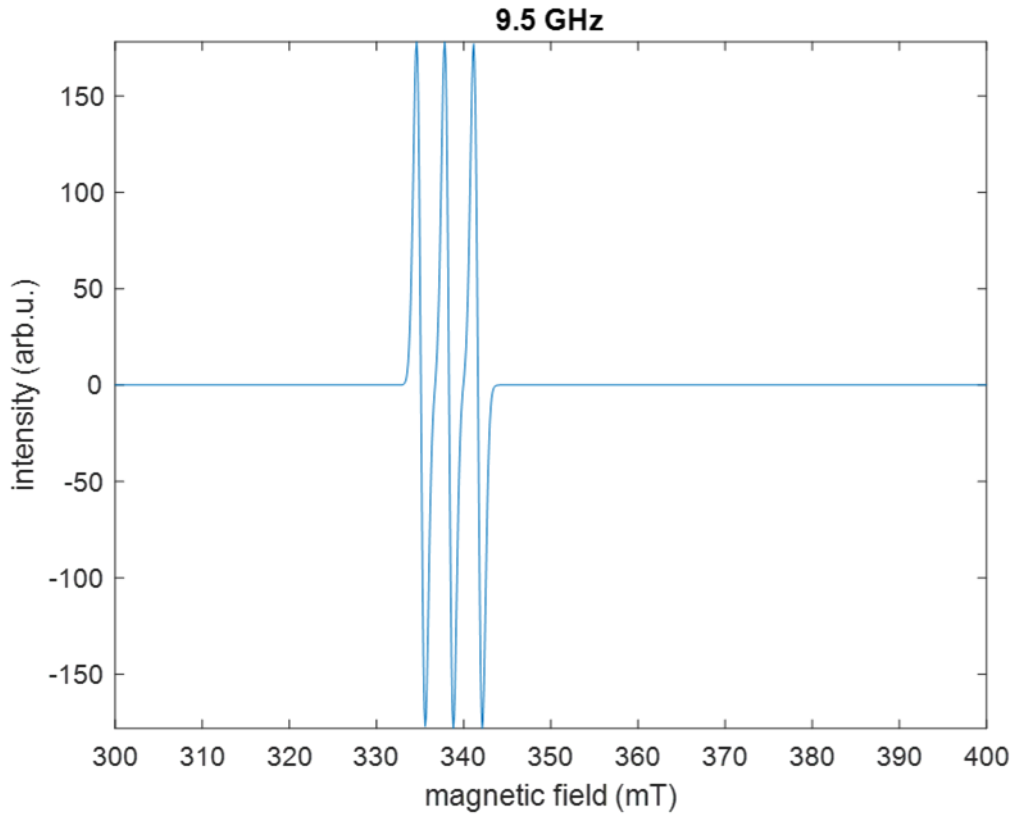
EPR of Nitrogen Dioxide (NO_2)

- I'm examining NO_2 because it is the molecule I studied for my Ph.D, thesis, it happens to be a free radical in its ground state. It combines with another NO_2 to form N_2O_4 which has no unpaired electrons. So, to see the free radical behavior, it should be studied at relatively low pressures to minimize the dimerization.
- Nitrogen dioxide has a free, unpaired electron in its ground state configuration.
- As a molecule it therefore has a spin $S=1/2$, and a multiplicity of $2S+1$, or 2 (i.e. a doublet state).
- The nitrogen nucleus of the N14 isotope has a nuclear spin $I=1$ with a multiplicity of $2I+1=3$, (i.e. a triplet state).
- The hyperfine coupling of the nitrogen nuclear spin to the microwave electronic spin transition of -½ to +½ should result in a triplet configuration.

Simulated NO2 EPR Spectra*



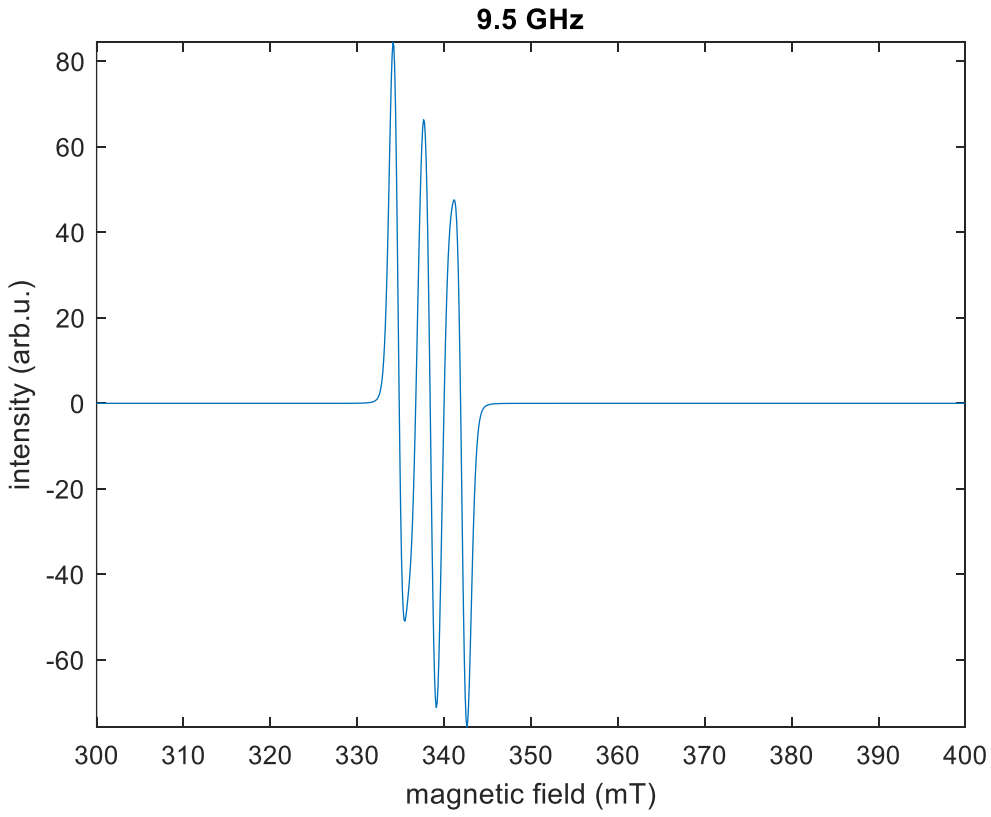
Rigid limit simulated EPR spectrum



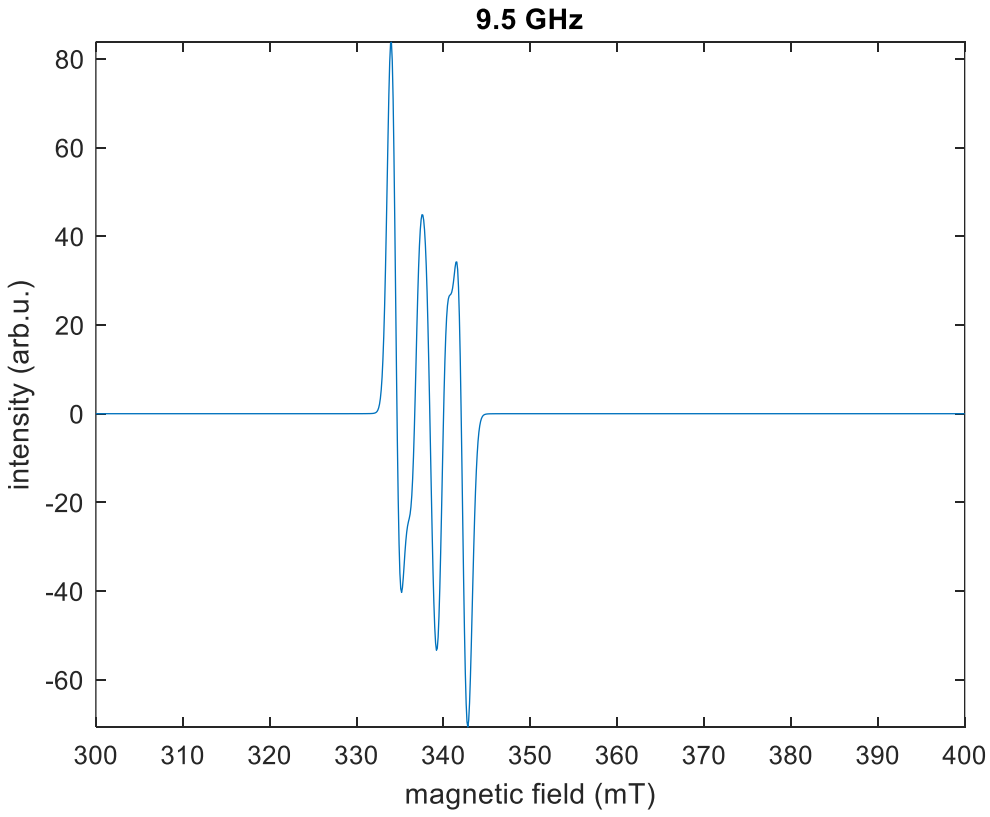
Isotropic limit simulated EPR spectrum

*from Easy Spin/ORCA

Simulated NO2 EPR Spectra*



Slow Motion Regime, tcorr=1e-8s



Slow Motion Regime, tcorr=1e-7s

*from Easy Spin/ORCA