Extracting Quantum Properties of Solid-State Polarized Targets

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Tensor Collaboration Meeting
Jefferson Lab

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U.S. DEPARTMENT of ENERGY


UNIVERSITY of VIRGINIA

Jefferson Lab

Outline

1. Motivation
2. Theoretical Background
3. Computational Modeling
4. Outcome
5. Future Prospects

Motivation

Importance of Polarized Targets:

- Spin structure of nucleons.
- Spin-dependent scattering/interactions.
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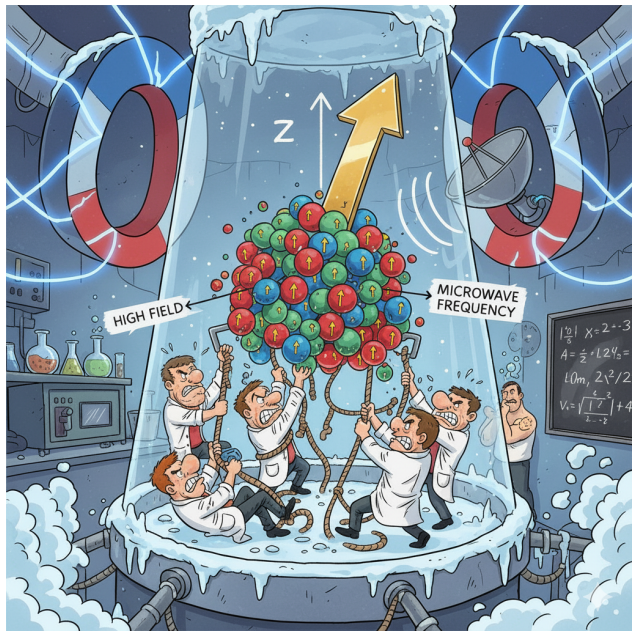
Today's Challenges:

- Achieving high polarization.
- Understanding the relaxation mechanism.



Big Picture

- We want to explore ESR parameters such as linewidth, intensities for radicals including NH_2. and ND_2..
- Other characteristics that we can use in our Rate Equations.

We try to understand and extract the properties/parameters governing polarization and relaxation in target materials.

Theoretical Framework

Density Functional Theory:

Uses the electron density approach to find the ground state of the system.

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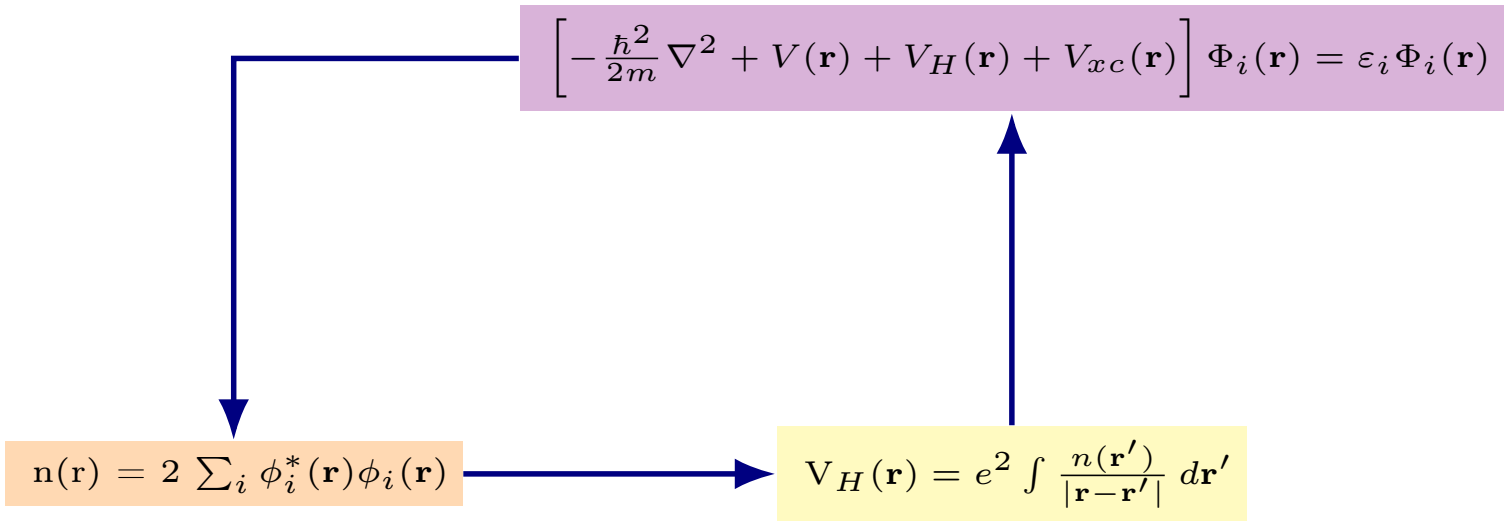
Self Consistency of Kohn-Sham Equation



Theoretical Framework

The ESR parameters form DFT

The g-Tensor:

Determines the position of the signal in the ESR spectra. There are four contributions to it.

$$\mathbf{g} = g_e \mathbf{1} + \mathbf{g}^{\mathrm{RMC}} + \mathbf{g}^{\mathrm{DSO}} + \mathbf{g}^{\mathrm{PSO}} \quad (1)$$

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$$\mathrm{g}^{\mathrm{DSO}}_{\mu\nu} = \frac{\alpha^2 g_e}{4S} \sum_{k,l} P^{\alpha-\beta}_{kl} \langle \phi_k | \xi(r_A) [\mathrm{r}_A r_O - r_{A,\mu} r_{O,\nu}] | \phi_l \rangle (4)$$

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Orbital Zeeman: usually the main source of deviation from free electron g-value.

$$g^{\mathrm{PSO}}_{\mu\nu} = -\frac{g_e}{2S} \sum_{k,l} \frac{\partial P^{\alpha-\beta}_{kl}}{\partial B_\nu} \langle \phi_k | \hat{h}^{SOC}_\nu | \phi_l \rangle \quad (5)$$

(Source: ORCA manual, Release 6.1.0)

Theoretical Background

Hyperfine Coupling (A) Tensor:

It characterizes the interaction between electron and nuclear spin that leads to splitting of the signal.

$$\mathbf{A}_N = A_{\text{iso}}\mathbf{1} + \mathbf{A}^{\text{dip}} + \mathbf{A}^{\text{orb}} + \mathbf{A}^{\text{GC}} \tag{6}$$

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$$A_{\text{iso}}(N) = \frac{4\pi}{3}\langle S_z\rangle^{-1} g_e g_N \beta_e \beta_N \, \rho(\mathbf{R}_N), \tag{7}$$

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$$A^{\text{dip}}_{\mu\nu}(N) = P_N \sum_{k,l} \rho_{kl} \left\langle \phi_k \left| r_N^{-5}(3 r_{N\mu} r_{N\nu} - \delta_{\mu\nu} r_N^2)\phi_l \right.\right. \tag{8}$$

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Spin-orbit contribution: comes from cross terms between spin orbit and nucleus orbit coupling operators

$$A^{\text{orb}}_{\mu\nu}(N) = -\frac{1}{2S} P_N \sum_{k,l} \frac{\partial \rho_{kl}}{\partial I_\nu} \left\langle \phi_k \left| \hat{h}^{\text{SOC}}_{\mu} \right| \phi_l \right\rangle \tag{9}$$

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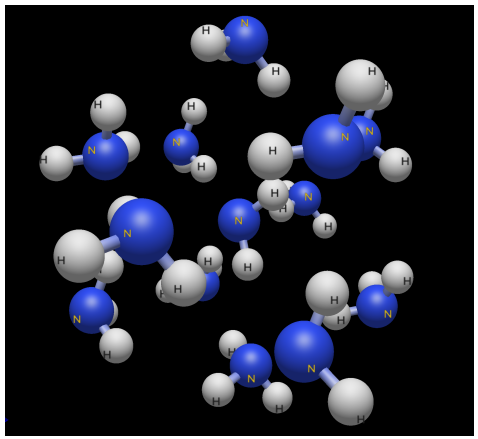

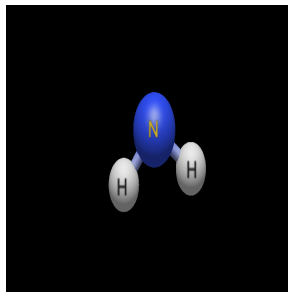

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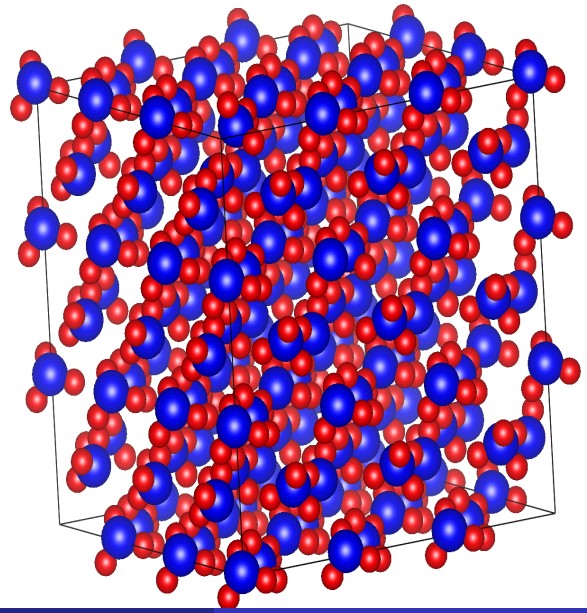

Results

Example output with anisotropic g and A tensors from ORCA.

```
-------------------
ELECTRONIC G-MATRIX
-------------------

Method          : SCF
Type of density    : Spin Density
Type of derivative : Magnetic Field (no GIAOs) (Direction=X)
Multiplicity       :  2
Irrep              :  0
Basis              : AO
The g-matrix:
          2.0055754   0.0021273   0.0008500
          0.0021272   2.0035016   0.0005473
          0.0008500   0.0005473   2.0040343

Breakdown of the contributions
 gel        2.0023193   2.0023193   2.0023193
 gRMC      -0.0002020  -0.0002020  -0.0002020
 gDSO(tot)  0.0000458   0.0000990   0.0001000
 gPSO(tot)  0.0000088   0.0014979   0.0050080
          ----------  ----------  ----------
 g(tot)     2.0021719   2.0037142   2.0072252 iso=  2.0043704
 Delta-g   -0.0001474   0.0013949   0.0049060 iso=  0.0020512

 Orientation:
  X         0.5284972   0.2605601   0.8079599
  Y        -0.8488948   0.1529278   0.5059553
  Z         0.0082722  -0.9532689   0.3020100
```

```
-------------------------------------------------------------
Nucleus  0H : A  : Isotope=   1 I=  0.5 P=533.5514 MHz/au**3
           Q  : Isotope=   2 I=  1.0 Q=  0.0029 barn
           HFC: iso  =YES dip=YES orb=YES gauge=YES
           EFG: fgrad= NO rho= NO
-------------------------------------------------------------

Total HFC matrix (all values in MHz):
-------------------------------------------------------------
          -25.4538         25.5939         -30.8252
           25.5948        -51.2955         -19.5230
          -30.7407        -19.4704        -101.0501

A(FC)       -59.3666         -59.3666         -59.3666
A(SD)        62.1955          -7.6721         -54.5234
A(ORB+DIA)    0.2198          -0.0030           0.0834   A(PC) =   0.1001
A(ORB)        0.2108          -0.0007           0.0811   A(PC) =   0.0971
A(DIA)        0.0090          -0.0023           0.0023   A(PC) =   0.0030
            ----------       ----------       ----------
A(Tot)        3.0488         -67.0417        -113.8066   A(iso)= -59.2665
Orientation:
 X         0.8025849        0.5285326        -0.2766059
 Y         0.4964997       -0.8488730        -0.1813911
 Z        -0.3306744        0.0082470        -0.9437089
```

```
-------------------------------------------------------------------------
        Euler rotation of hyperfine tensor to g-tensor
-------------------------------------------------------------------------

-------------------------------------------------------------------
 Atom |  Alpha    Beta    Gamma  |   Ax      Ay      Az
      |       [degrees]          |       [MHz]
-------------------------------------------------------------------
  2N     -0.0     0.0     0.0     110.64  -21.38  -19.92
  0H    -90.0    36.9    90.0     -67.04 -113.81    3.05
  1H     90.0    36.9   -90.0     -67.04 -113.81    3.05
-------------------------------------------------------------------
```

Results

EPR parameters for NH_2.

Experimental values are from references[1][2][3]. The **Hybrid B3LYP functional** was used for all calculations.

System Size	**Basis set**	g_{iso}	Δg	g_{exp}
Single radical	def2-TZVP	2.0043704	0.0020512	2.0034–2.0047
	EPR-III	2.0044454	0.0021261	–
Cluster (51 atoms)	def2-TZVP	2.0039831	0.0016639	–

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System Size	**Basis set**	A_{iso} **(MHz)**	A_{exp} **(MHz)**
Single radical	def2-TZVP	N: 23.1120, H: -59.2665, H: -59.2664	N: 19–27, H: 67–69
	EPR-III	N: 28.6276, H: -60.8941, H: -60.8883	—
Cluster (51 atoms)	def2-TZVP	N: 26.460, H: -57.202, H: -56.9775	—

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Results

EPR parameters for ND_2.

Experimental values are from[4] and[5].

g	g_{iso}	Δg	g_{exp}
	2.0044462	0.0021270	2.0034 - 2.0047
A_{iso} (MHz)	N	D	A_{exp}
	28.6327	-9.1423, -9.142305	N:27.8, D:-10.1

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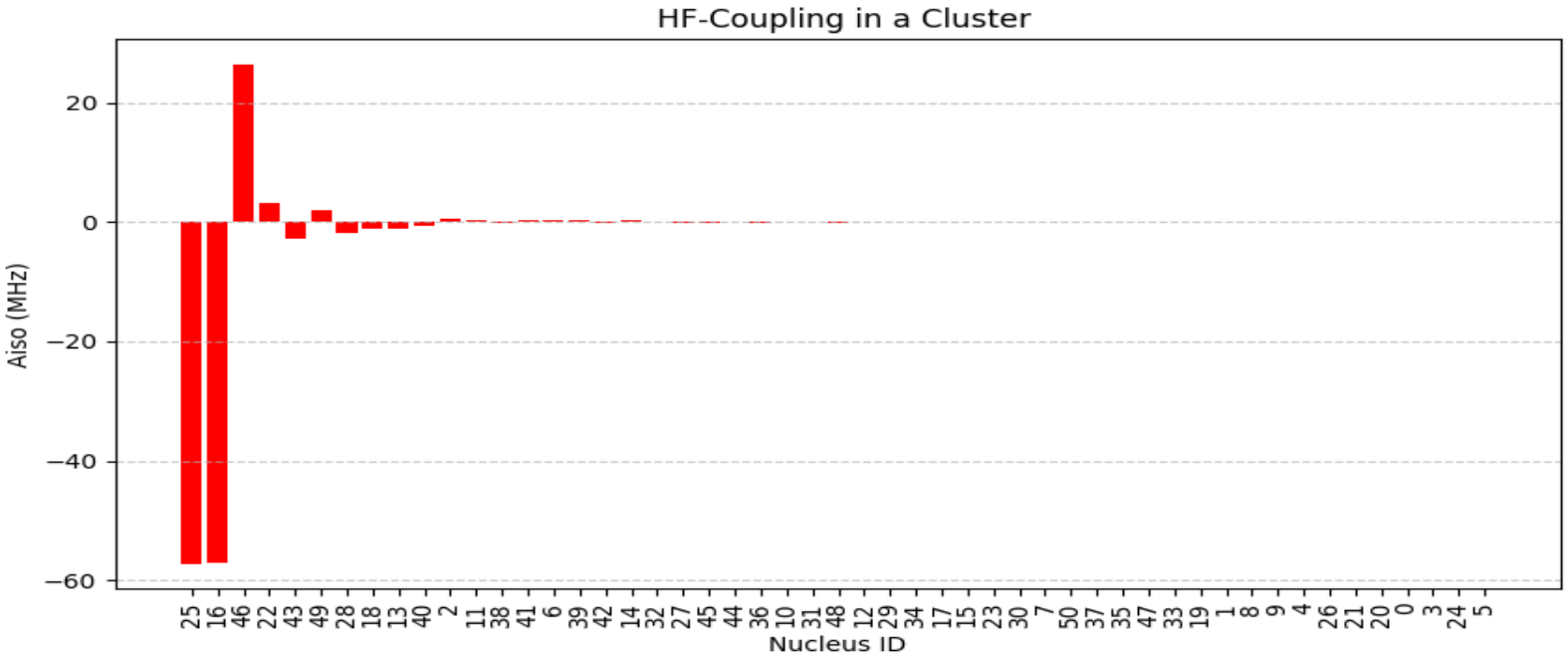
Cluster Effect

HF-Coupling with Surrounding Nuclei



ESR Spectra

Used the softwareEasyspin, which takes the ESR Hamiltonian: $\mathrm{H}_s = \mu_B \vec{B} \cdot g \cdot \hat{S} + \sum_i \hat{I}_i \cdot A_i \cdot \hat{S}$
The Microwave frequancy used is ≈ 9.5GHz based on $\Delta E = h\nu = \mu_B g_e \vec{B}$

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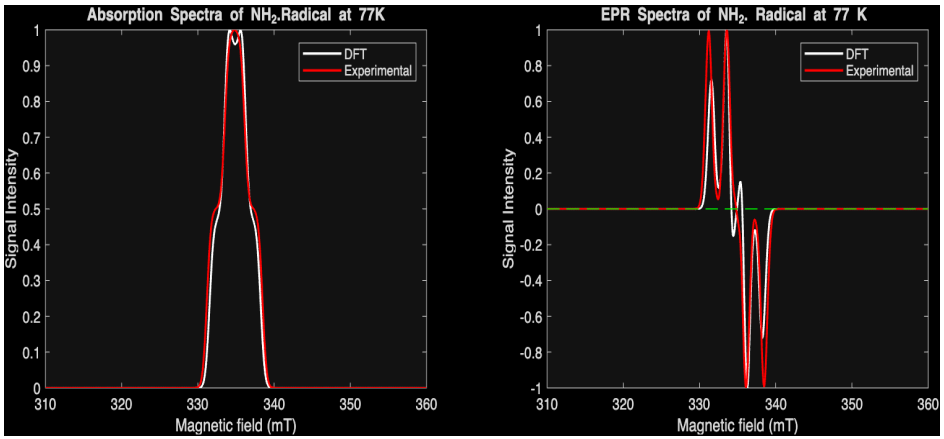
ESR Powder Spectra for NH2. Radical



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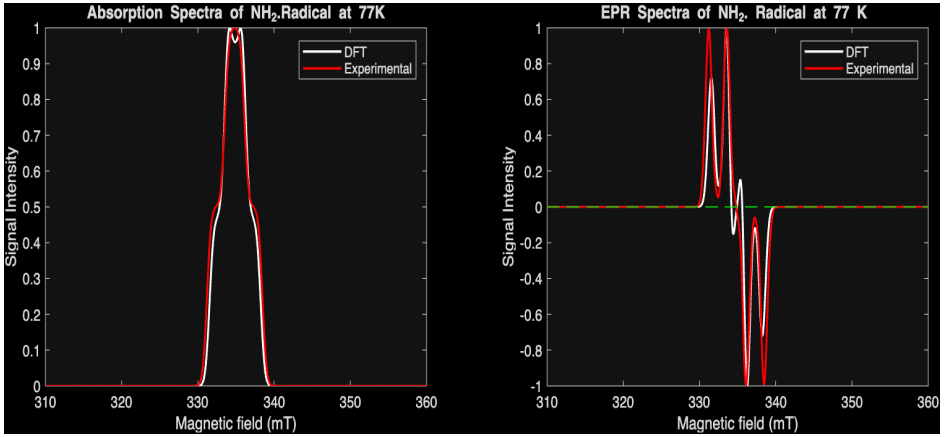
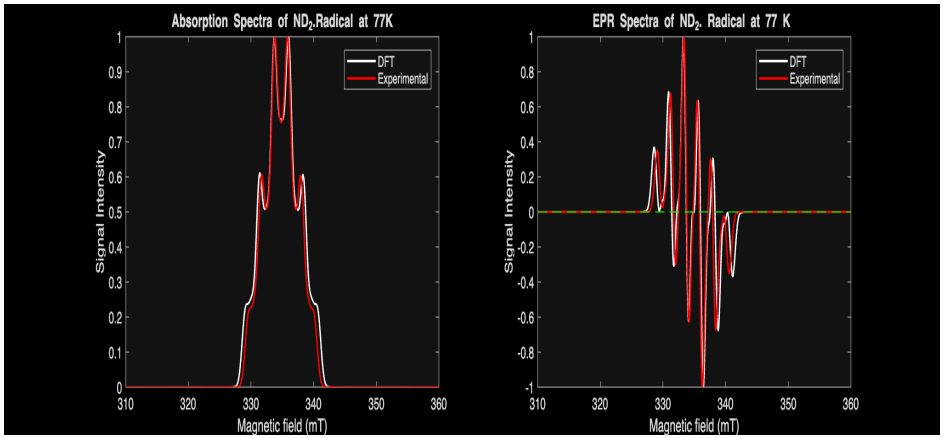


For ND2. radical



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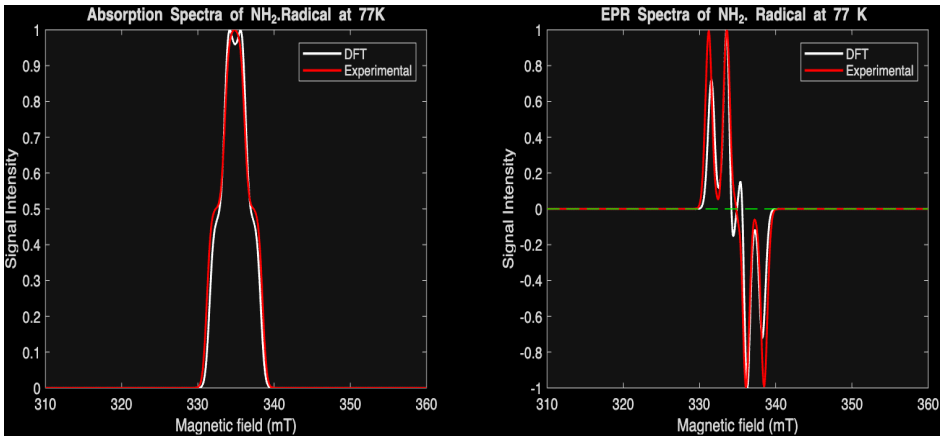
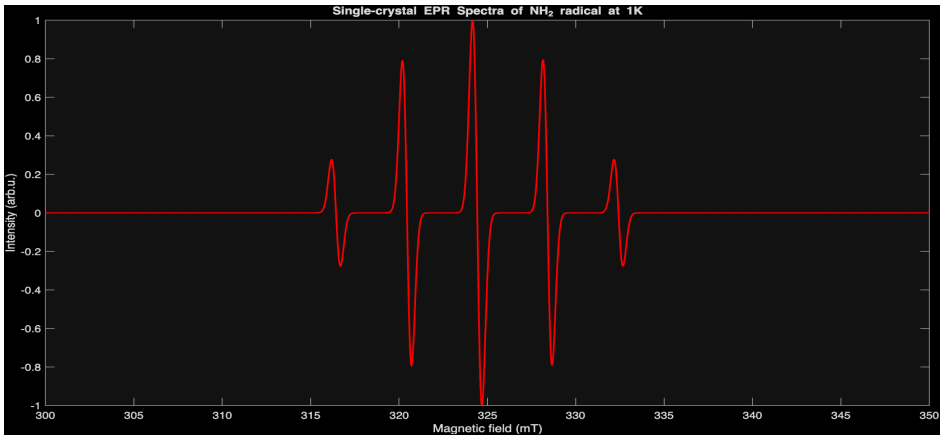


Single Crystal Spectra for NH_2.



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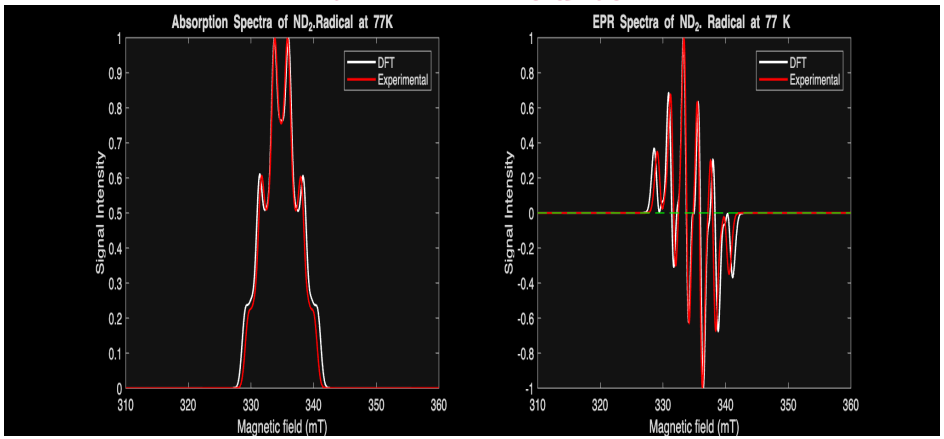
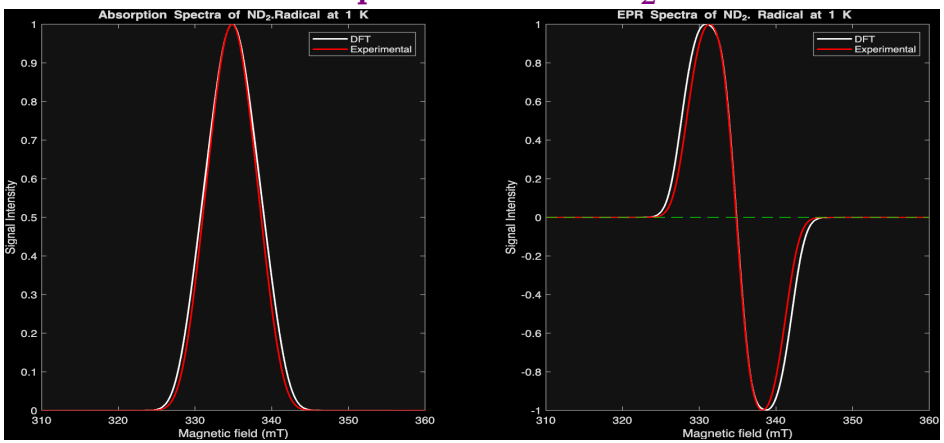


Powder Spectra for $ND_2.at1K.$



Future Prospects

- We are currently running a QE simulation to calculate the phonon dispersion relation / DOS for NH_3.

- Use DFT/ NNQMD (NN driven Path Integral Molecular Dynamics) to understand quantum level fluctuations at low temperature.
- We plan to generate INS data to study different contributions, such as nuclear quantum effects and different vibrational modes, that contribute to spin-lattice relaxation.
- If funding situation allows, we also plan to perform INS on our sample to verify these theoretical calculations.
- We plan to model the time constants T_1 and T_2 in different radical lattices.


THANK
YOU

Any Questions