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Abstract

Amino acids combine to form proteins in living organisms; most are chiral. On Earth amino acids appear only in the *L*- form, which is likely due to the amplification of enantiomeric excess (*ee*). However, a small *ee* for the *L*-form of amino acids has been observed in meteorites that have fallen on Earth. One possibility for this *ee* is the effect of antisymmetric components of the magnetic shielding tensor for ^{14}N nuclei in amino acids, which in NMR manifests as the antisymmetric chemical shift (ACS). This can result in preferential destruction of their *D*-form through interactions with polarized leptons (e.g., neutrinos) in high-field extraterrestrial environments, such as star formation or supernovae.

This study outlines the plan to measure the shielding tensor components of ^{14}N in single crystals of *N*-Acetyl Cysteine (NAC) and *N*-Acetyl Valine (NAV) amino acids. The ACS components will be measured using a custom, goniometer-based, single-crystal Nuclear Magnetic Resonance (NMR) probe to be deployed in a 600 MHz (14.1 T) magnet at the National High Magnetic Field Laboratory (NMHFL). The measurement will be done using the method described in Wi. *et al*. [1] — monitoring the chemical shifts of the two ^{14}N (I=1) resonances as a single crystal of the sample is rotated about the three principal laboratory-frame axes (*x*, *y*, *z*). This experiment will help verify the effect of ACS components in preferential destruction of *D*-form of amino acids in an extraterrestrial environment. Also, NMR is blind to chirality and this experiment should provide a new strategy to study chirality of molecules using NMR without the use of chiral auxiliaries.

Amino Acids

Amino acids have a carboxyl group (-COOH), an amine group (– NH_2), and an α carbon (C*) which is a chiral center with a molecule or atom (R) attached to it. The amino acids are named based on their R group:

R = H glycine (achiral)
R = CH_3 alanine
R = $CH(CH_3)_2$ valine
R = CH_2SH cysteine

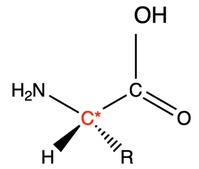
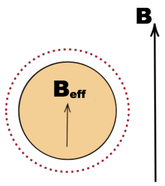


Figure 1. General Structure of Amino Acid

Magnetic Shielding in Molecules

The motion of electrons around a nucleus within a molecule changes the effective magnetic field experienced by that nucleus $\mathbf{B_{eff}}$. This is described as a magnetic shielding tensor σ.



$$\mathbf{B_{eff}} = (1-\sigma)\mathbf{B} \tag{1}$$

$$\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \tag{2}$$

$$\sigma_{ij} = \underbrace{\left(\tfrac{1}{3}\textstyle\sum_{i=1}^{3}\sigma_{ii}\right)}_{\text{[isotropic]}} + \underbrace{\frac{(\sigma_{ij}-\sigma_{ji})}{2}}_{\text{[Antisymetric Chemical Shift (ACS)]}} + \underbrace{\left(\frac{\sigma_{ij}+\sigma_{ji}}{2} - \tfrac{1}{3}\textstyle\sum_{i=1}^{3}\sigma_{ii}\right)}_{\text{[Chemical Shift Anisotropy (CSA)]}} \tag{3}$$

A chirality-dependent shift in nuclear magnetization ($\mathbf{\Delta M}$) is observed when a chiral molecule is placed in an electric ($\mathbf{E}$) and magnetic field ($\mathbf{B}$) [2]. This effect is a result of coupling of nuclear magnetic dipole and the molecular electric dipole moment of the molecule ($\mu_{\mathbf{E}}$) via shielding tensor (σ):

$$\mathbf{\Delta M} = \underbrace{\frac{1}{6kT}(\mathbf{M}\times\mathbf{E})}_{\text{external factor}}\underbrace{[(\sigma_{yz}-\sigma_{zy})\mu_{E,x} + (\sigma_{zx}-\sigma_{xz})\mu_{E,y} + (\sigma_{xy}-\sigma_{yx})\mu_{E,z}]}_{\text{molecular geometry factor } (\eta_M)} \tag{4}$$

Simulations

The magnetic shielding tensor components have been calculated using *ab initio* electronic structure calculations, typically at a B3LYP/6-31G(d,p)//HF/6-31G(d,p)/GIAO level of theory. From those components, we can calculate the change in chemical shift as the molecule, fixed in a single-crystal lattice, is rotated through the magnetic field of the spectrometer in the lab frame.

The magnitude of the raw data (**first row**) is expected to be in the order of a few MHz. The difference between the transition frequencies (**second row**) has contributions from quadrupolar coupling, CSA (**third row**), and ACS (**fourth and fifth row**). Usually, the ACS components are ignored in single-crystal experiments. However small, the difference between transition frequencies is sensitive to ACS.

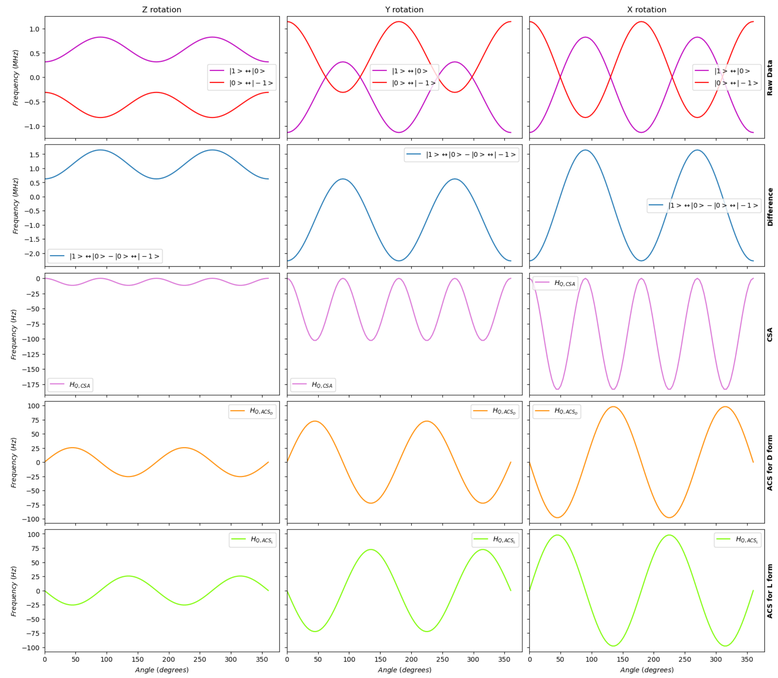


Figure 2. **First** row shows the expected raw data for the $|-1>\leftrightarrow|0>$ and $|0>\leftrightarrow|1>$ energy level transitions for the ^{14}N quadrupolar nucleus rotated about x, y, and z direction. **Second** row shows the difference of the two transition frequencies. This data will be fitted using Fourier equations [1] to extract the tensor components. **Third** row shows the CSA frequency for the ^{14}N nuclei in two chiral forms. **Fourth and Fifth** row shows the difference in data for the two chiral forms where off-diagonal shielding tensors of 50 ppm and -50 ppm are assumed.

Nuclear Magnetic Resonance Experiment

A single-crystal nuclear magnetic resonance (SCNMR) experiment has been planned at National High Magnetic Field Laboratory (MagLab) using a custom-made NMR probe with a 14.1 T magnet. The experiment will measure quadrupolar coupled antisymmetric chemical shift (ACS) tensor components for amino acids. The samples are grown at Western Michigan University (WMU).

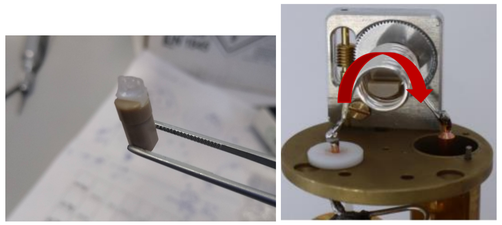


Figure 3. **Left**: Single crystal of N-Acetyl Cysteine on a goniometer mount. **Right**: The goniometer mount is placed in the goniometer. The crystal is then manually rotated inside the NMR probe.

Magneto Chiral Model

A magneto chiral model [3] describes a mechanism for the selection of amino acids in an extraterrestrial environment. The selection is made by weak interaction of nitrogen (^{14}N) nuclei in the amino acids with relativistic leptons (neutrino, electron, muon, etc.). The interaction cross section depends on spins of ^{14}N and lepton involved. An example of such interaction involving spin 1 ^{14}N and spin 1/2 anti-neutrino ($\bar{\nu}_e$) to give spin 0 ^{14}C and spin 1/2 positron (e^+) is:

$$^{14}\mathrm{N} + \bar{\nu}_e \rightarrow {}^{14}\mathrm{C} + e^+ \tag{5}$$

- if spins are aligned then reaction is suppressed
- if spins are anti-aligned then reaction is allowed

● Amino acid survives
● Amino acid is destroyed

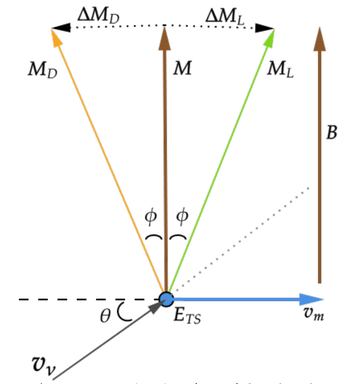


Figure 4. A possible scenario where amino acid containing meteorite moving with velocity $\mathbf{v_m}$ passes through an environment of magnetic field ($\mathbf{B}$) and relativistic lepton. The lepton is approaching the meteorite with velocity $\mathbf{v}_\nu$ at an angle θ and the meteorite experiences electric field ($\mathbf{E_{TS}}$) in its rest frame.

Shift in nuclear magnetization ($\mathbf{\Delta M}$) for the dextro (*D*) and levo (*L*) is responsible for the different alignment of nuclei in the two forms of amino acids. This can happen when an object containing amino acids (e.g. meteorite) passes through an environment of relativistic leptons, magnetic and electric fields. In space, supernovae explosions or neutron star mergers can result in this environment. Positive values of η_M result in aligned spin of ^{14}N with spins of the lepton. For several amino acids in meteorites $\eta_M > 0$ [3].

Future Experiments

Searching for ^{14}N transition signals is challenging considering the very low magnetic moments of the nucleus that result in low sensitivity of detection. Additionally, the quadrupolar effects play a significant role in the broadening of spectral signals [4].

To navigate these challenges, SCNMR experiments with other chiral single crystals and other nuclei such as boron (B) will be considered in the future.

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