Fast field cycling NMR relaxometry

An innovative tool for the comprehension of surface char properties

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Application of NMR

NMR is utilized widely not only in physics and/or chemistry but also in medical diagnostics (MRI) and so on.

For example:
- Physics
  - Condensed matter physics, Magnet, Superconductor, and so on
- Chemical
  - Analysis and/or identification of material
- Biophysics
  - Analysis of Protein structure
- Medical
  - MRI (Magnetic Resonance Image)
Why Interest In Dynamics?

- Function requires motion/kinetic energy
- Entropic contributions to binding events
- Protein Folding/Unfolding
- Uncertainty in NMR and crystal structures
- Effect on NMR experiments—spin relaxation is dependent on rate of motions → know dynamics to predict outcomes and design new experiments
- Quantum mechanics/prediction (masochism)
Magnetic moment \( \mu = \gamma \bar{I} \hbar = \gamma \hat{\hbar} \bar{I} \)

- \( \gamma \) gyromagnetic ratio
- \( \hbar = \frac{\hbar}{2\pi} \) Planck constant
Development of Energy States of Nuclei in an Applied Magnetic Field

Spin $\frac{1}{2}$ Nucleus = "Bar Magnet"
Development of Energy States of Nuclei in an Applied Magnetic Field

Spin $\frac{1}{2}$ Nucleus = "Bar Magnet"
Relaxation during NMR experiment

Responses Due to $T_1$ AND $T_2$

$T_1 = \text{time needed to re-align magnetization along z-axis}$

$T_2 = \text{time needed to null the xy component of the magnetization}$
Spin-Lattice Relaxation, $T_1$

The absorbed energy is lost through vibrational and rotational motion to the magnetic components of the "lattice" of the sample. Problem: The temperature of the sample can rise over time.
Spin-Lattice relaxation processes cause an exponential decay of the excited state population.

Spin-Lattice relaxation is the slowest of the relaxation processes.

Spin-Spin Relaxation, $T_2$

Several processes are "lumped" under this term, but one of the predominant techniques is spin diffusion, a process requiring neighboring nuclei to have the same precession rates, but different magnetic quantum numbers.
Another cause is a disruption in the homogeneity of the magnetic field through the sample caused by the sample itself. (e.g. - formation of dimers, trimers, etc. that change the relaxation rates of nuclei.)
Factors affecting relaxation

**Dipolar interactions**: the stronger the interactions, the faster is the nuclear relaxation (i.e. shorter $T_1$ and $T_2$ values = larger $R_1$ and $R_2$ values)
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Figure 4.2  Temperature dependences of the dipolar $T_1$, $T_2$ and $T_{1p}$ relaxation times in semilogarithmic coordinates at the Larmor frequency $\omega_0$. The dashed $T_1$ curve corresponds to a higher Larmor frequency than $\omega_0$. The regions with $1 \gg \omega_0^2 \tau_C^2$, $1 \sim \omega_0^2 \tau_C^2$ and $1 \ll \omega_0^2 \tau_C^2$ correspond to fast, intermediate and slow molecular motions on the frequency scale of NMR.
**Factors affecting relaxation**

**Dipolar interactions:** the stronger the interactions, the faster is the nuclear relaxation (i.e. shorter $T_1$ and $T_2$ values = larger $R_1$ and $R_2$ values)

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Fast motion regime. Molecules are weakly bound, the exchange is rapid. Longer relaxation times are retrieved when temperature is raised up due to the disruption of the interactions and the weakening of the dipolar interactions.

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*Figure 4.2.* Temperature dependences of the dipolar $T_1$, $T_2$ and $T_{1p}$ relaxation times in semilogarithmic coordinates at the Larmor frequency $\omega_0$. The dashed $T_1$ curve corresponds to a higher Larmor frequency than $\omega_0$. The regions with $1 \gg \omega_0^2 \tau_C$, $1 \sim \omega_0^2 \tau_C^2$ and $1 \ll \omega_0^2 \tau_C^2$ correspond to fast, intermediate and slow molecular motions on the frequency scale of NMR.
**Factors affecting relaxation**

**Dipolar interactions**: the stronger the interactions, the faster is the nuclear relaxation (i.e. shorter $T_1$ and $T_2$ values = larger $R_1$ and $R_2$ values)

**Slow motion regime.** Molecules are strongly bound, the exchange is slow. Shorter relaxation times are retrieved when temperature is raised up.
Surface interactions

Bulk water ($\tau \sim 10^{-12}$ s)

Fast diffusion

Protons belonging to different chemical or physical domains are relevant to FFC-NMR.
Comparison among different biochars
1. Poplar residues
2. Residues from coniferous trees
3. Marc residues

Chemical shift (ppm)

250  200  150  100  50  0  -50

SSB Poplar char
Marc char
Conifer char
How to measure $T_1$ relaxation time: fast field cycling
NMR relaxometry

Decreasing proton Larmor frequency
In the 1st Mediterranean Biochar Symposium held in Italy from January 17th to 18th, 2013, it was observed that poplar char is richer in small sized pores, whereas large pore sizes appear to be characteristic for the conifer char.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface area (m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marc char</td>
<td>42±4</td>
</tr>
<tr>
<td>Poplar char</td>
<td>98±6</td>
</tr>
<tr>
<td>Conifer char</td>
<td>66±5</td>
</tr>
</tbody>
</table>
Increase in relaxation rate is related to the different pore sizes. The smaller the pore size, the stronger are the dipolar interactions thereby leading to faster $R_1$ values.
The smaller the pore size, the stronger is the interaction of water with the pore walls, thereby providing longer correlation time values.
Biochar – hydrophobic
Water – hydrophilic
Do they chemically interact?

What do we expect?
Surface properties of poplar biochar

Temperature variation of $T_1$ values at 39 MHz

Graph showing the relationship between $T_1$ (ms) and $1000/T$ ($K^{-1}$) with three regimes indicated: fast motion, intermediate motion, and slow motion.
$R_1$ increases as temperature is enhanced.
Relaxation rate ($R_1$) is given by the combination of the outersphere and the innersphere contributions.

- Outersphere mechanism
  - Non mediated by H-bonding

- Innersphere mechanism
  - Mediated by H-bonding
  - Innersphere mechanism

Symbols:
- Water
- Metal impurity
- Hydrogen bonding
- Char/Biochar
Relaxation rate ($R_1$) is given by the combination of the outersphere and the innersphere contributions.

Outersphere mechanism

$$R_{\text{out}} = Y \left[ \frac{C}{dD} \left[ 7J(\omega_S \tau_D) + 3J(\omega_I \tau_D) \right] \right]$$

$$\tau_D \propto \frac{\eta d^2}{kT}$$

Correlation time measures the time needed for the molecular reorientation. The higher the temperature, the shorter is the time needed for a molecule to reorientate.

The outersphere mechanism does not explain the NMRD profiles.
Relaxation rate ($R_1$) is given by the combination of the outersphere and the innersphere contributions.

**Innersphere mechanism**

\[ R_{1_{\text{in}}} = \frac{f_M}{T_{1M} + \tau_M} \]

$f_M$ is the fraction of bound water; $T_{1M}$ is the proton longitudinal relaxation time of water coordinated to the biochar paramagnetic center; $\tau_M$ is the mean residence time of the bound water.
Relaxation rate ($R_1$) is given by the combination of the outersphere and the innersphere contributions.

\[ R_{1\text{in}} = \frac{f_M}{T_{1M} + \tau_M} \]

**Innersphere mechanism**

If $T_{1M} \gg \tau_M$ fast motion regime occurs; temperature increase is associated to $R_1$ decrease.

If $T_{1M} \ll \tau_M$ slow motion regime occurs; temperature increase is associated to $R_1$ increase.
Relaxation rate ($R_1$) is given by the combination of the outersphere and the innersphere contributions.

The innersphere mechanism is predominant.

Weak non conventional hydrogen bonds occur between metal impurities, aromatic biochar centers and water molecules.
Attempt to measure H-bond strength

Arrhenius graphs reporting the temperature variations of the relaxation rate values.

Activation energy of 6 kJ/mol

This activation energy value is consistent with H-bonds between water molecules and π-systems in aromatic molecules.
COEVOLUTION OF ORGANIC SUBSTANCES AND SOILS

Fast field cycling NMR relaxometry characterization of biochars obtained from an industrial thermochemical process

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Nature of water-biochar interface interactions

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