

## Computer practical 2: DD-CSA cross-correlation and TROSY

In this practical we will look at two aspects of the DD-CSA cross-correlation process. The principal effects of the DD-CSA cross-correlation are:

1. Creating a longitudinal cross-relaxation process connecting in-phase magnetisation  $L_Z$  to the anti-phase magnetisation  $L_Z S_Z$ :

$$\frac{d}{dt} \begin{bmatrix} 1 \\ H_Z \\ F_Z \\ H_Z F_Z \end{bmatrix} = - \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & r_{HH} & x_{HF} & 0 \\ 0 & x_{HF} & r_{FF} & c_{F,HF} \\ 0 & 0 & c_{F,HF} & r_{HF} \end{bmatrix} \begin{bmatrix} 1 \\ \Delta H_Z \\ \Delta F_Z \\ H_Z F_Z \end{bmatrix} \quad (1)$$

where the cross-relaxation rate  $x_{HF}$  and the cross-correlation rate  $c_{F,HF}$  have different dependence on the distance and the magnet field:

$$x_{HF} = \frac{1}{10} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_H^2 \gamma_F^2 \hbar^2 \tau_c}{r_{HF}^6} \left( \frac{6}{1 + (\omega_F + \omega_H)^2 \tau_c^2} - \frac{1}{1 + (\omega_F - \omega_H)^2 \tau_c^2} \right) \quad (2)$$
$$c_{F,HF} = \frac{2}{5} \frac{\mu_0}{4\pi} \frac{\gamma_F^2 \gamma_H \hbar B_0}{r_{HF}^3} \frac{\tau_c}{1 + \omega_F^2 \tau_c^2} \Delta \sigma_F$$

2. Creating a difference between the transverse relaxation rate of the left and the right component of a  $J$ -coupling doublet:

$$R[L_+ - 2L_+ S_Z] \neq R[L_+ + 2L_+ S_Z] \quad (3)$$

Our objective today is to evaluate both effects as functions of CSA amplitude and magnet field.

### Stage 1: specify the spin system

Spinach example set already contains 3-fluorotyrosine DFT calculation (*3\_fluoro\_tyr.log*). Find the file in *examples/standard\_systems*, copy it to a separate folder and import its contents:

```
% Read 3-fluorotyrosine DFT calculation
[sys,inter]=g2spinach(gparse('3_fluoro_tyr.log'),...
    {{ 'C', '13C' }, { 'F', '19F' } }, [186.38 192.97]);
```

- (a) We are only interested in atoms 7 and 8 in the resulting data structures. Inspect the two data structures and use Matlab commands to delete all other atoms and their interactions.
- (b) Optionally use *cst\_display* to visualise the chemical shielding tensors (there is an example for how to visualise chemical shielding tensors in *examples/visualisation*).

### Stage 2: specify other simulation parameters

We need to specify magnet field, the type of relaxation theory, and the associated parameters:

```
% Magnet field
sys.magnet=14.1;

% Relaxation theory
inter.relaxation={'redfield'};
inter.rlx_keep='labframe';
inter.equilibrium='zero';
inter.tau_c={25e-9};
```

This is a small spin system, and so the complete basis may be used:

```
% Basis set
bas.formalism='sphten-liouv';
bas.approximation='none';
```

### Stage 3: supply the information to Spinach and request the relaxation superoperator

Carefully read the console output of the data ingestion commands:

```
% Spinach housekeeping
spin_system=create(sys,inter);
spin_system=basis(spin_system,bas);
```

And get Spinach to calculate the relaxation superoperator:

```
% Relaxation superoperator
R=relaxation(spin_system);
```

### Stage 4: get the states of interest

We are interested in the relaxation rates of the longitudinal magnetisation  $L_z$ , transverse magnetisation  $L_+$ , the TROSY component of the transverse magnetisation  $L_+ + 2L_+S_z$ , and the anti-TROSY component  $L_+ - 2L_+S_z$ . These states are requested in the standard way:

```
% States of interest
LzF=state(spin_system,{'Lz'},{1});
LzC=state(spin_system,{'Lz'},{2});
LpF=state(spin_system,{'L+'},{1});
LpC=state(spin_system,{'L+'},{2});
F_t=state(spin_system,{'L+'},{1})-2*state(spin_system,{'L+', 'Lz'},{1,2});
F_a=state(spin_system,{'L+'},{1})+2*state(spin_system,{'L+', 'Lz'},{1,2});
C_t=state(spin_system,{'L+'},{2})-2*state(spin_system,{'L+', 'Lz'},{2,1});
C_a=state(spin_system,{'L+'},{2})+2*state(spin_system,{'L+', 'Lz'},{2,1});
```

Before matrix elements are calculated, all of these states must be normalised:

```
% Divide by the norm
LpF=LpF/norm(LpF,2);
LpC=LpC/norm(LpC,2);
LzF=LpF/norm(LzF,2);
LzC=LpC/norm(LzC,2);
F_t=F_t/norm(F_t,2);
F_a=F_a/norm(F_a,2);
C_t=C_t/norm(C_t,2);
C_a=C_a/norm(C_a,2);
```

### Stage 5: get relaxation rates of interest

For each of the states of interest, the corresponding relaxation rate is obtained by extracting an element of the relaxation superoperator, for example:

```
% Relaxation rates
r2c=-LpC'*R*LpC;
```

### Stage 6: exploration

By modifying and rearranging the programme code as necessary and creating loops over simulation parameters (where necessary), and plotting graphs, answer the following questions:

1. Is there a dominant longitudinal relaxation mechanism for fluorine? Proceed by deleting either the coordinates or the CSA and observing the effect.
2. What is the dominant transverse relaxation mechanism for fluorine?
3. What is the distance dependence of the longitudinal dipolar relaxation rate? Proceed by deleting both CSAs and varying the distance.
4. What is the distance dependence of the cross-relaxation rate between  $H_z$  and  $F_z$ ?
5. What is the distance dependence of the cross-correlation rate between  $H_z$  and  $H_zF_z$ ?
6. What is the magnetic field dependence of  $R_1$  and  $R_2$  on protons and fluorine?
7. What is the magnetic field dependence of the relaxation rate of the TROSY and the anti-TROSY components of the transverse magnetisation on (a) carbon; (b) fluorine?
8. What is the rotational correlation time dependence of the relaxation rate of the TROSY and the anti-TROSY components of the transverse magnetisation on (a) carbon; (b) fluorine in a 600 MHz magnet?