Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Tuning nuclear depolarization under MAS by electron T_{1e}

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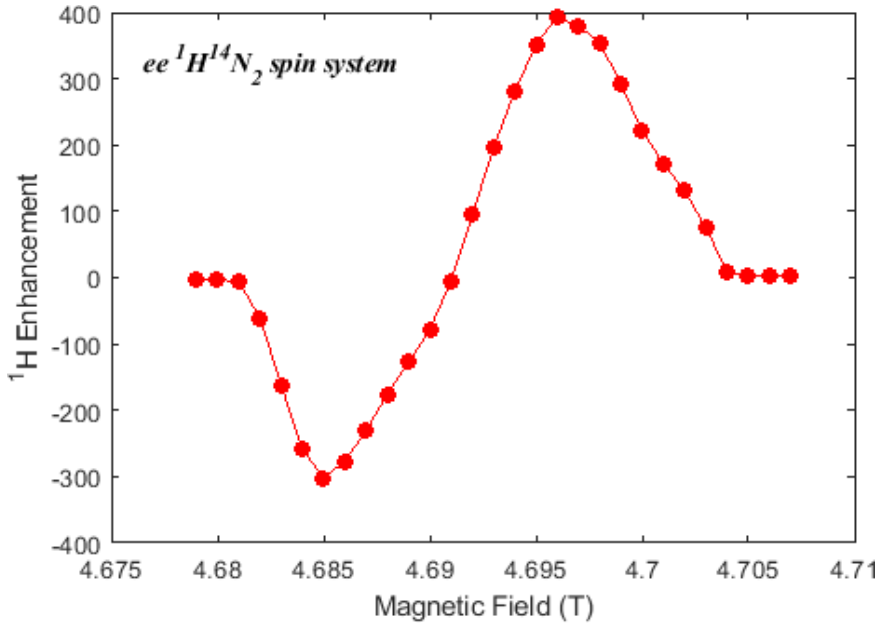
I. Numerical Simulations

1) Comparison of Spin Evolution simulation with a simulation shown in Fig. 5 by F. Mentink-Vigier *et. al.*, ***Phys. Chem. Chem. Phys.*, 19 (2017), 3506–3522**. This calculation is done to generate DNP field profile for bTbK radical which includes two ^{14}N spins. This calculation took a total time of 9 minutes using Intel(R) Xeon(R) CPU E5-2690 v2 @ 3.00 GHz CPU with 20 cores.



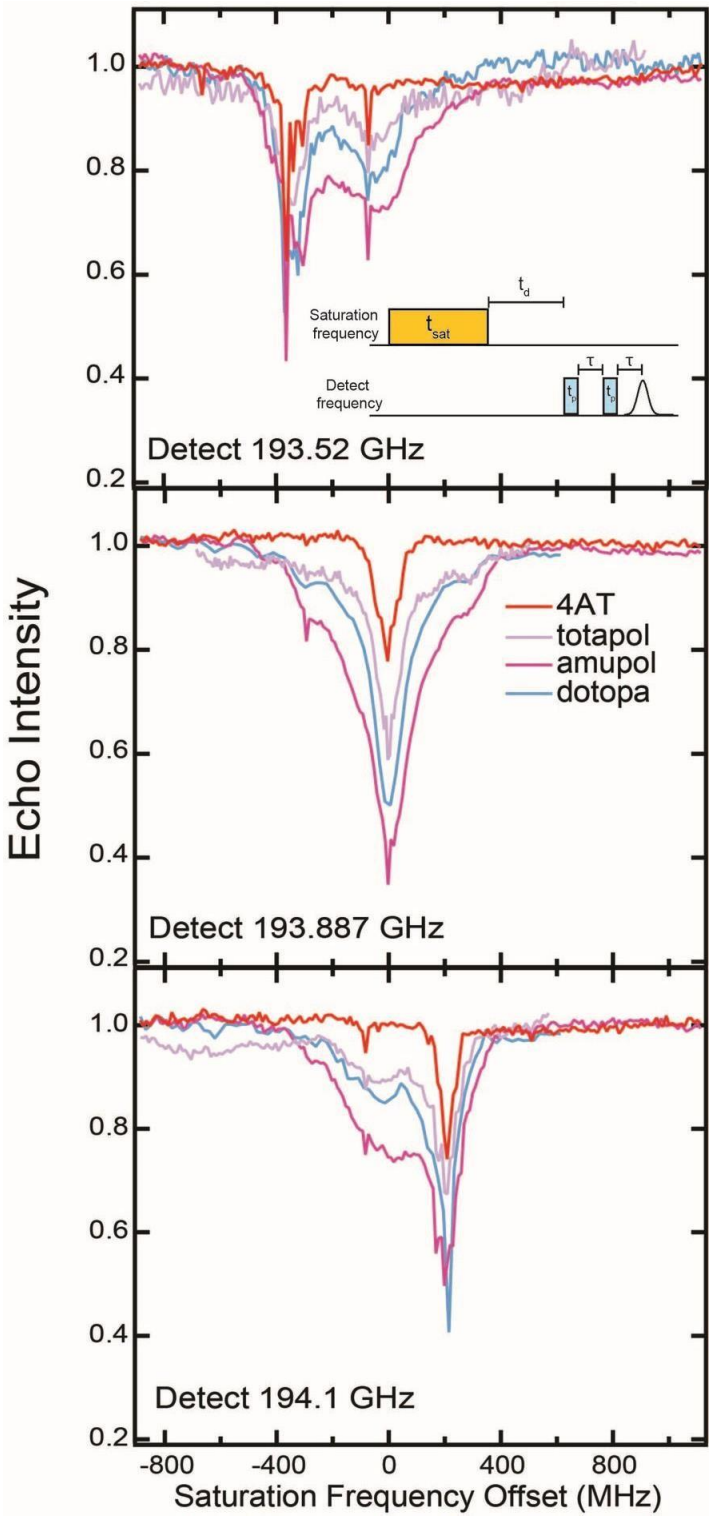
The Spin Evolution pulse program (https://spinevolution.com) is shown below.

```
****** The System**********************************

spectrometer(MHz)  200

spinning_freq(kHz) 5
channels            e H1 N14 N14b(14.457118 1)
nuclei              e e H1 N14 N14b
atomic_coords       *
cs_isotropic        *
csa_parameters      *
g-tensor            1 2.0097 2.0065 2.0024   0   0   0
g-tensor            2 2.0097 2.0065 2.0024 -58 79 -118
j_coupling          *
spin-spin_coupling 1 2 0 -60e3 0 0 65 0
spin-spin_coupling 1 3 0 3e3 0 0 0 0
spin-spin_coupling 1 4 42e3 53e3 0   0  0   0
spin-spin_coupling 2 5 42e3 53e3 0 -58 79 -118
quadrupole          *
dip_switchboard     *
csa_switchboard     *
exchange_nuclei     *
bond_len_nuclei     *
bond_ang_nuclei     *
tors_ang_nuclei     *
groups_nuclei       *
******* Pulse Sequence ******************************
CHN 1
timing(usec)        (200)x65536
power(kHz)          1000
phase(deg)          0
freq_offs(kHz)      0
CHN 2
timing(usec)        200
power(kHz)          0
phase(deg)          0
freq_offs(kHz)      0
CHN 3
timing(usec)        200
power(kHz)          0
phase(deg)          0
freq_offs(kHz)      0
```

```
CHN 4
timing(usec)        200
power(kHz)          0
phase(deg)          0
freq_offs(kHz)      0
******* Variables ***********************************
spin_temp=100
ref_freq_1=131.725e+3
scan_par B0_field/4.679:0.001:4.707/
T2e=0.001
T1e=0.3
T1n=200
set_T2(["1; 2"],"a",T2e)
set_T1(["1; 2"],"a",T1e)
set_T1(3,"a",T1n)
******* Options ***************************************
rho0                Ieq
observables         I3z
EulerAngles         leb50
n_gamma             *
line_broaden(Hz)    *
zerofill            *
FFT_dimensions      *
options             -ns1 -nsoff3 -nsoff4 -dp -re -id1e6 -v1 -vclk -lvc
-xtol8e-4 -split20
****************************************************************
***********
```

II. Experimental

The ELDOR spectra recorded for different radicals (4 amino TEMPO, TOTAPOL, AMUPOL, and DOTOPA) and for different probe frequencies (193.52, 193.887, and 194.1 GHz) are shown below. The experimental conditions are same as described in the main text, i.e., ~7T B_o field, 25 K sample temperature, and total electron spin concentration of 20 mM.


Echo Intensity
1.0
0.8
0.6
0.4
0.2
Detect 193.52 GHz
Saturation frequency
t_{sat}
t_d
Detect frequency
τ
τ
t_p
t_p
4AT
totapol
amupol
dotopa
Detect 193.887 GHz
Detect 194.1 GHz
-800
-400
0
400
800
Saturation Frequency Offset (MHz)