CHARACTERISATION OF INORGANIC MATERIALS USING SOLID-STATE NMR SPECTROSCOPY

Appendix A

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Appendix A

A.1 Origin of spinning sidebands

In the principal axis system (PAS) of the CSA tensor $\boldsymbol{\sigma}^{R}$ can be expressed in terms of $\boldsymbol{\sigma}^{PAS}$

$$\boldsymbol{\sigma}^{R} = \mathbf{R}^{-1}(\alpha, \beta, \gamma) \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix} \mathbf{R}(\alpha, \beta, \gamma) \ , \qquad (A.1)$$

where $\mathbf{R}(\alpha, \beta, \gamma)$ defines the rotation matrix, which rotates the PAS into the rotor frame using three Euler angles α, β and γ. When θ_R is equal to 54.736° then

$$\omega(\alpha, \beta, \gamma; t) = -\omega_0 \begin{Bmatrix} \sigma_{iso} + \left[A_1 \cos(\omega_R t + \gamma) + B_1 \sin(\omega_R t + \gamma) \right] \\ \left[A_2 \cos(2\omega_R t + 2\gamma) + B_2 \sin(2\omega_R t + 2\gamma) \right] \end{Bmatrix} \ , \qquad (A.2)$$

where A_1, B_1, A_2 and B_2 are defined as

$$A_1 = \frac{2}{3}\sqrt{2} \sin\beta \cos\left[\cos^2\alpha \left(\sigma_{11}^{PAS} - \sigma_{33}^{PAS} \right) \right] + \sin^2\alpha \left(\alpha_{22}^{PAS} - \sigma_{33}^{PAS} \right) \ ,$$

$$B_1 = \frac{2}{3}\sqrt{2} \sin\alpha \cos\alpha \sin\beta \left(\sigma_{11}^{PAS} - \sigma_{22}^{PAS} \right) \ ,$$

$$A_2 = \frac{1}{3} \begin{pmatrix} \left(\cos^2\beta \cos^2\alpha - \sin^2\alpha \right) \left(\sigma_{11}^{PAS} - \sigma_{33}^{PAS} \right) \\ + \left(\cos^2\beta \sin^2\alpha - \cos^2\alpha \right) \left(\sigma_{22}^{PAS} - \sigma_{33}^{PAS} \right) \end{pmatrix} \ ,$$

$$B_2 = -\frac{2}{3} \sin\alpha \cos\alpha \cos\beta \left(\sigma_{11}^{PAS} - \sigma_{22}^{PAS} \right) \ . \qquad (A.3)$$

A.2 Additional theory for the two-dimensional CSA-amplified PASS experiment

A.2.1 A carousel of spins

The orientation, Ω_{PR}, of the principal axis system, P, relative to the MAS rotor frame of reference, R, is described by three Euler angles $\{\alpha_{PR}, \beta_{PR}, \gamma_{PR}\}$, that remain fixed throughout the spinning of the MAS rotor. However, the orientation of R with respect to the laboratory frame of reference, L, changes as the rotor spins. The change in the orientation between these two frames of reference, R and L, can be described by a further set of Euler angles $\{\alpha_{PL}, \beta_{PL}, \gamma_{PL}\}$. The description of the rotations between these different frames of reference can be simplified by considering a 'carousel', c, of spins that have the same isotropic chemical shift, which can be brought into coincidence by the rotation around the MAS axis. The spins of the carousel undergo the same cycle of spin-precession frequencies, but at a range of different times, and the carousel is formed by the chemically-equivalent sites with the same value of α_{PR} and β_{PR}, but different values of γ_{PR}. From this point forward, for simplicity in the following equations, $\gamma_{PR} = \gamma$. The evolution of the transverse magnetisation can be described by the rotating frame precession frequency, $\omega_c^{(m)}(t ; \gamma)$, which can be written as a Fourier series,

$$\omega_c^{(m)}(t ; \gamma) = \sum_{m=-2}^{2} \omega_c^{(m)}(\gamma) \exp(i\, m\, \omega_r\, t) \quad , \tag{A.4}$$

with the Fourier components

$$\omega_c^{(m)} = \sum_{m'=-2}^{2} A_{2m'}^{P}\, D_{m',m}^{2}(\Omega_{PR})\, d_{m0}^{2}(\beta_{RL})\, \exp\left(-i\, m\, \alpha_{RL}^{0}\right) + \delta_{m0}\, \omega_{iso} \quad , \tag{A.5}$$

where m is limited to the range $-2 \leq m \leq 2$. $A_{2m'}$ defines the principal components of the chemical shielding tensor in the principal axis frame of reference, P, $D^2_{m',m}$ and d^2_{m0} are the Wigner rotations and the time and orientation dependencies of the precession frequency are now be separated by $\omega\left(t ; \Omega_{PR}\right)$. When $m = 0$, the Fourier component can be written as

$$\omega_c^{(m)} = \sum_{m'=2}^{2} A^P_{2m'} D^{(2)}_{m'0}\left(\Omega_{PR}\right) d^2_{00} \beta_{RL} + \omega_{iso} \quad . \tag{A.6}$$

When spinning at the magic angle, $\beta_{RL} = 54.756°$, $\omega^{(0)}\left(\Omega_{PR}\right) = \omega_{iso}$ and is now independent of the orientation Ω_{PR}. Therefore, the time-averaged precession frequency, *i.e.*, the isotropic frequency, now becomes $\omega^{(0)} = \omega_{iso}$ and only the isotropic peak appears in the MAS NMR spectrum. Furthermore, as the orientation of any crystallite within the carousel can be transformed to that of any other by rotation about the magic angle, the Fourier component in Equation A.6 obeys the following relationship

$$\omega_c^{(m)}\left(\gamma\right) = \omega_c^{(m)}\left(0\right) \exp\left(i\, m\, \gamma\right) \quad . \tag{A.7}$$

A.3 SIMPSON fitting programs

A3.1 Assuming ideal pulses

```
spinsys {
channels 13C
nuclei   13C
shift   1 0   $par(shift) $par(eta) 0 0 0
}

par {
    method           gcompute
    start_operator   I1x
    detect_operator  I1p
    spin_rate        4200
    gamma_angles     32
    sw               gamma_angles*spin_rate
    crystal_file     zcw376
    np               32
    proton_frequency 600e6
}

proc pulseq {} {
    maxdt 1
    delay 9999
}

proc fitfunction {val}  {
    global par stop
    set scale       [lindex [lindex $val 0] 1]
    set par(shift)  [lindex [lindex $val 1] 1]
    set par(eta)    [lindex [lindex $val 2] 1]
    set sim [fsimpson]
    set re [findex $sim 1 -re]
    set im [findex $sim 1 -im]
    fsetindex $sim 1 [expr $re*2] [expr $im*2]
    fft $sim
    fphase $sim -scale $scale
    set rms [frms $sim $par(exp)]
    if {$rms < $par(bestrms)} {
    set par(bestrms) $rms
    fsave $sim $par(name).spe
    puts -nonewline "*"
    }
```

```
    funload $sim
    puts "$par(iter) $rms $par(bestrms) $val"
    if {$stop || $rms < $par(maxrms) ||
    $par(iter) > $par(maxiter)} {
    exit
    }
    return $rms
}

proc main {} {
    global par
    set par(fitmethod)  simplex
    set par(function)  fitfunction
    set par(exp)  [fload 102.spe]
    set par(bestrms)  1e6
    set par(maxrms)  0.0001
    set par(maxiter)  500

    set par(values) {
    {scale  14000 100 1}
    {shift  20000 100 1}
    {eta  0.5 0.01 1}
        }
    fit par
}
```

A.3.2 Complete simulation

```
spinsys {
  channels 13C
  nuclei 13C
  shift  1 0   $par(shift) $par(eta) 0 0 0
}

par {
  spin_rate  2400
  np  32
  sw  38400
  crystal_file  LEBoct31
  start_operator  I1z
  detect_operator  I1p
  proton_frequency  600e6
  gamma_angles  32
  verbose  111
  variable rf  22727.27
  variable tr  1e6/spin_rate
  variable dw  1e6/sw
  variable  tdwell  1.0e6/sw

}

proc pulseq {} {
  global par
  maxdt 0.5
  set par(t90) [expr 0.25e6/$par(rf)]
    reset
    pulse $par(t90) $par(rf) y
    acq
    for {set i 1} {$i < $par(np)} {incr i} {
    delay $par(tdwell)
  acq $par(recph)
 }
}

proc fitfunction {val}  {
    global par stop
    set scale  [lindex [lindex $val 0] 1]
    set par(shift)  [lindex [lindex $val 1] 1]
    set par(eta)   [lindex [lindex $val 2] 1]
    set sim [fsimpson]
```

```
    set re [findex $sim 1 -re]
    set im [findex $sim 1 -im]
    fsetindex $sim 1 [expr $re*2] [expr $im*2]
    fft $sim
    fphase $sim -scale $scale
    set rms [frms $sim $par(exp)]
    if {$rms < $par(bestrms)} {
    set par(bestrms) $rms
    fsave $sim $par(name).spe
#   puts -nonewline "*"
    }

funload $sim
    set out [open "result.txt" a]
    puts $out "$par(iter) $rms $par(bestrms) $val"
    close $out
    if {$stop || $rms < $par(maxrms) ||
    $par(iter) > $par(maxiter)} {
    exit
    }
    return $rms
}

proc main {} {
  global par
  set par(oddph)  0
  set par(recph) 0
  #set f [fsimpson]
  set par(fitmethod)      simplex
  set par(function)       fitfunction
  set par(exp)            [fload 1058.spe]
  set par(bestrms)  1e6
  set par(maxrms)         0.005
  set par(maxiter)  1000
  set par(values) {
    {scale 3094 1000 1}
    {shift 11255 10 1}
    {eta 0.2 0.1 1}
  }
fit par
}
```

A.3.3 Contour error plot – array

```
spinsys {
  channels 31P
  nuclei 31P
  shift      1      0p     $par(aniso)  $par(eta)     0      0      0
}

par {
  method           gcompute
  start_operator   I1x
  detect_operator  I1p
  spin_rate  1400
  gamma_angles  32
  sw  gamma_angles*spin_rate
  crystal_file  zcw376
  np  32
  proton_frequency 600e6
}
proc pulseq {} {
    maxdt 5.0
    delay 1e6
}
proc main {} {
    global par

set par(span_start) 1
set par(span_stop) 300
set par(span_inc) 1
set par(skew_inc) 0.1
set par(larmor_freq) 242.938

set par(skew_par) [expr {int(-10*$par(skew_inc))}]
# set skew range and step size
  for {set m 10} {$m >= -10} {incr m $par(skew_par)} {
  set par(kappa) [expr $m/10.0]
# set span range and step size
  for {set p $par(span_start)} {$p <= $par(span_stop)} {incr p
$par(span_inc)} {
  set par(span) [expr $p*$par(larmor_freq)]
  set par(oddph)  0
  set par(recph) 0
if {$m>= 0} {
  set par(aniso) [expr  -($par(span)/2.0)*(1.0+$par(kappa)/3.0)]
  set par(eta)  [expr  (1.0-$par(kappa))/(1.0+$par(kappa)/3.0)]
} else {
  set par(aniso) [expr  ($par(span)/2.0)*(1.0-$par(kappa)/3.0)]
```

```
  set par(eta)  [expr  (1.0+$par(kappa))/(1.0-$par(kappa)/3.0)]
}

puts "kappa $par(kappa) omega $par(span) aniso $par(aniso) eta $par(eta)"

  set f [fsimpson]
  set re [findex $f 1 -re]
  set im [findex $f 1 -im]
  fsetindex $f 1 [expr $re*2] [expr $im*2]
  fft $f
  fsave $f $par(name)_[expr $par(span)/$par(larmor_freq)]_[expr
$par(kappa)*10].spe
}
}
}
```

A.3.4 Contour error plot – plot

```
spinsys {
  channels 31P
  nuclei   31P
  shift  1  0  $par(shift) $par(eta) 0 0 0
}

par {
}

proc pulseq {} {}
proc main {} {
  global par
set par(span_start) 1
set par(span_stop) 300
set par(span_inc) 1
set par(skew_inc) 0.1
set par(larmor_freq) 242.938

set par(skew_par) [expr {int(-10*$par(skew_inc))}]
  set exp  [fload $par(name).spe]
  set outputfile [open $par(name)_result.txt w]
set rmsarray [list]
  set spanarray [list 0]
# set span range and step size
  for  {set  p  $par(span_start)}  {$p  <=  $par(span_stop)}  {incr  p
$par(span_inc)} {
  set par(span) [expr $p*$par(larmor_freq)]
  lappend spanarray [expr $par(span)/$par(larmor_freq)]
}

 puts $outputfile "$spanarray"
# set skew range and step size
  for {set m 10} {$m >= -10} {incr m $par(skew_par)} {
  set par(kappa) [expr $m/10.0]
  set spanrmsarray [list $par(kappa)]
# set span range and step size
for  {set  p  $par(span_start)}  {$p  <=  $par(span_stop)}  {incr  p
$par(span_inc)} {
set par(span) [expr $p*$par(larmor_freq)]
set  sim    [fload  array_mas_[expr  $par(span)/$par(larmor_freq)]_[expr
$par(kappa)*10].spe]
fautoscale $sim $exp -re
    set rms [frms $sim $exp]
    funload $sim
    lappend spanrmsarray $rms
```

```
  }
 puts $outputfile "$spanrmsarray"
 }
}
```

A.4 Spin- and transition-dependent coefficients

Table A.1: Spin- and transition-dependent coefficients

I	m_I	A^0 (I, m_I)	A^2 (I, m_I)	A^4 (I, m_I)
I = 3/2	1/2	−2/5	−8/7	54/35
	3/2	6/5	0	−6/5
I = 5/2	1/2	−16/15	−64/21	144/35
	3/2	−4/5	−40/7	228/35
	5/2	20/3	40/21	−60/7
I = 7/2	1/2	−30/15	−120/21	270/35
	3/2	−54/15	−96/7	606/35
	5/2	30/15	−240/21	330/35
	7/2	294/15	168/21	−966/35
I = 9/2	1/2	−48/15	−192/21	432/35
	3/2	−108/15	−168/7	1092/35
	5/2	−60/15	−600/21	1140/35
	7/2	168/15	−336/21	168/35
	9/2	648/15	432/21	−2332/35

A.5 References

1.