

Supporting information for “¹⁴N Overtone transition in double-rotation solid-state NMR”

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MATERIALS AND METHODS

Characterisation of *N*-(Acetyl- d_3)valine- d_{10}

Melting point = 159–161 °C; ^2H NMR data in Fig. S3 (76.8 MHz, CH_3OH): δ 5.60 (s, 2H), 4.98 (s, 1H), 2.78 (s, 1H), 2.66 (s, 3H), 1.61 (s, 6H); ^{13}C NMR in Fig. S4 (100 MHz, CD_3OD) δ 175.8, 174.3, 59.5 (t, $J_{\text{C-D}} = 21$ Hz), 31.4 (t, $J_{\text{C-D}} = 20$ Hz), 22.4 (t, $J_{\text{C-D}} = 20$ Hz), 19.2 (m), 18.0 (m); IR (powder) ν 3000, 1755, 1518, 1399, 1221, 1092 cm^{-1} ; MS (ESI+) m/z $\text{C}_7\text{H}_3\text{D}_{11}\text{NO}_3^+$ Calc. 171.16, found 170.92; Calc. for $\text{C}_7\text{H}_2\text{D}_{11}\text{NNaO}_3$ 193.15, found 193.07; $\text{C}_7\text{H}_2\text{D}_{12}\text{NO}_3^+$ Calc. 172.16, found 172.00; Calc. for $\text{C}_7\text{HD}_{12}\text{NNaO}_3$ 194.15, found 194.11.

FIGURE S1:

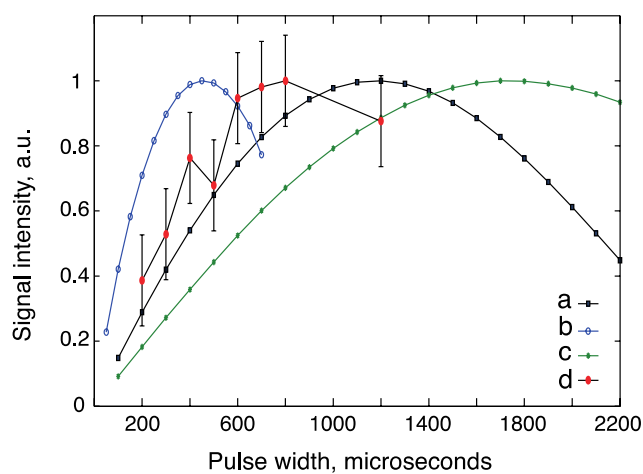


Figure S1. Selected calculated and experimental nutation curves for some of the ^{14}N overtone spinning sidebands of deuterated glycine and deuterated NAV at 20.0 T on the DOR probe, using a nominal RF amplitude of 21 kHz, as calibrated from the ^{17}O signal from water, with the spinning frequency specified in Table S1. (a) simulation of the $-2, -2$ spinning sideband of glycine, (b) simulation of the $-2, -2$ spinning sideband of NAV, (c) simulation of the $-1, -2$ spinning sideband of glycine, (d) experimental data the $-2, -2$ spinning sideband of glycine acquired with 8000 scans. The simulations were performed using parameters in Table S1.

FIGURE S2:

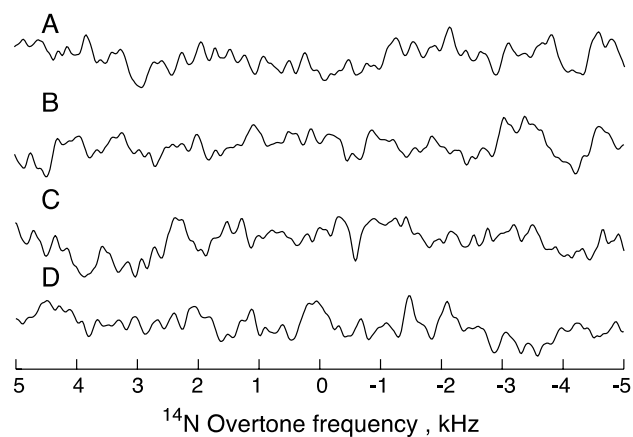


Figure S2. Experimental data for some of the ^{14}N overtone spinning sidebands for deuterated glycine under DOR at 20.0 T and a spinning frequency $\nu_{out}= 1.425$ kHz and $\nu_{in}= 6.95$ kHz, acquired with 8000 scans using a nominal RF amplitude of 21 kHz with 800 μs pulse length. All spectra are recorded near specific overtone spinning sidebands, therefore each spectrum appears at a different position. For the sake of convenience, the spectra are plotted on an arbitrary scale where 0 is set as the center of each spinning sideband. (A) (-1, -2) spinning sideband, (B) (0, -2) spinning sideband, (C) (-2,0) spinning sideband, (D) (-1,0) spinning sideband.

FIGURE S3:

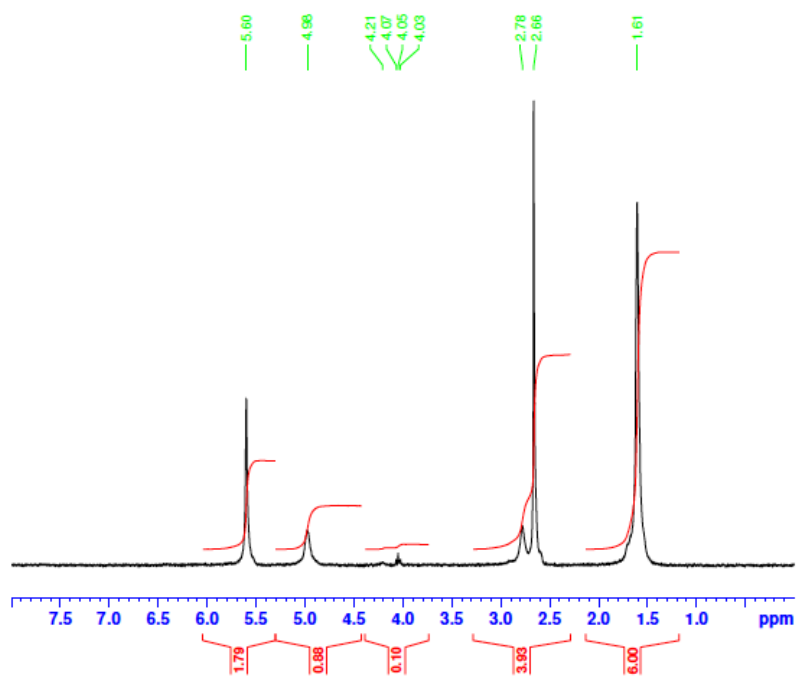


Figure S3: ^2H NMR of *N*-(acetyl- d_3)valine- d_{10} (76.8 MHz, CH_3OH)

FIGURE S4:

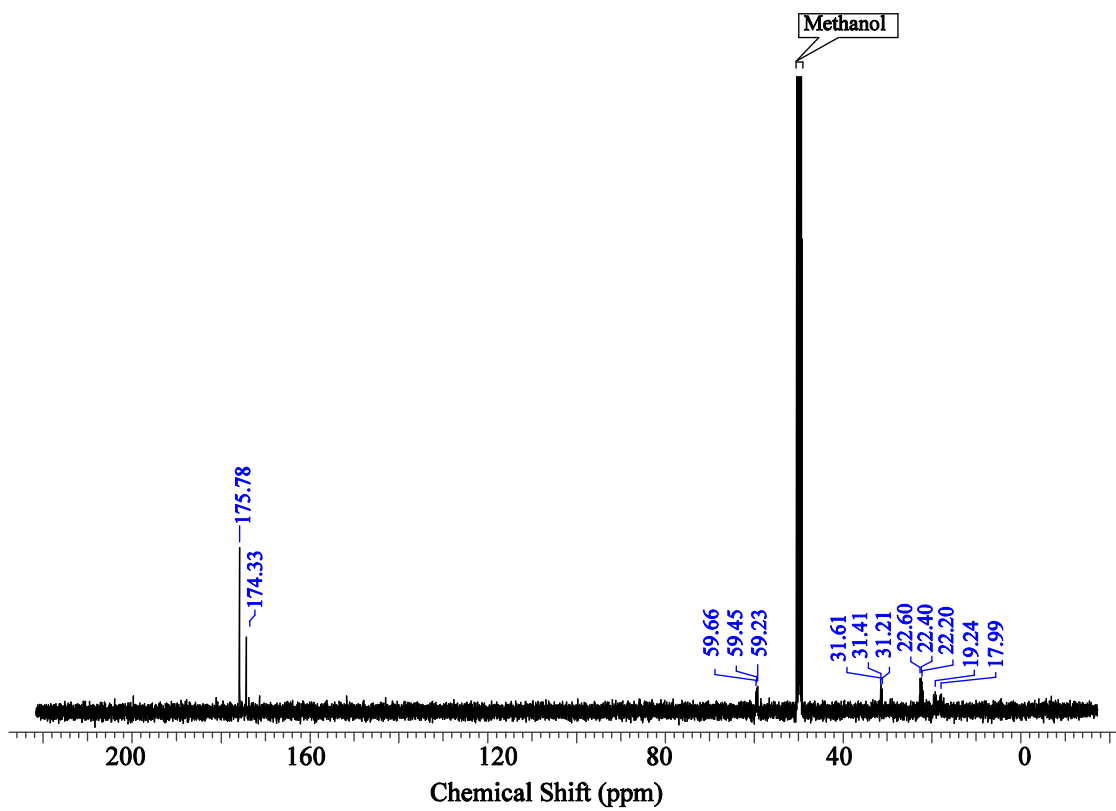


Figure S4: ^{13}C NMR of *N*-(acetyl- d_3)valine- d_{10} (100 MHz, CD_3OD)

SPINACH INPUT FILE FOR THE SIMULATION ON GLYCINE IN FIGURE 1.

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% Panoramic double rotation overtone 14N spectrum of glycine. A short pulse
% with instrumentally inaccessible power is given to make the excitation
% pattern uniform.
% Note: slower spinning rates require larger spatial ranks.
% i.kuprov@soton.ac.uk
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% i.haies@soton.ac.uk

function glycine_dor_overtone()
% System specification
sys.magnet=14.1; sys.isotopes={'14N'};
inter.coupling.matrix{1,1}=eeqq2nqi(1.18e6,0.53,1,[0 0 0]);

% Relaxation theory
inter.relaxation='damp';
inter.damp_rate=500;

% Basis set
bas.formalism='sphten-liouv';
bas.approximation='none';
sys.disable={'trajlevel'};

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

% Experiment setup
theta=atan(sqrt(2));
parameters.rate_outer=-1500;
parameters.rate_inner=-7000;
parameters.rank_outer=4;
parameters.rank_inner=3;
parameters.axis_outer=[sin(theta) 0 cos(theta)]; % 54.74 degrees
parameters.axis_inner=[sqrt(20-2*sqrt(30)) 0 sqrt(15+2*sqrt(30))]; % 30.56 degrees
parameters.grid='lebedev_ab_rank_5';
center=2*spin_system.inter.basefrqs(1)/(2*pi);
parameters.sweep=[(center-3e4) (center+2e4)];
parameters.npoints=256;
parameters.spins={'14N'};
parameters.axis_units='MHz';
parameters.invert_axis=1;
parameters.rho0=state(spin_system,'Lz','14N');
parameters.coil=cos(theta)*state(spin_system,'Lz','14N')+...
    sin(theta)*(state(spin_system,'L+','14N')+...
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state(spin_system,'L-', '14N'))/2;
parameters.rframes={};

% Experiment parameters
expt.n_power=3.0e6;
expt.n_pulse=1.0e-6;
carrier_frequency=22e3;

% Get the Hamiltonian
[H,Q]=hamiltonian(assume(spin_system,'labframe'));

% Get the relaxation matrix
R=relaxation(spin_system);

% Get the averaging grid
sph_grid=load([spin_system.sys.root_dir '/kernel/grids/' parameters.grid '.mat']);

% Inform the user and shut up
report(spin_system,['powder average being computed over '
num2str(numel(sph_grid.weights)) ' orientations.']);
report(spin_system,'pulse sequence silenced to avoid excessive output. ');
spin_system.sys.output='hush';

% Build pulse operator
N_pulse=cos(theta)*operator(spin_system,'Lz','14N')+sin(theta)*(operator(spin_system,'L+', '
14N')+operator(spin_system,'L-', '14N'))/2;
F_pulse=2*pi*expt.n_power*kron(speye(2*parameters.rank_outer+1),kron(speye(2*parame
ters.rank_inner+1),N_pulse));

% Project the relaxation matrix
R=kron(speye(2*parameters.rank_outer+1),kron(speye(2*parameters.rank_inner+1),R));

% Powder averaged spectrum
spectrum=zeros(1,parameters.npoints);
parfor k=1:numel(sph_grid.weights) %#ok<*PFBNS>

% Get the Fokker-Planck Liouvillian

[L,M,P]=doublerot(spin_system,{},H,Q,parameters,[sph_grid.alphas(k),sph_grid.betas(k),sph_
grid.gammas(k)]);

% Get the pulse Hamiltonian
omega=2*spin_system.inter.basefrqs(1)-2*pi*carrier_frequency;
F_aver=average(spin_system,F_pulse,L+1i*M,F_pulse,omega,'matrix_log');

% Project the states into Fokker-Planck space
local_parameters=parameters;

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local_parameters.rho0=P*parameters.rho0;
local_parameters.rho0=local_parameters.rho0/norm(local_parameters.rho0);
local_parameters.coil=P*parameters.coil;
local_parameters.coil=local_parameters.coil/norm(local_parameters.coil);

% Apply the pulse

local_parameters.rho0=propagator(spin_system,F_aver+1i*R,expt.n_pulse)*local_parameter
s.rho0;

% Run the detection in the frequency domain

spectrum=spectrum+sph_grid.weights(k)*slowpass(spin_system,local_parameters,L+1i*M+1
i*R,0*L,0*L)

end

% Phasing
spectrum=spectrum*exp(1.25i);

% Plotting
spectrum_axis=linspace(-3e4,+2e4,parameters.npoints)/1e3;
subplot(2,1,1); plot(spectrum_axis,real(spectrum)); xlabel('kHz');
subplot(2,1,2); plot(spectrum_axis,imag(spectrum)); xlabel('kHz');
end

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