

BCMB/CHEM 8190
ANSWERS TO PROBLEM SET 2

1) $T_2^* = 1/(\pi \times \Delta\nu_{1/2}) = 1/(\pi \times 2) = 0.16 \text{ s} = T_2$ if line width is totally dictated by spin relaxation (no magnetic field inhomogeneity).

If 1 Hz of the 2 Hz width is from inhomogeneity, T_2^* is still 0.16 s, but T_2 is 0.32.

The FID decays with T_2^* and multiplying with an exponential with a 1 s decay constant (T_e) adds to the decay constant: $\exp(-t/T_2^*) \times \exp(-t/T_e) = \exp(-t/T_2^* - t/T_e) = \exp(-t(T_2^* + T_e)/(T_2^* \times T_e))$, so, effective decay constant is $(T_2^* + T_e)/(T_2^* \times T_e) = 0.138$, and line width becomes 2.3 Hz. These decay constants are often entered as line broadening (LB) or effective $1/T_2^* = 1/(\pi \times \text{LB}) + 1/0.16$. An LB of 1 Hz would add 1 Hz to the line width.

2) a) acquisition time should be approximately T_2^* , or 0.3s

b) spectral width (Hz) for 200 ppm @ 50 MHz = $200 \text{ ppm} \times 50 \text{ Hz/ppm} = 10,000 \text{ Hz}$
the dwell time should be $1/(2 \times \text{spectral width})$ or $1/20000 = 5 \times 10^{-5} \text{ s}$. For a 0.3 s acquisition one needs at least $0.3/(5 \times 10^{-5}) = 6000$ complex points.

c) the Ernst formula says optimal pulse angle = $\cos^{-1}[\exp(-aq/T_1)]$; optimum pulse angle is 20 degrees

d) none if signal to noise is to be optimized

e) line broadening should be about $1/(\pi \times T_2)$ or 1 Hz if signal to noise is to be optimized.

3) 4 minutes is long enough to reach steady state so S/N increases on averaging are well approximated by the square root of the length of time. Hence S/N after 100 min is 25:1 ($5 \times \sqrt{100/\sqrt{4}}$).

4) $J_{P,H} = 21 \times \cos(\theta)^2 - 2.25 = 18.8$ for 180° , and 3.0 for 60°

	Ideal Couplings		
	Trans	Gauche-	Gauche+
$^3J_{PH'}$	3.0	18.8	3.0
$^3J_{PH''}$	3.0	3.0	18.8

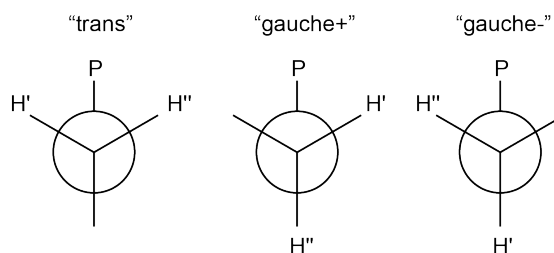
Experimental

$$^3J_{PH'} = f_T (3.0) + f_{G+} (3.0) + f_{G-} (18.8) = 6.0$$

$$^3J_{PH''} = f_T (3.0) + f_{G+} (18.8) + f_{G-} (3.0) = 8.0$$

$$f_T + f_{G+} + f_{G-} = 1.0$$

Implies: $f_T = 0.5$, $f_{G+} = 0.3$, $f_{G-} = 0.2$



5) The carbonyl carbon uses an sp^2 hybrid orbital to bond to the nitrogen as opposed to an sp^3 orbital for the C_α carbon. Hence the s character ratio is $1/3$ vs $1/4$ and the coupling to the α carbon should be $3/4$ of 15 or about 11 Hz – this is approximately correct. If we consider the nitrogen of the $C'-N$ bond to also use an sp^2 hybrid, the only difference from $C=C$ in ethylene would come from the magnetogyric ratios and the $C=C$ coupling in ethylene would be about $10/4 = 2.5$ times larger – again approximately correct.