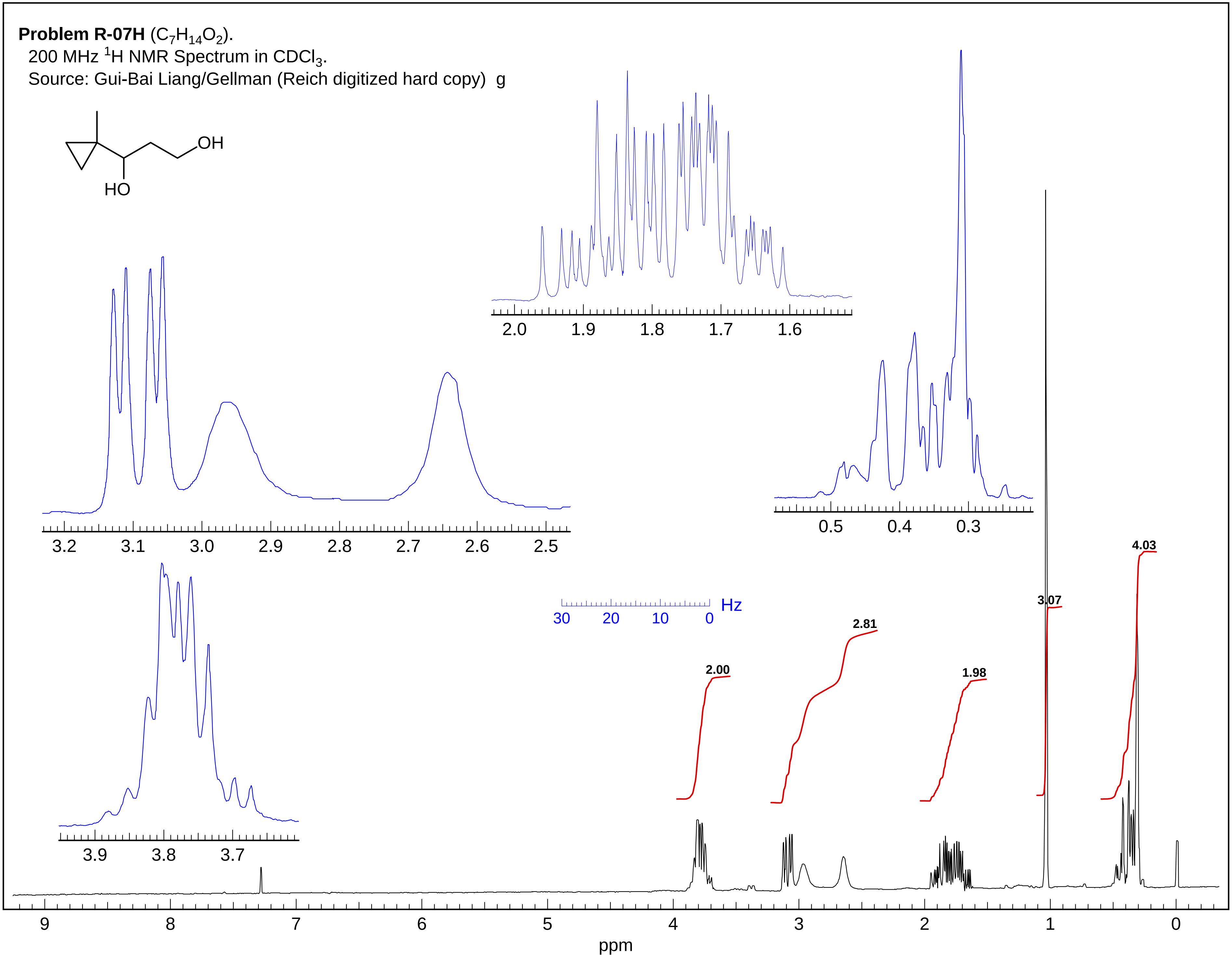
Problem R-07H ($C_7H_{14}O_2$).
200 MHz ^1H NMR Spectrum in $CDCl_3$.
Source: Gui-Bai Liang/Gellman (Reich digitized hard copy) g



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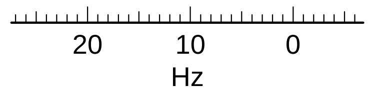
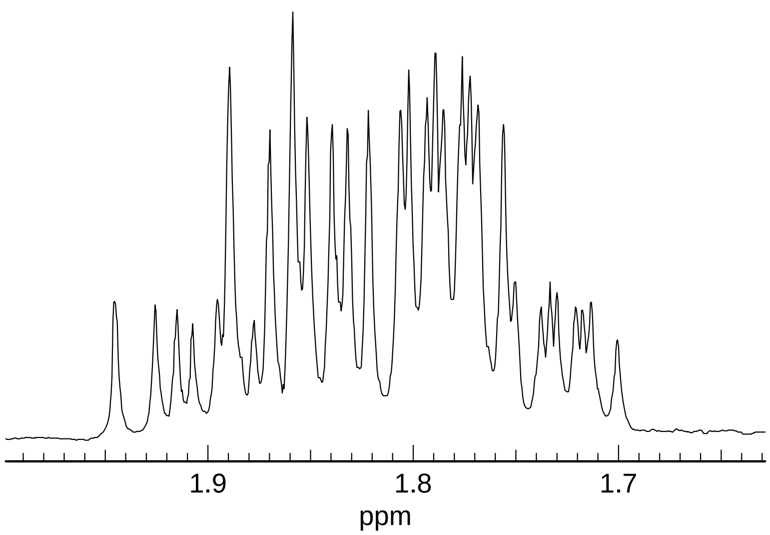
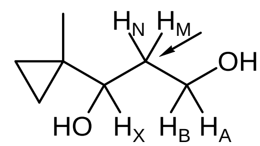
Problem R-07H ($C_7H_{14}O_2$). Interpret a proton NMR spectrum (next page).

(a) Identify H_X (give δ and J values)

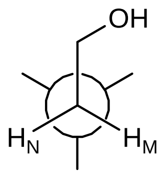
(b) Below is reproduced the multiplet at δ 1.8. Which protons are these (circle: A, B, M, N, X). Label the spectrum and extract the coupling constants (you may use first-order analysis) and report the couplings (e.g., J_{PQ} = 33 Hz). Draw a coupling tree to show you understand the pattern







(c) Show the probable conformation looking down the bond marked with an arrow (fill in the Newman projection below).



(d) Which of the couplings you extracted in part (a) using first-order analysis do you expect to be accurate?

Which will be only approximate? Explain, and predict the direction of the expected error for these couplings (be specific).

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Problem R-07H ($C_7H_{14}O_2$). Interpret a proton NMR spectrum (next page).

(a) Identify H_X (give δ and J values)

2 δ 3.09, dd, J = 10.8, 3.7

(b) Below is reproduced the multiplet at δ 1.8. Which protons are these (circle: A, B, M, N, X). Label the spectrum and extract the coupling constants (you may use first-order analysis) and report the couplings (e.g., J_{PQ} = 33 Hz). Draw a coupling tree to show you understand the pattern

Coupling tree: 3

MN assignment: 1

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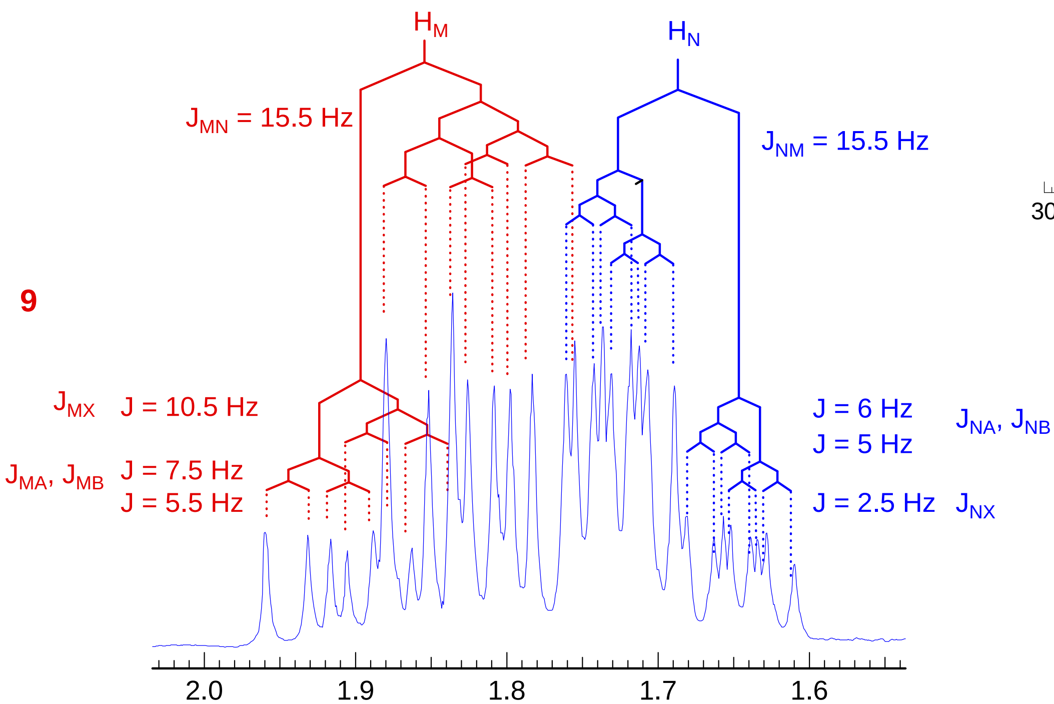
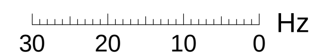
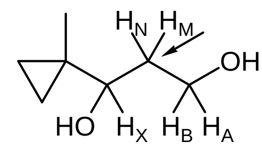
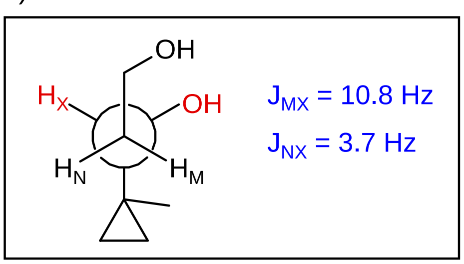


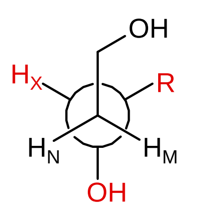




(c) Show the probable conformation looking down the bond marked with an arrow (fill in the Newman projection below).

3





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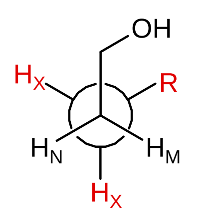

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(d) Which of the couplings you extracted in part (a) using first-order analysis do you expect to be accurate?

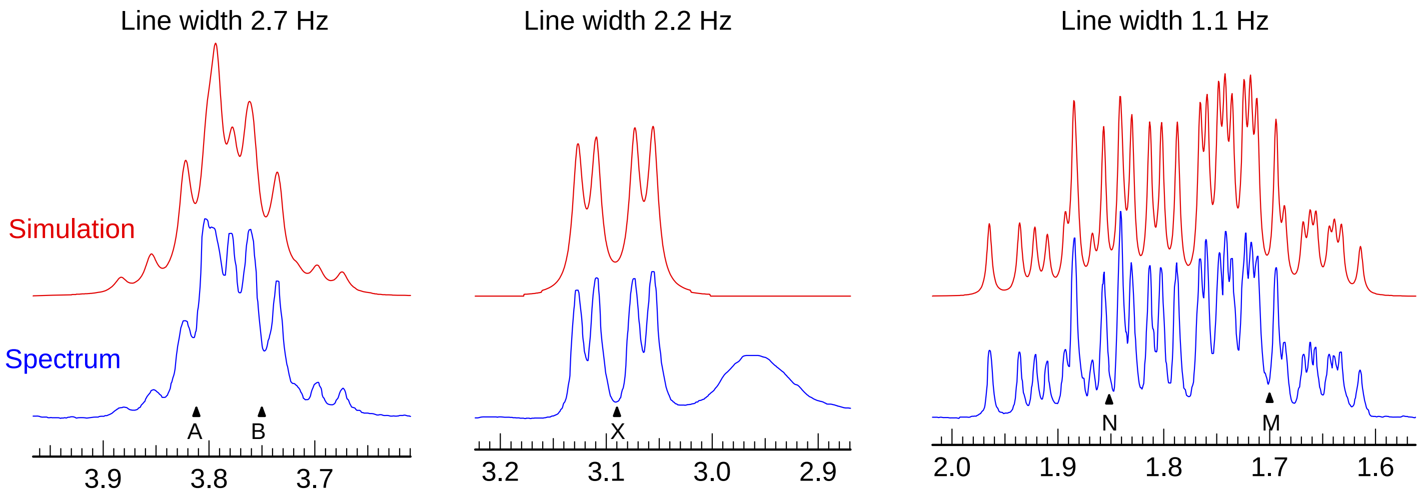
2 Only the J_{MN} coupling will be accurate.

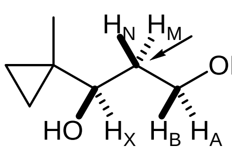
Which will be only approximate? Explain, and predict the direction of the expected error for these couplings (be specific).

2 Since the AB protons are strongly coupled ($\Delta\nu_{AB} < J_{AB}$), then all couplings to them will be changed (virtual coupling effects will be seen). Thus the true values of J_{MA} and J_{MB} will be further apart than the measured numbers (true values might be 7 and 3 instead of 6 and 4). Similarly, the values for J_{MX} and J_{NX} will be affected since M and N are fairly close, but the errors here will be smaller, since $\Delta\nu_{MN} > J_{MN}$

See simulation and a more detailed analysis on next page.

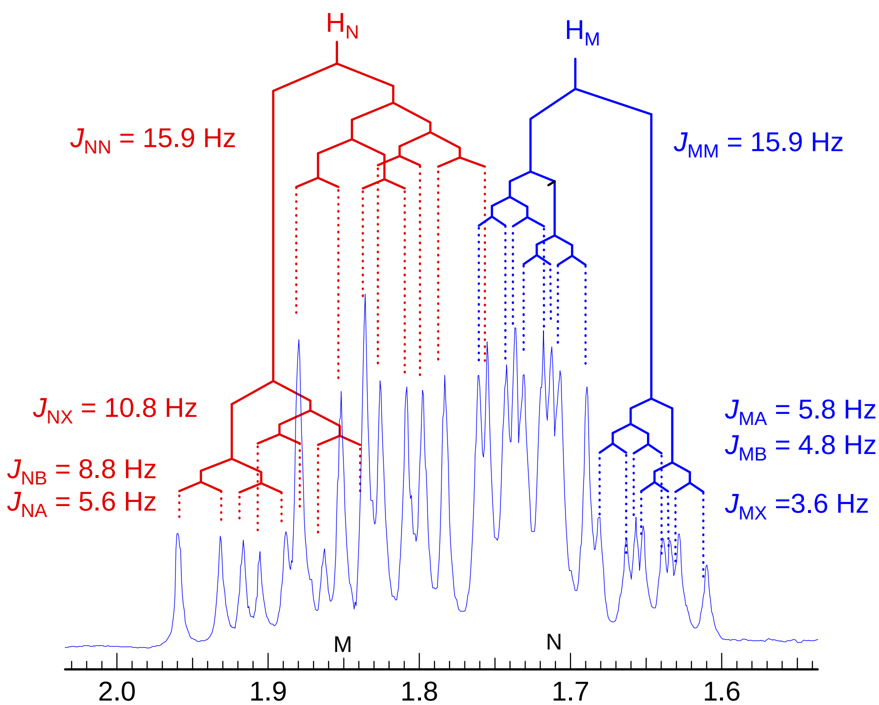
Simulation with WINDNMR (http://www.chem.wisc.edu/areas/reich/plt/windnmr.htm)





Parameters

ν_M = 339.15	ν_N = 369.58	ν_X = 618.37	ν_A = 750.05	ν_B = 762.04
	J_{MN} = -16.00	J_{MX} = 3.00	J_{MA} = 4.20	J_{MB} = 6.30
		J_{NX} = 11.40	J_{NA} = 9.70	J_{NB} = 4.90
			J_{XA} = 0.00	J_{XB} = 0.00
				J_{AB} = -12.20

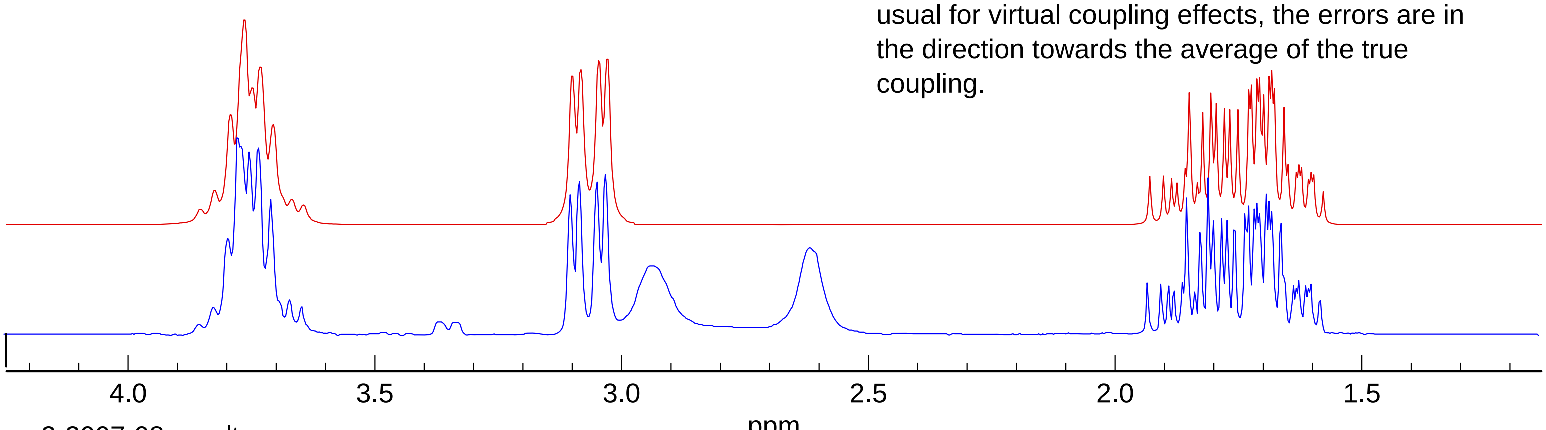


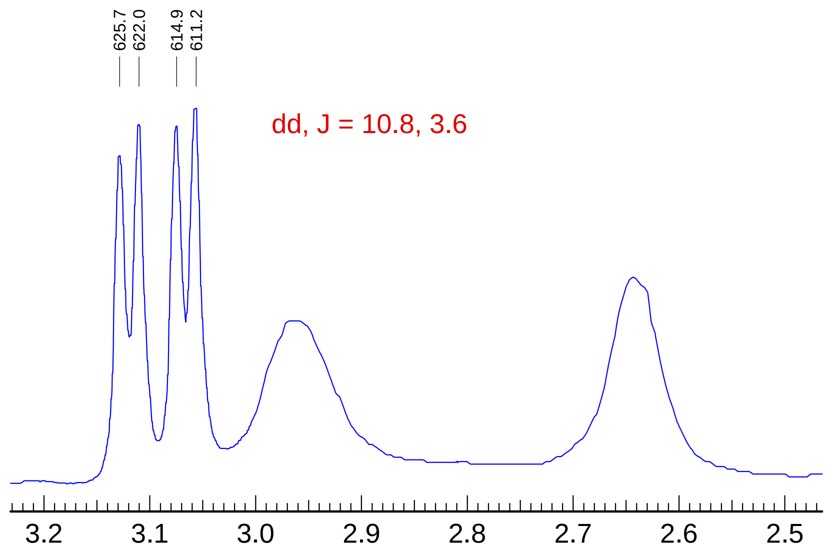
$\Delta\nu_{AB}$ = 8 Hz (J_{AB} = -12.1)

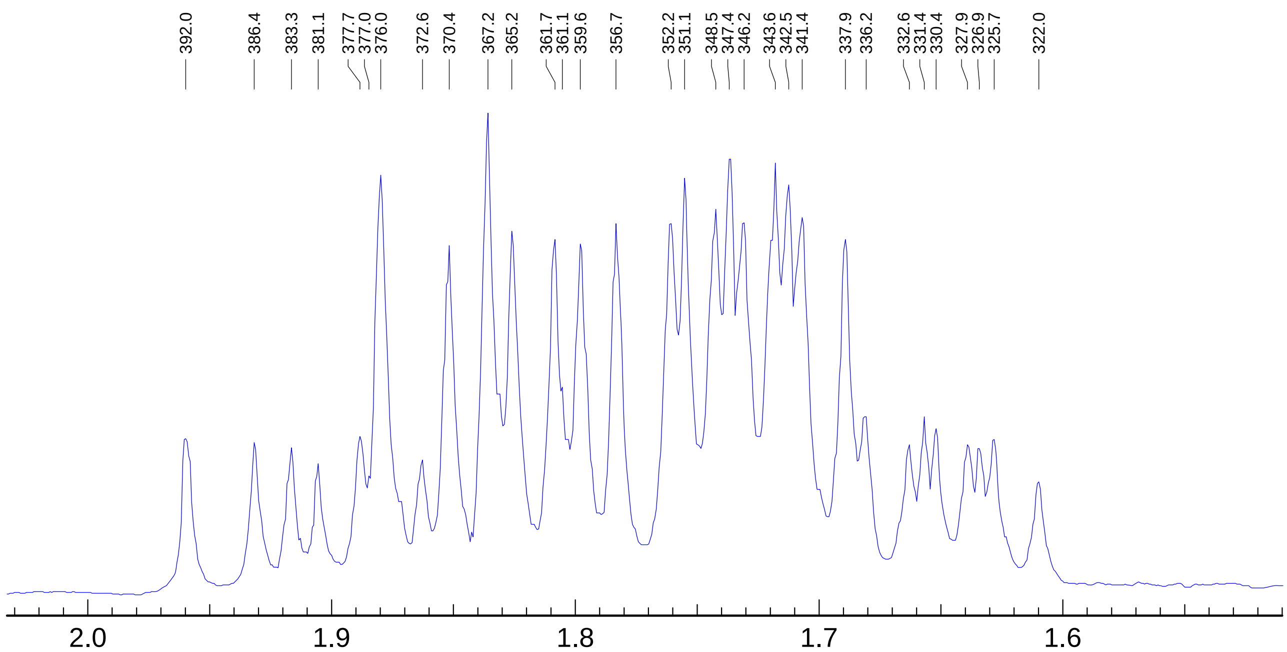
$\Delta\nu_{MN}$ = 20.2 Hz (J_{MN} = -16 Hz)

Simulation (actual *J*)	**First order analysis *J***
J_{MA} = 4.20	J_{MA} = 5.8 Hz
J_{MB} = 6.30	J_{MB} = 4.8 Hz
J_{NA} = 9.70	J_{NB} = 8.8 Hz
J_{NB} = 4.90	J_{NA} = 5.6 Hz
J_{MX} = 3.00	J_{MX} = 3.6 Hz
J_{NX} = 11.40	J_{NX} = 10.8 Hz

For coupling to M, N *J* errors from a first order analysis are 1.6, 1.5, 0.9 and 0.7 Hz for coupling to A and B, but only 0.6 and 0.6 Hz for coupling to X. The errors are larger for coupling to A and B because ν_{AB} (8 Hz) is smaller than J_{AB}. As is usual for virtual coupling effects, the errors are in the direction towards the average of the true coupling.







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