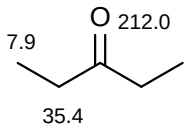
Problem R-07A $C_8H_{16}O$

Calculate the ^{13}C chemical shifts of the carbons marked c and d in the 75 MHz ^{13}C NMR spectrum of 5-methyl-3-heptanone below. Use as a model the appropriate shifts of 3-pentanone shown. Show the parameters you used. (15 points)

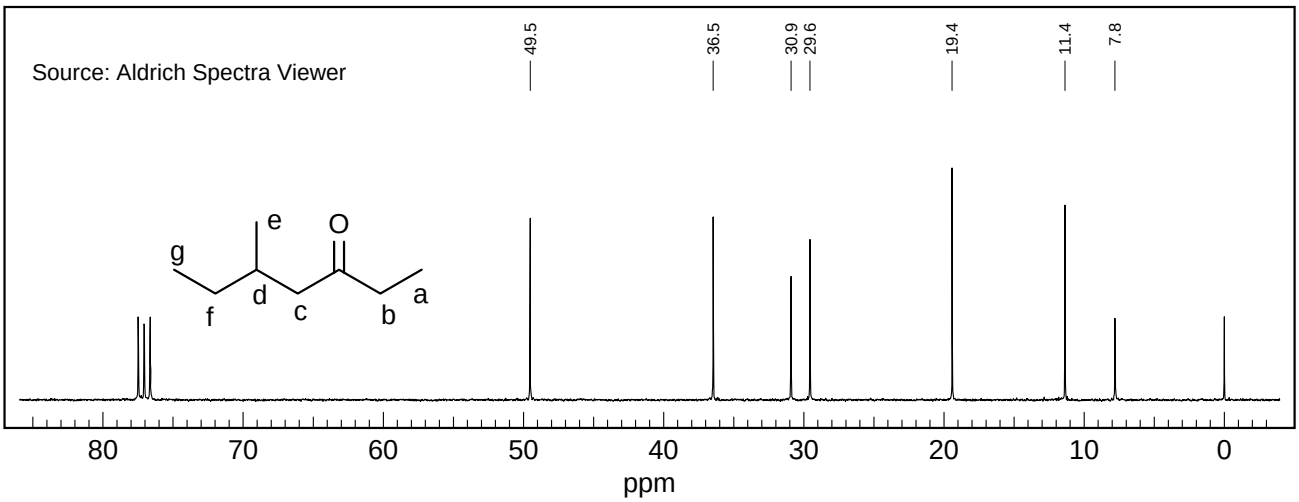
δ_c =

δ_d =



Calculate f using any sound method.

δ_f =



Using this and any other calculations or model compounds needed, assign the carbons a-g (mark the letters on the spectrum). Note any remaining ambiguities. What spectroscopic information would be needed to complete the assignment?

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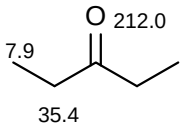


3 δ_c = 35.4 + 2β + γ + 2°(3°) - 2°(1°) = 49.2 (obs: 49.5)

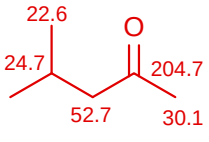
3 δ_d = 7.9 + 2α + β + 3°(1°) + 3°(2°) + 3°(2°) - 1°(2°) = 28.1 (obs: 29.6)

Calculate f using any sound method.

3 From CH_4:

δ_f = -2.1 + 2α + 2β + $\gamma_{C=O}$ + 2°(1°) + 2°(3°) = 30.4 ($\gamma_{C=O}$ is from the "n- iso- table, -2 ppm)

Calculations using another model compound:



Model

δ_c = 52.7 + γ = 50.2 (obs: 49.5)

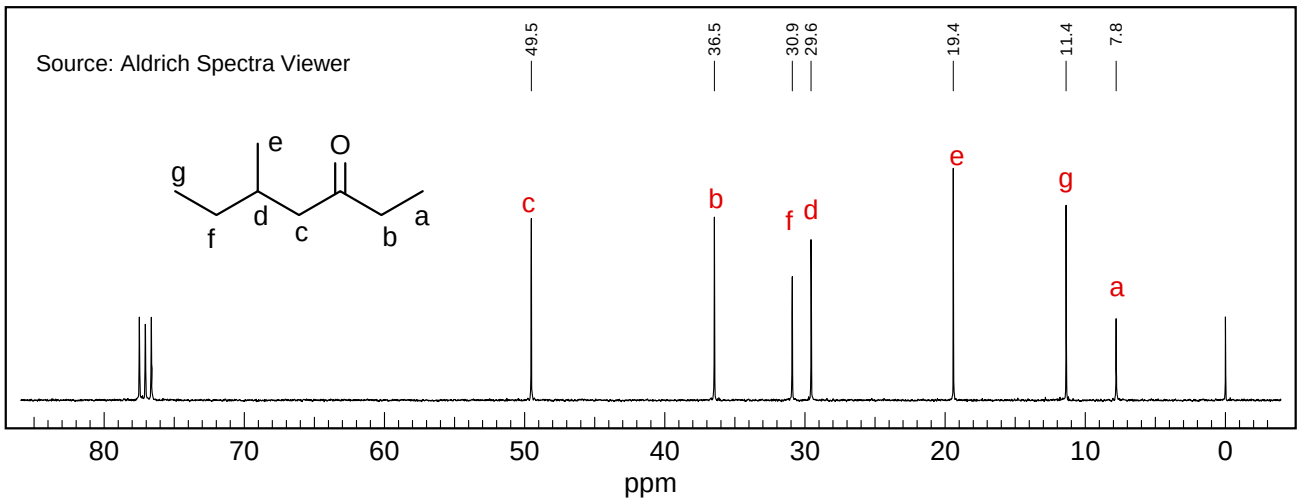
δ_d = 24.7 + β - 3°(1°) + 3°(2°) = 30.4 (obs: 29.6)

δ_e = 22.6 + γ = 20.1 (obs: 19.4)

δ_f = 22.6 + α - 1°(3°) + 2°(3°) = 30.3 (obs: 30.4)

Note: all calculations are within 1.5 ppm of the observed values

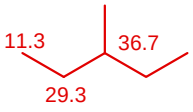
3



Using this and any other calculations or model compounds needed, assign the carbons a-g (mark the letters on the spectrum). Note any remaining ambiguities. What spectroscopic information would be needed to complete the assignment?

3 δ_g = 11.3

δ_f = 29.3



Model

The signals at 30.9 and 29.6 are too close to call - would need an APT experiment (DEPT or coupled ^{13}C spectrum) to distinguish the CH_2 from the CH

Grant-Paul Parameters

δ_C = -2.1 + Σ n_iA_i + Σ (branching corrections) (in δ from TMS)

	A_i	**Branching Corrections (1°(3°) = a CH_3 (1°) with a CHR_2 carbon (3°) attached to it).**							
α	+9.1	1°(1°)	0	2°(1°)	0	3°(1°)	0	4°(1°)	-1.5
β	+9.4	1°(2°)	0	2°(2°)	0	3°(2°)	-3.7	4°(2°)	-8.4
γ	-2.5	1°(3°)	-1.1	2°(3°)	-2.5	3°(3°)	-9.5	4°(3°)	-15.0
δ	+0.3	1°(4°)	-3.4	2°(4°)	-7.5	3°(4°)	-15.0	4°(4°)	-25.0
ε	+0.1								