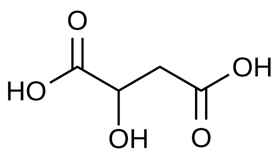
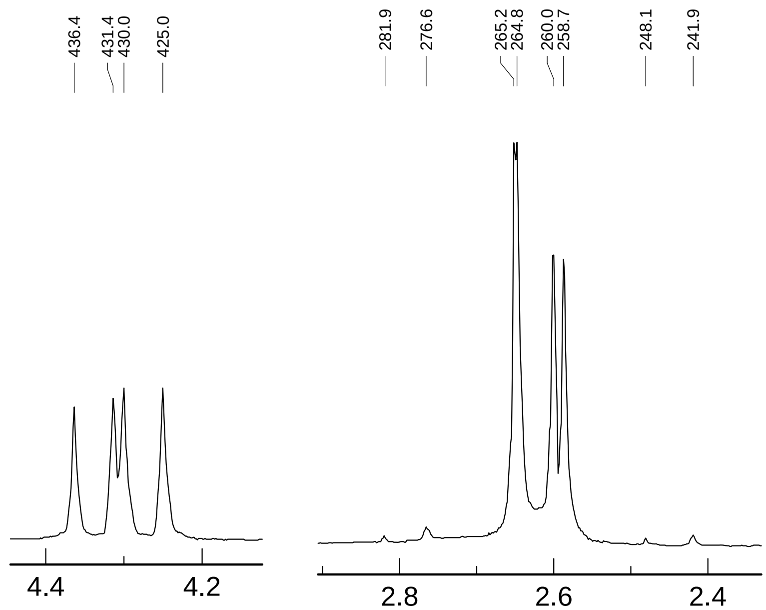
Problem R-08I ($C_4H_6O_5$). The 100 MHz NMR spectrum of malic acid in D_2O is shown below.

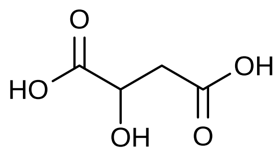


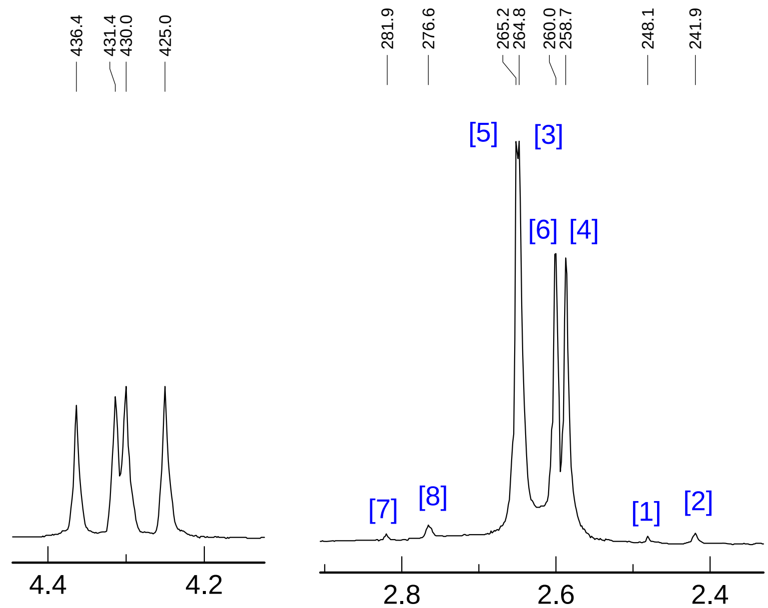


(a) Do a mathematically accurate analysis of this spectrum. If there are two solutions, report them both. Show a coupling tree.

(b) If you are proposing two solutions, suggest at least one criterion which allows you to identify the correct one.

Problem R-08I ($C_4H_6O_5$). The 100 MHz NMR spectrum of malic acid in D_2O is shown below.





(a) Do a mathematically accurate analysis of this spectrum. If there are two solutions, report them both. Show a coupling tree.

15

$c_+ = (6+4)/2 \quad = 259.37$

$\Delta\nu_{ab}+ = \delta_+ = \text{sqrt}((8-2)(6-4)) \quad = 6.6$

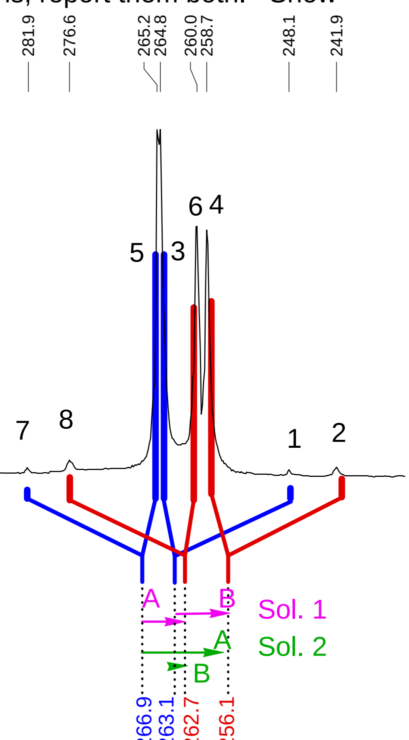
$c_+ \pm \Delta\delta_+/2 = \quad 262.7 \quad 256.1$

$c_- = (5+3)/2 \quad = 264.98$

$\Delta\nu_{ab}- = \delta_- = \text{sqrt}((7-1)(5-3)) \quad = 3.8$

$c_- \pm \Delta\delta_-/2 = \quad 266.9 \quad 263.1$

	Solution 1	**Solution 2**
J_{AB}	16.7	16.7
J_{AX}	4.2	0.4
J_{BX}	7.0	10.8
ν_A	264.8	262.9
ν_B	259.6	261.5
$\Delta\nu_{AB}$	5.2	1.4
δ_A	2.65	2.63
δ_B	2.59	2.61



2

Intensity Calculation

Solution 1

$\Phi 1+ = 0.5 \arcsin(J_{AB}/2D+) = 34.2$

$\Phi 1- = 0.5 \arcsin(J_{AB}/2D-) = 38.6$

$i_{10} = i_{11} = 0.994$

$i_{14} = i_{15} = 0.006$

Solution 2

$\Phi_2+ = \Phi 1 = 34.2$

$\Phi_2- = 90 - \Phi 1- = 51.4$

$i_{10} = i_{11} = 0.913$

$i_{14} = i_{15} = 0.087$

(b) If you are proposing two solutions, suggest at least one criterion which allows you to identify the correct one.

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In both solutions the J_{AX} and J_{BX} couplings are both positive, thus appropriate for a ^3J, although magnitude is better for solution 1 (vicinal couplings of 0.4 Hz in an acyclic $CH\text{-}CH_2$ system probably are never seen).

The intensity calculation predicts 9% size for the extra peaks 14 and 15 in the X part for Solution 2, and these should have been clearly visible in the spectrum

So solution 1 is probably correct.