Chemical Shift Calculation for AB Spectra

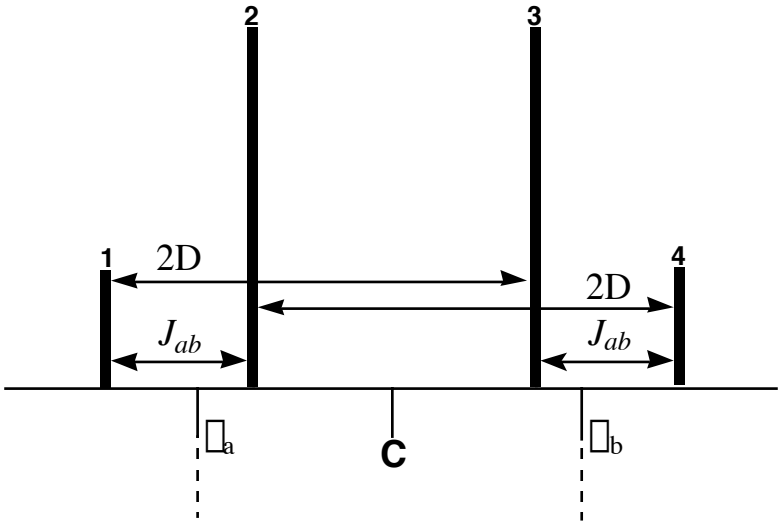
An AB spectrum usually exhibits the 'roofing effect' characteristic of higher order coupling systems. In such systems, you cannot think of each line representing a single transition of a nucleus as is possible with a first-order spectrum. Instead, the peaks of a higher-order spectrum should be thought of as a combination of all spins in the system.

Four lines are present in an AB system, and the coupling constant, *J*, is the same for each line:

$$|J_{ab}| = (\nu_1 - \nu_2) = (\nu_3 - \nu_4)$$

The line intensities (*i*) are no longer 1:1:1:1 as in an AX system, but are given by the ratios:

$$\frac{i_2}{i_1} = \frac{i_3}{i_4} = \frac{(\nu_1 - \nu_4)}{(\nu_2 - \nu_3)}$$



ν_a and ν_b are not exactly centered between lines 1 & 2 and 3 & 4. Instead, their chemical shifts are given by the centers of gravity for each doublet. This can be calculated using the following formulae:

c = center of spectrum = $0.5(\nu_2 + \nu_3) = 0.5(\nu_1 + \nu_4)$

$$\Delta\nu = (\nu_a - \nu_b) = \sqrt{\left[(\nu_1 - \nu_4)(\nu_2 - \nu_3)\right]} = \sqrt{\left[(2D)^2 - J^2\right]}$$

$$\nu_a = c + \frac{\Delta\nu}{2} \qquad \nu_b = c - \frac{\Delta\nu}{2}$$