

AB Proton NMR Analysis for 2,3-dibromothiophene

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The purpose of this tutorial is to obtain the chemical shifts and coupling constant of 2,3-dibromothiophene by analysis of its proton nmr spectrum.

The nuclear magnetic energy operator for the AB system is given below.

$$\hat{H}_{mag} = -\nu_A \hat{I}_z^A - \nu_B \hat{I}_z^B + J_{AB} \hat{I}^A \cdot \hat{I}^B \quad \text{where} \quad \nu_A = g_n \beta_n B_z (1 - \sigma_A) \hat{I}_z^A \quad \nu_B = g_n \beta_n B_z (1 - \sigma_B) \hat{I}_z^B$$

$$\text{and} \quad \hat{I}^A \cdot \hat{I}^B = \hat{I}_x^A \hat{I}_x^B + \hat{I}_y^A \hat{I}_y^B + \hat{I}_z^A \hat{I}_z^B$$

The nuclear spin operators (using atomic units, $h = 2\pi$) in the x-, y- and z-directions, plus the identity operator are shown below.

$$I_x := \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad I_y := \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad I_z := \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad I := \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Tensor matrix multiplication is used to construct the magnetic energy operator in two steps. Please see <http://www.users.csbsju.edu/~frioux/nmr/AB-NMR-TENSOR.pdf> for details.

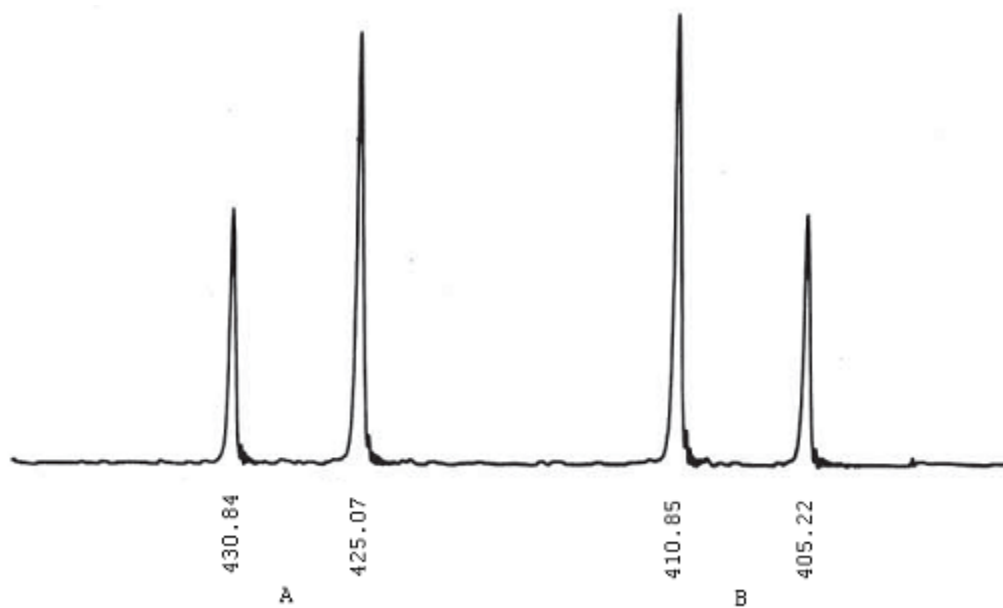
$$-\nu_A \hat{I}_z^A - \nu_B \hat{I}_z^B \rightarrow -\nu_A \hat{I}_z^A \otimes \hat{I} - \hat{I} \otimes \nu_B \hat{I}_z^B = -\frac{1}{2} \begin{pmatrix} \nu_A + \nu_B & 0 & 0 & 0 \\ 0 & \nu_A - \nu_B & 0 & 0 \\ 0 & 0 & -\nu_A + \nu_B & 0 \\ 0 & 0 & 0 & -\nu_A - \nu_B \end{pmatrix}$$

$$J_{AB} (\hat{I}_x^A \otimes \hat{I}_x^B + \hat{I}_y^A \otimes \hat{I}_y^B + \hat{I}_z^A \otimes \hat{I}_z^B) = J_{AB} \hat{I}^A \otimes \hat{I}^B = \frac{J_{AB}}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

The magnetic Hamiltonian can now be written in Mathcad code.

$$H_{mag} := \begin{pmatrix} -\frac{\nu_A}{2} - \frac{\nu_B}{2} + \frac{J_{AB}}{4} & 0 & 0 & 0 \\ 0 & \frac{\nu_B}{2} - \frac{\nu_A}{2} - \frac{J_{AB}}{4} & \frac{J_{AB}}{2} & 0 \\ 0 & \frac{J_{AB}}{2} & \frac{\nu_A}{2} - \frac{\nu_B}{2} - \frac{J_{AB}}{4} & 0 \\ 0 & 0 & 0 & \frac{\nu_A}{2} + \frac{\nu_B}{2} + \frac{J_{AB}}{4} \end{pmatrix}$$

Next, approximate values for the chemical shifts and the coupling constant are extracted from the nmr spectrum. Initially we will assume the chemical shifts to be at the center of each of the doublets and the coupling constant will be taken to be the separation between the resonances in each doublet. The resonance frequencies are given in Hz.



This procedure yields the following approximate values: $\nu_A := 428$ $\nu_B := 408$ $J_{AB} := 5.7$

The eigenvalues of the magnetic Hamiltonian can now be calculated using these approximate values. Inspection of H_{mag} makes it clear that two states are pure nuclear spin states and two are superpositions. It is therefore straightforward to make the nuclear spin assignments shown below.

$$\text{eigenvals}(H_{\text{mag}}) \rightarrow \begin{pmatrix} -\frac{J_{AB}}{4} - 8 \cdot \sqrt{\frac{J_{AB}^2}{256} + \frac{\nu_A^2}{256} - \frac{\nu_A \cdot \nu_B}{128} + \frac{\nu_B^2}{256}} \\ 8 \cdot \sqrt{\frac{J_{AB}^2}{256} + \frac{\nu_A^2}{256} - \frac{\nu_A \cdot \nu_B}{128} + \frac{\nu_B^2}{256}} - \frac{J_{AB}}{4} \\ \frac{J_{AB}}{4} - \frac{\nu_A}{2} - \frac{\nu_B}{2} \\ \frac{J_{AB}}{4} + \frac{\nu_A}{2} + \frac{\nu_B}{2} \end{pmatrix} = \begin{pmatrix} -11.82 \\ 8.97 \\ -416.57 \\ 419.43 \end{pmatrix} \begin{matrix} \alpha\beta + \beta\alpha \\ \alpha\beta - \beta\alpha \\ \alpha\alpha \\ \beta\beta \end{matrix}$$

The nmr selection rule requires that only one nuclear spin can flip in a transition, giving four possible transitions with the following approximate frequencies.

$$\begin{array}{llll} \alpha\alpha \rightarrow \alpha\beta + \beta\alpha & -11.82 + 416.57 = 404.75 & \alpha\alpha \rightarrow \alpha\beta - \beta\alpha & 8.97 + 416.57 = 425.54 \\ \alpha\beta + \beta\alpha \rightarrow \beta\beta & 419.43 + 11.82 = 431.25 & \alpha\beta - \beta\alpha \rightarrow \beta\beta & 419.43 - 8.97 = 410.46 \end{array}$$

We now refine the approximate values for the shifts and coupling constant using the actual transition frequencies from the nmr spectrum. In other words 405.22 replaces 404.75, 410.85 replaces 410.46, 425.07 replaces 425.44, and 430.84 replaces 431.25.

We set up a Given/Minerr Mathcad solve block using the four allowed transitions with the experimental resonant frequencies and employing energy conservation explicitly. The approximate shifts and coupling constant from above serve as seed values for this numeric algorithm.

Given

$$\frac{J_{AB}}{4} - \frac{\nu_A}{2} - \frac{\nu_B}{2} + 405.22 = -\frac{J_{AB}}{4} - 8 \cdot \sqrt{\frac{J_{AB}^2}{256} + \frac{\nu_A^2}{256} - \frac{\nu_A \cdot \nu_B}{128} + \frac{\nu_B^2}{256}} \quad \alpha\alpha + 405.22 \rightarrow (\alpha\beta + \beta\alpha)$$

$$\frac{J_{AB}}{4} - \frac{\nu_A}{2} - \frac{\nu_B}{2} + 425.07 = 8 \cdot \sqrt{\frac{J_{AB}^2}{256} + \frac{\nu_A^2}{256} - \frac{\nu_A \cdot \nu_B}{128} + \frac{\nu_B^2}{256}} - \frac{J_{AB}}{4} \quad \alpha\alpha + 425.07 \rightarrow (\alpha\beta - \beta\alpha)$$

$$-\frac{J_{AB}}{4} - 8 \cdot \sqrt{\frac{J_{AB}^2}{256} + \frac{\nu_A^2}{256} - \frac{\nu_A \cdot \nu_B}{128} + \frac{\nu_B^2}{256}} + 430.84 = \frac{J_{AB}}{4} + \frac{\nu_A}{2} + \frac{\nu_B}{2} \quad (\alpha\beta + \beta\alpha) + 430.84 \rightarrow \beta\beta$$

$$8 \cdot \sqrt{\frac{J_{AB}^2}{256} + \frac{\nu_A^2}{256} - \frac{\nu_A \cdot \nu_B}{128} + \frac{\nu_B^2}{256}} - \frac{J_{AB}}{4} + 410.85 = \frac{J_{AB}}{4} + \frac{\nu_A}{2} + \frac{\nu_B}{2} \quad (\alpha\beta - \beta\alpha) + 410.85 \rightarrow \beta\beta$$

The refined values for the coupling constant and chemical shifts are:

$$\begin{pmatrix} J_{AB} \\ \nu_A \\ \nu_B \end{pmatrix} := \text{Minerr}(J_{AB}, \nu_A, \nu_B) \quad \begin{pmatrix} J_{AB} \\ \nu_A \\ \nu_B \end{pmatrix} = \begin{pmatrix} 5.70 \\ 427.54 \\ 408.45 \end{pmatrix}$$