In a recent issue of Science, investigators reported the synthesis and characterization of fused porphyrin systems, as illustrated here. To be more complete, they characterized a series of constructs of varying lengths and measured their absorption properties. Absorption spectra are shown below:

1. Assuming that the largest fused system (19) is a one-dimensional particle in a box, with box size 100 Å, calculate the energy (in cm\(^{-1}\)) of the predicted lowest energy electronic transition.

\[
E_n = \frac{n^2 \hbar^2}{8mL^2} = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8(9.109 \times 10^{-31} \text{ kg}) (100 \text{ Å})^2 n^2} = \left( \frac{6.626 \times 10^{-34} \text{ J s}}{8(9.109 \times 10^{-31} \text{ kg} \text{ m}^2 \text{ s}^2)} \right) n^2 = (6.025 \times 10^{-22} \text{ J}) n^2
\]
Relating that to wavelength (we’ll go to nm, and then back to cm⁻¹):

\[ \lambda_{m,n \rightarrow m',n'} = \frac{hc}{E_{m,n} - E_{m',n'}} = \frac{(6.626 \times 10^{-34} J s)(2.998 \times 10^4 m s^{-1})}{(6.025 \times 10^{-22} J)(n+1)^2 - n^2} = 3.297 \times 10^5 \frac{m}{nm} = 3.297 \times 10^3 \frac{nm}{cm} \]

\[ \frac{1}{\lambda_{m,n \rightarrow m',n'}} = \frac{(n+1)^2 - n^2}{3.297 \times 10^5 nm/cm} = \left( \frac{n+1}{n} \right)^2 = \left( \frac{120}{1} \right)^2 \approx 30.33 cm^{-1} \]

Finally, answer the question (two ways):

a) Assuming a simple situation with only 1 electron:

\[ \frac{1}{\lambda_{1 \rightarrow 2}} = \left( \frac{2}{1} \right)^2 \approx 30.33 cm^{-1} = 91 cm^{-1} \]

Not so great…

b) Treat it more realistically. From the Figure Legend, system (19) has 10 fused porphyrin rings. Counting π electrons in each porphyrin, I get about 24 electrons/porphyrin (anyone care to tell me otherwise?), leading to 240 electrons in the box in total. This means that the lowest 120 energy levels will be filled.

\[ \frac{1}{\lambda_{120 \rightarrow 121}} = \left( \frac{121}{120} \right)^2 \approx 1.2 \times 30.33 cm^{-1} = 7310 cm^{-1} \]

The answer is off by about a factor of two (observed is 12,000 cm⁻¹). Not bad, given the approximations involved.

2. Assuming that the largest fused system (19) is a TWO dimensional particle in a box, with well size 100 Å x 7 Å, calculate the energy (in cm⁻¹) of the predicted lowest energy electronic transition.

\[ E_{n_1 \rightarrow n_2} = \frac{\hbar^2}{8m} \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} \right) = \frac{(6.626 \times 10^{-34} J s)^2}{8 \times (9.109 \times 10^{-31} kg) \left( \frac{10^{-10} m}{A} \right)} \left( \frac{n_1^2}{l_1^2} + \frac{n_2^2}{l_2^2} \right) = \frac{(6.025 \times 10^{-18} J)(n_1^2}{l_1^2} + \frac{n_2^2}{l_2^2} \right) \]

Note that I’ve switched from L to l, taking out units (in other words, I should be dimensions in Angstroms, but is unitless in the above…)

\[ \lambda_{m,n \rightarrow m',n'} = \frac{hc}{E_{m,n} - E_{m',n'}} = \frac{(6.626 \times 10^{-34} J s)(2.998 \times 10^4 m s^{-1})}{(6.025 \times 10^{-18} J)} \left( \frac{m^2 - m'^2}{l_1^2} + \frac{n^2 - n'^2}{l_2^2} \right) = \frac{32.97 nm}{cm} \]

\[ \frac{1}{\lambda_{m,n \rightarrow m',n'}} = \frac{\left( \frac{m^2 - m'^2}{l_1^2} + \frac{n^2 - n'^2}{l_2^2} \right)}{32.97 nm} \approx \left( \frac{120}{1} \right)^2 \approx 30.33 cm^{-1} \]

Finally, answer the question (two ways):

a) Assuming a simple situation with only 1 electron:

\[ \frac{1}{\lambda_{1 \rightarrow 2}} = \left( \frac{1^2 - 1^2}{100^2} + \frac{2^2 - 2^2}{7^2} \right) \approx 30.33 \times 10^3 cm^{-1} = 18600 cm^{-1} \]

\[ \frac{1}{\lambda_{1 \rightarrow 2}} = \left( \frac{2^2 - 1^2}{100^2} + \frac{1^2 - 1^2}{7^2} \right) \approx 30.33 \times 10^3 cm^{-1} = 91.0 cm^{-1} \]
Note that the lowest energy transition would be the latter (despite the fact that the former is fortuitously closer to the real value)…

b) Treat it more realistically. 240 electrons in the box in total. But life gets complicated… Have to use Excel or the equivalent (I did not expect you to go through this…). Evaluating a large range of n1 and n2, it turns out that 120\textsuperscript{th} and 121\textsuperscript{st} lowest energy levels are (43,2) and (29,3), corresponding to (100Å,7Å).

\[
\frac{1}{\lambda_{43,2 \to 29,3}} = \left[ \frac{29^2 - 43^2}{100^2} + \frac{3^2 - 2^2}{7^2} \right] 30.33 \times 10^5 \text{ cm}^{-1} = (-0.1008 + 0.1020) 30.33 \times 10^5 \text{ cm}^{-1} = 3640 \text{ cm}^{-1}
\]

Whoops. Farther off than with 1D system (observed is 12,000 cm\textsuperscript{-1}). Still not bad, given the approximations involved.

3. Why measure spectra of constructs 7-12? Explain their spectra.

In these constructs, the \( \pi \) systems are effectively decoupled. The resulting spectra correspond to the isolated porphyrins, and so are independent of the numbered of linked systems.