

2.12: Absorption Spectrum of Formaldehyde

We can now turn to H_2CO again and look at the measured spectrum in the laboratory.

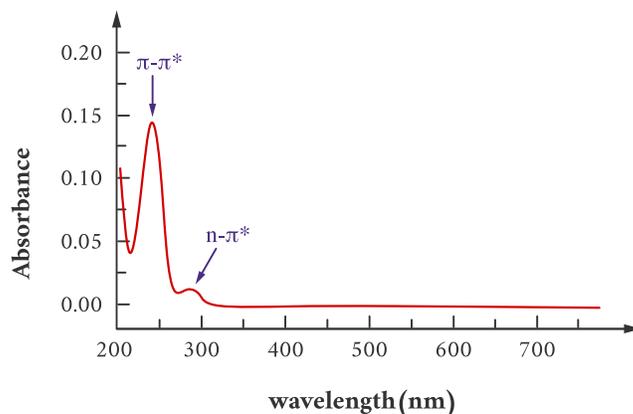
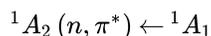


Figure 2.12.1: Electronic absorption spectrum of Formaldehyde in water. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

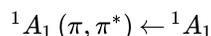
Two UV absorption bands are observed experimentally (Figure 2.12.1):

- 270 nm with $\epsilon = 100$ and
- 185 nm with $\epsilon > 10,000$

As discussed earlier, the lowest energy transitions are $n_b \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. As far as the states are concerned, the transitions are



and



respectively.

The Cartesian translational coordinates, x, y, z form a bases for the B_1, B_2 and A_1 representations in C_{2v} . Of course, x, y, z have the same transformation properties as \hat{M}_x, \hat{M}_y and \hat{M}_z , respectively. Hence we can represent as

$$\hat{M} = \begin{pmatrix} \hat{M}_x \\ \hat{M}_y \\ \hat{M}_z \end{pmatrix}$$

or in the C_{2v} point group as

$$\begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} = \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix}.$$

Class, please confirm this with the character table!

✓ Example 2.12.1: Forbidden Transition

Let's look at ${}^1A_2(n, \pi^*) \leftarrow {}^1A_1$

Evaluate this integrand for all components of \hat{M} :

$$A_2 \otimes \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} \otimes A_1 = \begin{pmatrix} B_2 \\ B_1 \\ A_2 \end{pmatrix}$$

And looking at each component:

- For \hat{M}_x :

$$A_2 \otimes B_1 \otimes A_1 = B_2$$

- For \hat{M}_y :

$$A_2 \otimes B_2 \otimes A_1 = B_1$$

- For \hat{M}_z :

$$A_2 \otimes A_1 \otimes A_1 = A_2$$

Therefore the ${}^1A_2 \leftarrow {}^1A_1$ transition is **forbidden** by electronic symmetry since there the symmetry is ODD for all the three \hat{M} components. That is, integration over all space with an integrand of non- A_1 symmetry will always results in zero!

However, in reality, other coupling elements like vibronic coupling and spin-orbit coupling will make this a weakly allow transition (Figure 2.12.1) instead of explicitly forbidden.

✓ Example 2.12.2: Allowed Transition

Let's look at ${}^1A_1 (\pi, \pi^*) \leftarrow {}^1A_1$

Evaluate this integrand for all components of \hat{M} :

$$A_1 \otimes \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} \otimes A_1 = \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix}$$

Therefore ${}^1A_1 \leftarrow {}^1A_1$ is **allowed** by since

- For \hat{M}_x :

$$A_1 \otimes B_1 \otimes A_1 = B_1$$

- For \hat{M}_y :

$$A_1 \otimes B_2 \otimes A_1 = B_2$$

- For \hat{M}_z :

$$A_1 \otimes A_1 \otimes A_1 = A_1$$

when \hat{M}_z the dipole moment operation (A_1) is used we get an integrand that has A_1 symmetry. This electronic transition is thus polarized (preferential absorption of one polarization vs. another) and is only allowed when the oscillating electric field vector, is aligned along the molecular z-axis (along the C=O bond direction).

✓ Example 2.12.3: Higher Lying Transitions

Let's consider higher energy transitions can occur such as

$${}^1B_1 (\pi, \sigma^*) \leftarrow {}^1A_1$$

$$B_1 \otimes \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} \otimes A_1 = \begin{pmatrix} A_1 \\ A_2 \\ B_1 \end{pmatrix}$$

So this transition is \hat{M}_x polarization **allowed** and is expected to lie further in the vacuum ultraviolet.

References

- <https://www.chem.ucla.edu/~bacher/UV...lone.html.html>
- http://web.gps.caltech.edu/~gab/ch21...ure16_2018.pdf

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