Just an info

Dipole-dipole interaction of molecules

Skip this $\Rightarrow$

H and J aggregates

$$E_{int} = \frac{1}{R_{AB}^3}\left[\vec{\mu}_A \cdot \vec{\mu}_B - 3(\vec{\mu}_A \cdot \vec{R}_{AB})(\vec{R}_{AB} \cdot \vec{\mu}_B)\right]$$

a)  $E_{int} > 0$

$$\begin{pmatrix} \varepsilon & J \\ J & \varepsilon \end{pmatrix} \to \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} \varepsilon & J \\ J & \varepsilon \end{pmatrix}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}\frac{1}{\sqrt{2}}$$

b)  $E_{int} < 0$

$$= \begin{pmatrix} \varepsilon + J & J + \varepsilon \\ -\varepsilon + J & \varepsilon - J \end{pmatrix}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}\frac{1}{2}$$

$$= \begin{pmatrix} 2(\varepsilon + J) & 0 \\ 0 & 2(\varepsilon - J) \end{pmatrix}\frac{1}{2} = \begin{pmatrix} \varepsilon + J & 0 \\ 0 & \varepsilon - J \end{pmatrix}$$

ad a) $\begin{pmatrix} \varepsilon & J \\ J & \varepsilon \end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}(\varepsilon + J)\begin{pmatrix} 1 \\ 1 \end{pmatrix}$

$|+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ has energy $(\varepsilon + J)$ —— $|+\rangle$ $\sqrt{2}\vec{d}$

$|-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$ has energy $(\varepsilon - J)$ —— $|-\rangle$ 0

ad b) $\begin{pmatrix} \varepsilon & -J \\ -J & \varepsilon \end{pmatrix} \Rightarrow |+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \to (\varepsilon - J)$ —— $|-\rangle$ $-\sqrt{2}\vec{d}$

$|-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \to (\varepsilon + J)$ —— $|+\rangle$ 0

Now add groundstate:

$$H_{mig} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \varepsilon & +J \\ 0 & +J & \varepsilon \end{pmatrix}$$

ad a) $\vec{\mu} = \begin{pmatrix} 0 & \vec{d} & \vec{d} \\ \vec{d} & 0 & 0 \\ \vec{d} & 0 & 0 \end{pmatrix}$ same direction

$$d_{+g} = \langle + | \vec{\mu} | g \rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 1 \end{pmatrix}\vec{d}\begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} =$$

$$= \frac{1}{\sqrt{2}}\vec{d}\begin{pmatrix} 0 & 1 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} = \frac{2}{\sqrt{2}}\vec{d}$$

$$d_{-g} = \langle - | \vec{\mu} | g \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & -1 \end{pmatrix} \vec{d} \begin{pmatrix} 0 & 1 & +1 \\ 1 & 0 & 0 \\ +1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} =$$

$$= \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & -1 \end{pmatrix} \vec{d} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} = 0$$

ad b)

$$\vec{\mu} = \begin{pmatrix} 0 & \vec{d} & -\vec{d} \\ \vec{d} & 0 & 0 \\ -\vec{d} & 0 & 0 \end{pmatrix}$$

$$d_{+g} = \langle + | \vec{\mu} | g \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 1 \end{pmatrix} \vec{d} \begin{pmatrix} 0 & 1 & -1 \\ 1 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} =$$

$$= \frac{1}{\sqrt{2}} \vec{d} \begin{pmatrix} 0 & 1 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} = \underline{\underline{0}}$$

$$d_{-g} = \langle - | \vec{\mu} | g \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 1 \end{pmatrix} \vec{d} \begin{pmatrix} 0 & 1 & -1 \\ 1 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$= \frac{\vec{d}}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} = -\frac{2\vec{d}}{\sqrt{2}} = \underline{\underline{-\sqrt{2}\,\vec{d}}}$$

Conclusion: in the dimer with parallel or antiparallel dipoles the upper excitonic level will be allowed.

For the conformation  it is always the lower exciton that is allowed

 H-aggregate  J-aggregates