

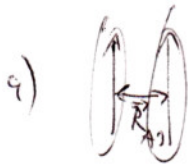
Mistake info

Dipole-dipole interaction of molecules

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How aggregates \Rightarrow

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



$E_{int} > 0$

$$\begin{pmatrix} \epsilon & J \\ J & \epsilon \end{pmatrix}$$

$$\rightarrow \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} \epsilon & J \\ J & \epsilon \end{pmatrix} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \frac{1}{\sqrt{2}}$$



$E_{int} < 0$

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

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

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

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

— $|+\rangle \sqrt{2} \vec{d}$

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

— $|-\rangle 0$

ad b) $\begin{pmatrix} \epsilon & -J \\ -J & \epsilon \end{pmatrix} \Rightarrow |+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \rightarrow (\epsilon - J)$

— $|-\rangle -\sqrt{2} \vec{d}$

$|-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \rightarrow (\epsilon + J)$

— $|+\rangle 0$

Now add quadrupole:

$$H_{int} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \epsilon & +J \\ 0 & +J & \epsilon \end{pmatrix}$$

ad a)

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

same direction

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

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

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

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

add)

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


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

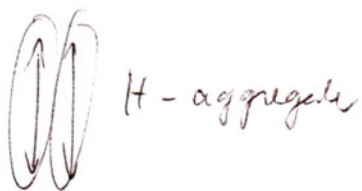
$$= \frac{1}{\sqrt{2}} \vec{d}' \overline{0 \ 1 \ 1} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} = \underline{\underline{0}}$$

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

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

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

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



J-aggregates