Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Optical spectra of molecular aggregates and crystals: testing approximation schemes
Electronic Supplementary Information

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Electrostatic intermolecular interactions are treated in the point dipole approximation, so that

$$\begin{aligned} J_{i,j} &= \frac{1}{4\pi\varepsilon}\left(\frac{\vec{\mu}_i\cdot\vec{\mu}_j - 3(\vec{\mu}_i\cdot\vec{d}_{ij})(\vec{\mu}_j\cdot\vec{d}_{ij})}{d_{ij}^3}\right) \\ &= \frac{\mu_0^2}{4\pi\varepsilon d_{ij}^3}\left[\vec{m}_i\cdot\vec{m}_j - 3(\vec{m}_i\cdot\vec{d}_{ij})(\vec{m}_j\cdot\vec{d}_{ij})\right], \end{aligned} \tag{1}$$

where $\vec{\mu}_i$ is the transition dipole moment on molecule i, $\vec{m}_i = \vec{\mu}_i/\mu_0$ is the unit vector that defines the direction of $\vec{\mu}_i$, $\vec{d}_{ij}$ is the unit vector connecting i and j sites, whereas d_{ij} is the distance between the two dipoles. The term in the squared parenthesis in the right hand side of the second line of the above equation is the D_{ij} quantity in Eq. 2 in the main text.

To relate the total oscillator strength of a system to a ground-state expectation value, we define the velocity dipole operator, $\hat{v}$:

$$i\hbar\hat{v} = [\hat{\mu}, \hat{H}], \tag{2}$$

where, to simplify the notation, we have suppressed the vector notation on both $\hat{v}$ and $\hat{\mu}$ operators. The oscillator strength associated with the $G \rightarrow E$ transition is:

$$f_{EG} = \frac{2}{3}\frac{m_e}{\hbar e^2}\omega_{EG}\langle G|\hat{\mu}|E\rangle\langle E|\hat{\mu}|G\rangle. \tag{3}$$

To eliminate the transition frequency from the above expression we use:

$$i\langle G|\hat{v}|E\rangle = \omega_{EG}\langle G|\hat{\mu}|E\rangle \tag{4}$$

and its complex conjugate, thus getting:

$$F = \sum_E f_{EG} = \frac{-im_e}{3\hbar e^2}\langle G|[\hat{\mu},\hat{v}]|G\rangle, \tag{5}$$

thus proving Eq.12 in the main text. Furthermore, using Eqs. 3 and 9 (main text) and remembering the Paulions algebra (see Eq. 4 in the main text), the commutator $[\hat{\mu}, \hat{v}]$ can be easily calculated. In particular, we have:

$$\begin{aligned} [\hat{\mu},\hat{v}] &= \frac{1}{i\hbar}\Big[\hat{\mu},[\hat{\mu},\hat{H}]\Big], \\ &= \frac{1}{i\hbar}\mu_0^2\sum_i[\hbar\omega_0 - \lambda(\hat{a}_i^\dagger + \hat{a}_i)](4\hat{n}_i - 2), \end{aligned} \tag{6}$$

that is Eq. 14 in the main text.

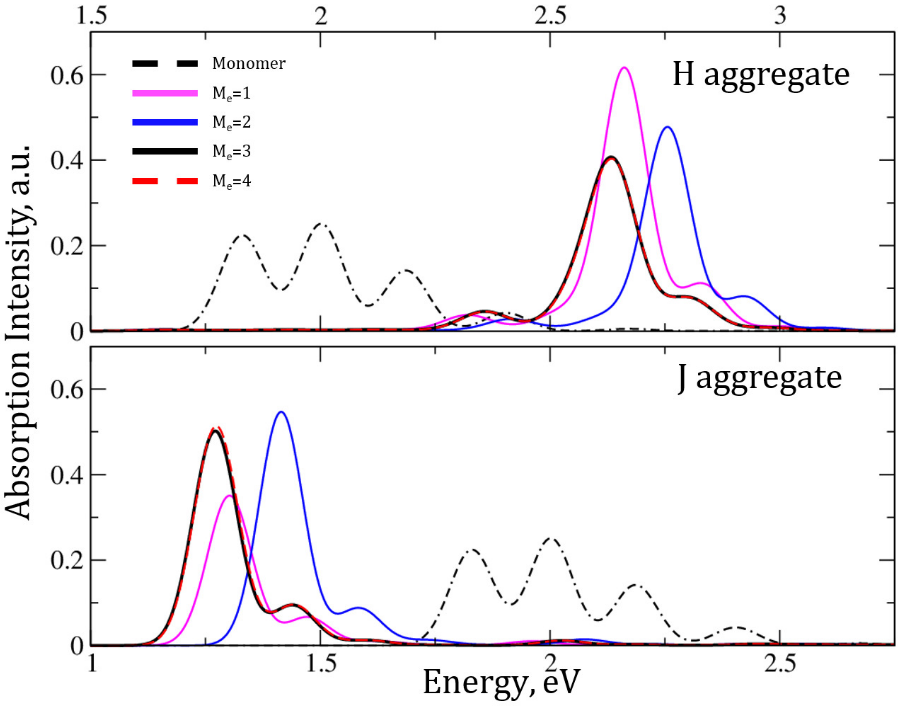

Figure 1: The same results as in Fig. 2, main text, but accounting for long-range electrostatic interactions.

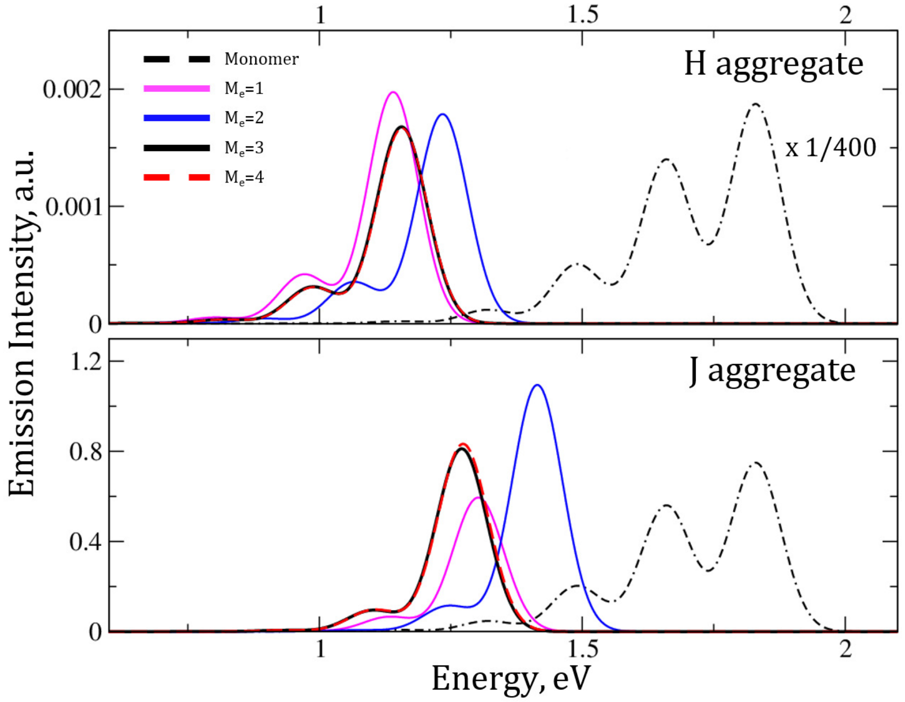

Figure 2: The same results as in Fig. 3, main text, but accounting for long-range electrostatic interactions.

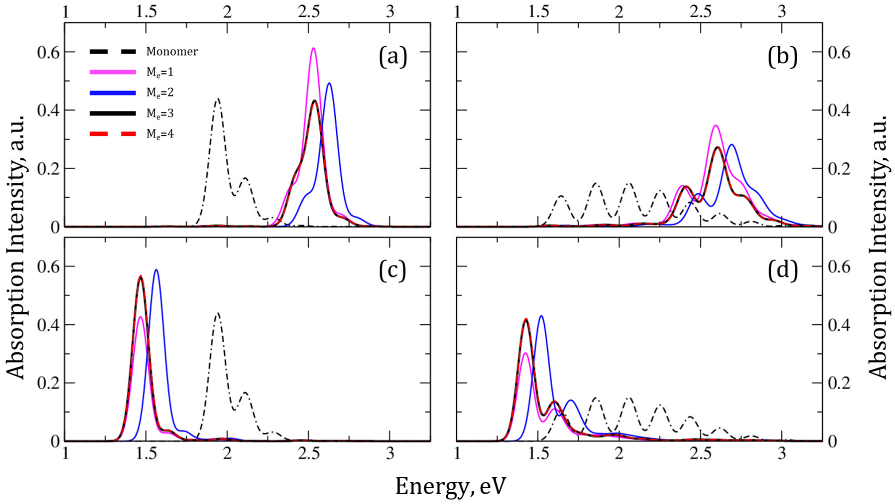

Figure 3: The same results as in Fig. 2, main text, but for different electron-vibration coupling strength. *a*) $J_1 = 0.255$ eV, $\lambda = 0.10$ eV; *b*) $J_1 = 0.255$ eV, $\lambda = 0.22$ eV; *c*) $J_1 = -0.255$ eV, $\lambda = 0.10$ eV; *d*) $J_1 = -0.255$ eV, $\lambda = 0.22$ eV.

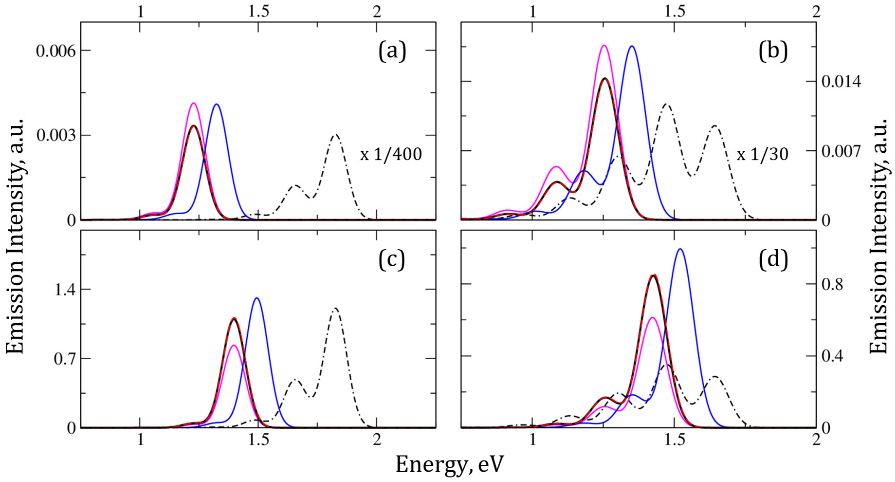

Figure 4: The same results as in Fig. 3, main text, but for different electron-vibration coupling strength. *a*) $J_1 = 0.255$ eV, $\lambda = 0.10$ eV; *b*) $J_1 = 0.255$ eV, $\lambda = 0.22$ eV; *c*) $J_1 = -0.255$ eV, $\lambda = 0.10$ eV; *d*) $J_1 = -0.255$ eV, $\lambda = 0.22$ eV. Please notice the different emission intensity scales on the y axis.

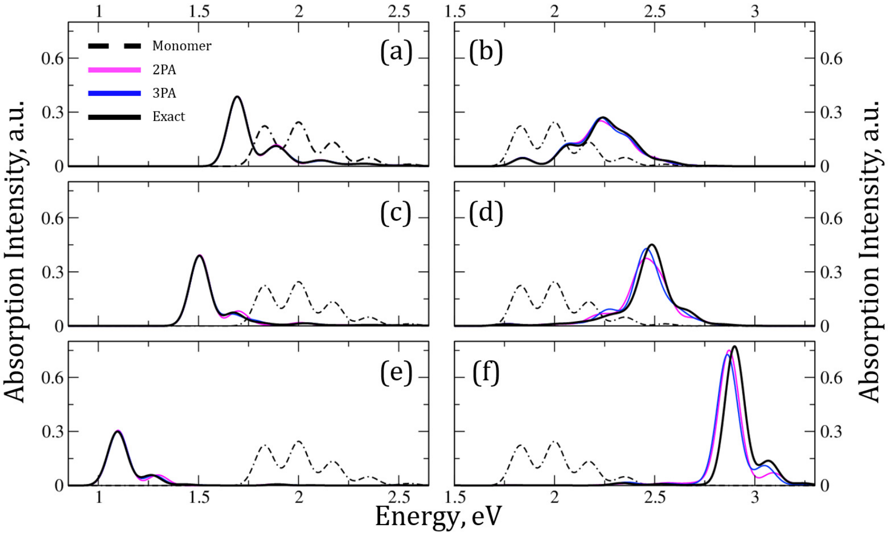

Figure 5: The same results as in Fig. 7, main text, but accounting for long-range electrostatic interactions. The number of molecules included in the calculation has been set to 6, the biggest aggregate that can be computed with a 3PA-lr basis.

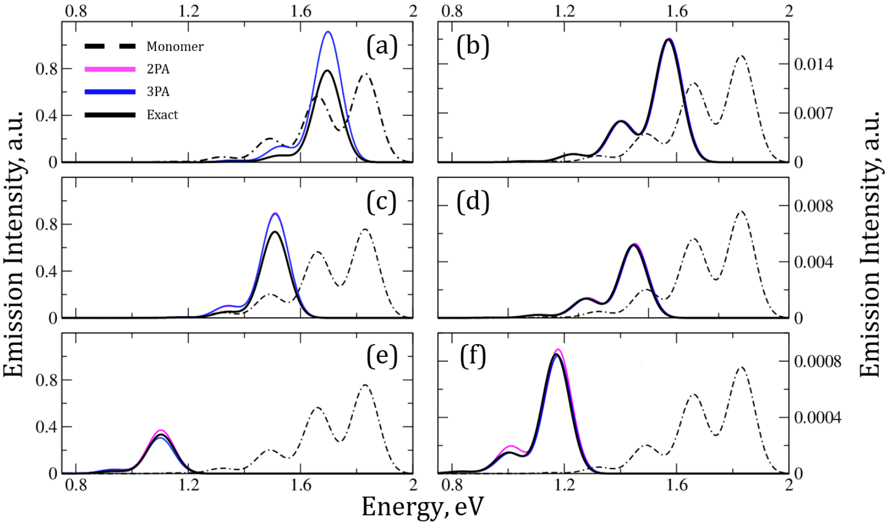

Figure 6: The same results as in Fig. 8, main text, but accounting for long-range electrostatic interactions. The number of molecules included in the calculation has been set to 6, the biggest aggregate that can be computed with a 3PA-lr basis. For H aggregates the monomer emission intensity is rescaled by a factor of 1/50, 1/100 and 1/1000 in panels (b), (d) and (f), respectively.