Theory of Transition-Dipole Coupling in Dye-Sensitized Semiconductor Nanoparticles

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SUPPORTING INFORMATION

Appendix A. Orientation factor in the point dipole approximation

Fig. A1 Relative alignment of semiconductor and molecule transition dipole moments.

Fig. A1 defines the angles that specify the relative alignment of the semiconductor and molecule transition moments. With this convention, the geometry factor is give by
Appendix B. Rearranging the determinant of \( \mathcal{J}(E) \)

The solutions to \( \mathcal{J}(E) = 0 \) are found by recognizing the special form of the \( \mathcal{J}(E) \) matrix:

\[
\mathcal{J}(E) = \begin{bmatrix}
E_{\phi_1} - E + Tc_1 * c_1 & Tc_1 * c_2 & Tc_1 * c_3 & \cdots \\
Tc_2 * c_1 & E_{\phi_2} - E + Tc_2 * c_2 & Tc_2 * c_3 & \cdots \\
Tc_3 * c_1 & Tc_3 * c_2 & E_{\phi_3} - E + Tc_3 * c_3 & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{bmatrix}
\]  \hspace{1cm} (B1)

where \( T \equiv G^2 |\mu_i|^2 Z_D(E) \) and \( c_i \equiv \Pi_{k=1}^{3P-6} \langle 0_k | \nu_k(i) \rangle \). Eq. B1 can be rearranged to give

\[
1 = T \left( \frac{c_1^2}{(E - E_{\phi_1})} + \frac{c_2^2}{(E - E_{\phi_2})} + \frac{c_3^2}{(E - E_{\phi_3})} + \cdots \right)
\]  \hspace{1cm} (B2)

Substituting the definitions for \( c_i \) and \( T \) and solving for \( Z_D(E) \) leads to Eq. 24.

Appendix C. Singular nature of the secular equations

Fig. 2 illustrates that the solution to the secular equations in their original form leads to a much larger calculated shift for the lowest vibrational energy level compared to all the rest. The cause of this problem is the form of Eq. 7, which is now rewritten without surface states included.

\[
\bar{H} = \begin{bmatrix}
\bar{E} & \bar{V}^* \bar{r} \\
\bar{V} & \bar{E}_i
\end{bmatrix}
\]  \hspace{1cm} (C1)

The submatrix \( \bar{V} \) has \( M \) columns and \( S \) rows, and each element can be written as a product of three terms:

\[
V_{x,m} = \langle \nu_x | \hat{H} | \phi_m \rangle = (G \mu_M \mu_s) \langle \Pi_{i=1}^{3P-6} \chi_{\nu_i} | \Pi_{j=1}^{3P-6} \chi_{\nu_j(m)} \rangle
\]  \hspace{1cm} (C2)
where for generality we permit the semiconductor transition moment to vary with state:

\[ \mu_s \equiv \langle \psi_s | \hat{\mu} | \psi_0 \rangle. \]

The first term is related to the previously defined coupling strength \( K \) and is the product of the semiconductor and molecule transition dipole moments and the orientation factor which is considered to be a constant for the entire manifold of molecule and semiconductor states. The second term is the vibrational Franck-Condon (overlap) factor for the \( m \)th vibronic state. Defining a new constant \( K' \),

\[ K' \equiv G \mu_M \]

the submatrix \( \bar{V} \) becomes an outer product due to the separated defining terms:

\[ \bar{V} = K'(s \cdot m^\top) \]

where the two vectors are

\[ s \equiv \left[ \langle \psi_{s=1} | \hat{\mu} | \psi_0 \rangle, \langle \psi_{s=2} | \hat{\mu} | \psi_0 \rangle, ..., \langle \psi_{s=5} | \hat{\mu} | \psi_0 \rangle \right]^\top \]

\[ m \equiv \left[ \Pi_{j=1}^{3P-6} \mathcal{Z}_{\nu',\nu=0} \left| \Pi_{j=1}^{3P-6} \mathcal{Z}_{\nu_j,nu=0} \right| \right]^\top \]

Eq. C1 can be recast as

\[ \bar{H} = \begin{bmatrix} \bar{E}_\phi & K'(s \cdot m^\top)^\top \\ K'(s \cdot m^\top) & \bar{E}_i \end{bmatrix} \]

Because submatrix \( \bar{V} \) is defined by an outer product, it is singular. Also, submatrices \( \bar{E}_\phi \) and \( \bar{E}_i \) are diagonal. When one seeks the eigenvalues of Eq. C7, it is found that only two of the eigenvalues (the largest and smallest) are different from the corresponding diagonal terms in \( \bar{E}_\phi \).

To avoid this problem, consider that the harmonic mean tends towards the value of the smallest element in the list. For each root of Eq. 28, the energy \( E_{\nu_s} \) closest to the root \( E \) will dominate the
summation in the denominator of the right hand side. Therefore, we will separate this term, denoted below by the index \( n \), from rest of the summation:

\[
K \ln \left( \frac{E_1 - E}{E_2 - E} \right) = \frac{1}{\Pi_{k=1}^{3P-6} \langle 0_k | \nu_k(m) \rangle^2} \left( e - E_\psi - \sum_{m=1}^{M} \frac{\Pi_{k=1}^{3P-6} \langle 0_k | \nu_k(m) \rangle^2}{E - E_\psi} \right)
\]

(C8)

Next, we set \( E = E_\psi \) in the summation.

\[
K \ln \left( \frac{E_1 - E}{E_2 - E} \right) = \frac{1}{\Pi_{k=1}^{3P-6} \langle 0_k | \nu_k(n) \rangle^2} \left( e - E_\psi - \sum_{m=1}^{M} \frac{\Pi_{k=1}^{3P-6} \langle 0_k | \nu_k(m) \rangle^2}{E_\psi - E_\psi} \right)
\]

(C9)

This approximation is justified because the new energy \( E \) is approximately equal to \( E_\psi \). Now the second term in the denominator of Eq. C9 is independent of \( E \), and we define a new function,

\[
T(n) = \sum_{m=1}^{M} \frac{\Pi_{k=1}^{3P-6} \langle 0_k | \nu_k(m) \rangle^2}{E_\psi - E_\psi}
\]

(C9)

which results in the following equation for the perturbed energy \( E \):

\[
K \ln \left( \frac{E_1 - E}{E_2 - E} \right) = \frac{1}{\Pi_{k=1}^{3P-6} \langle 0_k | \nu_k(n) \rangle^2} \left( e - E_\psi - T(n) \right)
\]

(C10)

One additional simplification is required, because terms in the summation for \( T(n) \) are discontinuous whenever \( E_\psi = E_\psi \), as in the case of a degenerate state. By recognizing that the function \( \frac{1}{(E_\psi - E_\psi)} \) in our theory results from the approximations we have made, it seems justifiable to make a simple adjustment to the equation which eliminates the nonphysical divergence while retaining the essential shape of the function. Such an approach is similar to the phenomenological lifetime term typically added as an imaginary component of the energy in...
calculations of transition rates, or the imaginary term in the denominator of a Greens function. Here, we use a mathematical expression which approximates \( \frac{1}{(E_{\phi_n} - E_{\phi_m})} \), yet without the singularity, as shown in Eq. C11.

\[
T'(n) = \sum_{m=1}^{M} \left\{ \prod_{k=1}^{3p-6} \left| \langle 0_k | \nu_k (n) \rangle \right|^2 \left| e^{\alpha |E_{\phi_n} - E_{\phi_m}|} \right| \text{sgn}(E_{\phi_n} - E_{\phi_m}) \right\}
\]

(C11)

Fig. C1. Plot of \( \frac{1}{(E_{\phi_n} - E_{\phi_m})} \) (in black) and \( e^{\alpha |E_{\phi_n} - E_{\phi_m}|} \text{sgn}(E_{\phi_n} - E_{\phi_m}) \) (in red), for \( E_{\phi_n} = 0.5 \) and \( \alpha = -100 \), in arbitrary units of energy and inverse energy respectively.

Fig. C1 shows a plot of \( \frac{1}{(E_{\phi_n} - E_{\phi_m})} \) in comparison to \( e^{\alpha |E_{\phi_n} - E_{\phi_m}|} \text{sgn}(E_{\phi_n} - E_{\phi_m}) \).

The parameter \( \alpha < 0 \) is chosen as a function of the specific problem such that \( \frac{1}{(E_{\phi} - E_{\phi_m})} \) is best approximated in the range of interest.