

1 Reaction Rate Derivation for Unimolecular Plasmonic Systems

This uses the formalism from the following paper: <https://arxiv.org/pdf/2205.04755> and here: [link](#)

Eventual data comparison: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC9642349/pdf/NA-004-D2NA00486K.pdf>

and <https://arxiv.org/pdf/2205.04755>

<https://pubs.acs.org/doi/10.1021/acs.jpcc.6b02314>

1.1 Hamiltonian with Plasmon-Molecule Interaction

The system Hamiltonian, incorporating the interaction between molecules and plasmons, is given by: (This is FOR N MOLECULES, I am first calculating for the single molecule case)

$$H_S = H_{mol} + H_{pl} + H_{int} \quad (1)$$

$$H_{mol} = \sum_{n=1}^{N_m} \left[\sum_{a_n} E_{na} |a_n\rangle \langle a_n| + \sum_{a_n \neq b_n} V_{a_n b_n} |a_n\rangle \langle b_n| \right] \quad (2)$$

$$H_{pl} = \sum_k \hbar \omega_{pl,k} b_k^\dagger b_k \quad (3)$$

$$H_{int} = - \sum_{nI} \left(\vec{\mu}_n \cdot \vec{g}_{n,k} b_k + \vec{\mu}_n \cdot \vec{g}_{n,k}^* b_k^\dagger \right) \quad (4)$$

$$\begin{aligned} \hat{E}_{pl} &\propto \sum_I \left(\vec{g}_I b_I + \vec{g}_I^* b_I^\dagger \right) \\ \Rightarrow H_{int} &\propto -\vec{\mu} \cdot \hat{E}_{pl} \propto - \sum_I \left(\vec{\mu} \cdot \vec{g}_I b_I + \vec{\mu} \cdot \vec{g}_I^* b_I^\dagger \right) \\ H_{int}^{ij} &= \begin{cases} \mu_{S_i S_j} \cdot \mathbf{E}_{pl,0} \sqrt{n+1} & \text{if } m = n+1, \text{ mdir} = \text{ndir} \\ \mu_{S_i S_j} \cdot \mathbf{E}_{pl,0} \sqrt{n} & \text{if } m = n-1, \text{ mdir} = \text{ndir} \text{ Or for many modes :} \\ 0 & \text{otherwise} \end{cases} \\ H_{int}^{ij,k} &= \begin{cases} \mu_{S_i S_j} \cdot \mathbf{E}_{pl,k} \sqrt{n+1} & \text{if } m = n+1, \text{ mdir} = \text{ndir} \\ \mu_{S_i S_j} \cdot \mathbf{E}_{pl,k} \sqrt{n} & \text{if } m = n-1, \text{ mdir} = \text{ndir} \\ 0 & \text{otherwise} \end{cases} \end{aligned} \quad (5)$$

where $h_{S_i S_j}$ is a projection operator onto the product state $|S_i\rangle$, constructed using the Heaviside step function $\theta(x)$:

$$\begin{aligned} h_{S_i S_j} &= \sum_{n, n_{dir}} \theta \left(\left(\frac{\text{basis.index}(S_i, n, n_{dir})}{\text{len}(\text{basis})} - x_{ds} \right) \right) |S_i, n, n_{dir}\rangle \langle S_j, n, n_{dir}| \\ \theta(x) &= \begin{cases} 0, & \text{if } x < 0 \\ 1, & \text{if } x \geq 0 \end{cases} \end{aligned}$$

This effectively captures the flux associated with transitions to the product state $|S_i\rangle$, with the Heaviside function acting as an implicit dividing surface.

1.2 Flux Correlation Function and Reaction Rate

The flux correlation function is:

$$\begin{aligned} C_f(t) &= \langle F(0)F(t) \rangle \\ F(t) &= e^{\frac{i}{\hbar}H_S t} F e^{-\frac{i}{\hbar}H_S t} \\ C_f(t) &= \langle F e^{\frac{i}{\hbar}H_S t} F e^{-\frac{i}{\hbar}H_S t} \rangle \\ C_f(t) &= \text{Tr} \left[\rho_0 F e^{\frac{i}{\hbar}H_S t} F e^{-\frac{i}{\hbar}H_S t} \right] \\ C_f(t) &= \text{Tr} \left[F e^{-\frac{i}{\hbar}H_S t} \rho_0 F e^{\frac{i}{\hbar}H_S t} \right] \end{aligned}$$

assuming ρ_0 can be written as $(1/Q_{eq}) * e^{-H_{mol}/2k_B T} (1-h)e^{-H_{mol}/2k_B T}$ due to thermodynamic conditions before the excitation occurs.

and the reaction rate constant is:

$$k_{S_i S_j} = \int_0^\infty dt C_f^{S_i S_j}(t)$$

The flux correlation function is:

$$C_f(t) = \langle F(0)F(t) \rangle = \text{Tr} \left[F e^{-\frac{i}{\hbar}H_S t} \rho_0 F e^{\frac{i}{\hbar}H_S t} \right] \quad (7)$$

assuming ρ_0 can be written as $(1/Q_{eq}) * e^{-H_{mol}/2k_B T} (1-h)e^{-H_{mol}/2k_B T}$ due to thermodynamic conditions before the excitation occurs. and the reaction rate constant is:

$$k = \int_0^\infty dt C_f(t) \quad (8)$$

Where Q_{eq} is $e^{-\frac{E_{S_0}}{k_b T}} + e^{-\frac{E_{S_1}}{k_b T}} + e^{-\frac{E_{S_2}}{k_b T}}$

1.3 Weak coupling attempt 1

Now to approach finding a tractable expression for $e^{-\frac{it}{\hbar}H_S}$ and $e^{\frac{it}{\hbar}H_S}$

$$\begin{aligned} e^{-\frac{it}{\hbar}H_S} &= e^{-\frac{it}{\hbar}(H_{mol}+H_p l + H_i n t)} \\ [H_{mol}, H_{pl}] &= 0, [H_{int}, H_{pl}] \neq 0 \\ H_0 &= H_p l + H_{mol} \\ \implies e^{-\frac{it}{\hbar}(H_0+H_{int})} &\approx e^{-\frac{it}{\hbar}(H_0)} e^{-\frac{it}{\hbar}(H_{int})} e^{\frac{it}{2\hbar}[H_0, H_{int}]} \\ \implies e^{\frac{it}{\hbar}(H_0+H_{int})} &\approx e^{\frac{it}{\hbar}(H_0)} e^{\frac{it}{\hbar}(H_{int})} e^{-\frac{it}{2\hbar}[H_0, H_{int}]} \end{aligned}$$

Now

$$\begin{aligned}
C_f(t) &\approx \text{Tr} \left[F e^{-\frac{i}{\hbar} H_{pl} t} e^{-\frac{i}{\hbar} H_{mol} t} e^{-\frac{i}{\hbar} H_{int} t} e^{\frac{i}{\hbar} \frac{\beta}{2} [H_0, H_{int}]} \rho_0 F e^{\frac{i}{\hbar} H_{pl} t} e^{\frac{i}{\hbar} H_{mol} t} e^{\frac{i}{\hbar} H_{int} t} e^{-\frac{i}{\hbar} \frac{\beta}{2} [H_0, H_{int}]} \right] \\
C_f(t) &\approx \text{Tr} \left[F e^{-\frac{i}{\hbar} H_{pl} t} e^{-\frac{i}{\hbar} H_{mol} t} e^{-\frac{i}{\hbar} H_{int} t} e^{\frac{i}{2\hbar} [H_0, H_{int}]} \right. \\
&\quad \times \frac{1}{Q_{eq}} * (|S_0\rangle\langle S_0| e^{-E_{S_0}/k_B T} + |S_1\rangle\langle S_1| e^{-E_{S_1}/k_B T} + |S_2\rangle\langle S_2| e^{-E_{S_2}/k_B T}) \\
&\quad \left. \times F e^{\frac{i}{\hbar} H_{pl} t} e^{\frac{i}{\hbar} H_{mol} t} e^{\frac{i}{\hbar} H_{int} t} e^{-\frac{i}{2\hbar} [H_0, H_{int}]} \right]
\end{aligned}$$

Assume a largely homogenous field in the cavity:

$$\begin{aligned}
F_{S_1 S_0} &= \frac{i}{\hbar} (-\mu_{S_1 S_0} \cdot \mathbf{E}_{pl,0}) (|S_1\rangle\langle S_0| - |S_0\rangle\langle S_1|) \\
F_{S_2 S_0} &= \frac{i}{\hbar} (-\mu_{S_2 S_0} \cdot \mathbf{E}_{pl,0}) (|S_2\rangle\langle S_0| - |S_0\rangle\langle S_2|) \\
F_{S_2 S_1} &= \frac{i}{\hbar} (-\mu_{S_2 S_1} \cdot \mathbf{E}_{pl,0}) (|S_2\rangle\langle S_1| - |S_1\rangle\langle S_2|) \\
\implies \langle S_m, n | F_{S_i S_j} | S_n, n \rangle &= \frac{i}{\hbar} (-\mu_{S_i S_j} \cdot \mathbf{E}_{pl,0}) (\delta_{mi} \delta_{nj} - \delta_{mj} \delta_{ni}) \\
e^{-\frac{i}{\hbar} H_0 t} &= e^{-\frac{i}{\hbar} H_{pl} t} e^{-\frac{i}{\hbar} H_{mol} t} \\
C_f(t) &\approx \frac{1}{Q_{eq}} \sum_{S_n} \text{Tr} \left[F e^{-\frac{i}{\hbar} H_{pl} t} e^{-\frac{i}{\hbar} H_{int} t} e^{\frac{i}{2\hbar} [H_0, H_{int}]} t |S_n\rangle\langle S_n| e^{-E_{S_n}/k_B T} F e^{\frac{i}{\hbar} H_{pl} t} e^{\frac{i}{2\hbar} H_{int} t} e^{-\frac{i}{\hbar} [H_0, H_{int}]} t \right] \\
&\approx \frac{1}{Q_{eq}} \sum_{S_n} \sum_n e^{-n\hbar\omega_{pl}/k_B T} e^{-i(E_{S_n} - E_{S_0})t/\hbar} \\
&\quad \times \text{Tr} \left[F e^{-\frac{i}{\hbar} H_{int} t} e^{\frac{i}{2\hbar} [H_0, H_{int}]} t |S_n, n\rangle\langle S_n, n| e^{-E_{S_n}/k_B T} F e^{\frac{i}{2\hbar} H_{int} t} e^{-\frac{i}{\hbar} [H_0, H_{int}]} t \right]
\end{aligned}$$

Therefore:

The flux correlation functions for the relevant transitions are:

$$\begin{aligned}
C_f^{S_1 S_0}(t) &\approx \frac{1}{Q_{eq}} \sum_{S_n} \sum_n e^{-n\hbar\omega_{pl}/k_B T} e^{-i(E_{S_n} - E_{S_0})t/\hbar} * T_{S_1 S_0}^{S_n, n}(t) \\
C_f^{S_2 S_0}(t) &\approx \frac{1}{Q_{eq}} \sum_{S_n} \sum_n e^{-n\hbar\omega_{pl}/k_B T} e^{-i(E_{S_n} - E_{S_0})t/\hbar} * T_{S_2 S_0}^{S_n, n}(t)
\end{aligned}$$

where the simplified trace terms are:

$$\begin{aligned}
T_{S_1 S_0}^{S_0, n}(t) &= \text{Tr} \left[F_{S_1 S_0} e^{-\frac{i}{\hbar} H_{int} t} e^{\frac{i}{2\hbar} [H_0, H_{int}]} t |S_0, n\rangle\langle S_0| e^{-E_{S_0}/k_B T} F_{S_1 S_0} e^{\frac{i}{2\hbar} H_{int} t} e^{-\frac{i}{\hbar} [H_0, H_{int}]} t \right] \\
T_{S_1 S_0}^{S_1, n}(t) &= \text{Tr} \left[F_{S_1 S_0} e^{-\frac{i}{\hbar} H_{int} t} e^{\frac{i}{2\hbar} [H_0, H_{int}]} t |S_1, n\rangle\langle S_1| e^{-E_{S_1}/k_B T} F_{S_1 S_0} e^{\frac{i}{2\hbar} H_{int} t} e^{-\frac{i}{\hbar} [H_0, H_{int}]} t \right] \\
T_{S_2 S_0}^{S_0, n}(t) &= \text{Tr} \left[F_{S_2 S_0} e^{-\frac{i}{\hbar} H_{int} t} e^{\frac{i}{2\hbar} [H_0, H_{int}]} t |S_0, n\rangle\langle S_0| e^{-E_{S_0}/k_B T} F_{S_2 S_0} e^{\frac{i}{2\hbar} H_{int} t} e^{-\frac{i}{\hbar} [H_0, H_{int}]} t \right] \\
T_{S_2 S_0}^{S_2, n}(t) &= \text{Tr} \left[F_{S_2 S_0} e^{-\frac{i}{\hbar} H_{int} t} e^{\frac{i}{2\hbar} [H_0, H_{int}]} t |S_2, n\rangle\langle S_2| e^{-E_{S_2}/k_B T} F_{S_2 S_0} e^{\frac{i}{2\hbar} H_{int} t} e^{-\frac{i}{\hbar} [H_0, H_{int}]} t \right]
\end{aligned}$$

And in the strong-coupling regime (my claim is that I'll be able to include a lot of chebyshev terms, since it has exponentially decreasing error it should quickly give a good global approximation given that I have found the eigenvalues of the Hamiltonian at hand:

$$\begin{aligned}
e^{-\frac{i}{\hbar}H_S t} &\approx \sum_{n=0}^N c_n T_n \left(-\frac{i}{\hbar} H'_S t \right) \\
H'_S &= \frac{H'_S - E_{mid}}{\Delta E} \\
E_{mid} &= \frac{E_{max} + E_{min}}{2} \\
\Delta E &= \frac{E_{max} - E_{min}}{2} \\
c_n &= \begin{cases} \frac{1}{\pi} \int_{-1}^1 \frac{e^{in \arccos(x)}}{\sqrt{1-x^2}} dx, & \text{for } n = 0 \\ \frac{2}{\pi} \int_{-1}^1 \frac{e^{in \arccos(x)}}{\sqrt{1-x^2}} dx, & \text{for } n > 0 \end{cases} \\
T_0(x) &= 1 \\
T_1(x) &= x \\
T_{n+1}(x) &= 2xT_n(x) - T_{n-1}(x) \\
C_f(t) &\approx \text{Tr} \left[F \left(\sum_{n=0}^N c_n T_n \left(-\frac{i}{\hbar} H'_S t \right) \right) \rho_0 F \left(\sum_{m=0}^N c_m T_m \left(\frac{i}{\hbar} H'_S t \right) \right) \right] \\
k &= \int_0^\infty C_f(t) dt
\end{aligned}$$

Actually, after implementing the chebyshev expansion, I saw that it wasn't converging very well, so now I am working on

Recall that these systems are naturally dissipative.. therefore I MAY need to properly address the following

$$H_S = H_{\text{mol}} + H_{\text{pl}} + H_{\text{int}} - i \frac{\Gamma}{2} \quad (9)$$

where Γ is a diagonal matrix representing the relaxation rates. The diagonal elements are given by:

$$\Gamma_{nn} = \begin{cases} 0 & \text{for } n = S_0 \text{ (ground state)} \\ \gamma_{S_1}^{\text{IC}} + \gamma_{S_1}^{\text{FL}} & \text{for } n = S_1 \\ \gamma_{S_2}^{\text{IC}} & \text{for } n = S_2 \end{cases} \quad (10)$$

Where IC denotes internal conversion clearly, with $\gamma_{S_1}^{\text{IC}} \mapsto 10^{11}$, $\gamma_{S_1}^{\text{FL}} \mapsto 10^8$, and $\gamma_{S_2}^{\text{IC}} \mapsto 10^{13}$ that uses Krylov subspaces instead.

2 Model Predictions

3 Gathering Azobenzene Data for Calculations

<https://opg.optica.org/josab/fulltext.cfm?uri=josab-15-11-2721id=35596>

$$\rho_{trans}(E) = 0.23\delta(E - 5.72) + 0.027\delta(E - 5.68) + 0.046\delta(E - 5.59) + 0.071\delta(E - 5.44) \\ + 0.029\delta(E - 4.48) + 1.16\delta(E - 3.41) + 0.049\delta(E - 2.75)$$

$$\rho_{cis}(E) = 0.14\delta(E - 5.66) + 0.051\delta(E - 5.56) + 0.04\delta(E - 4.7) + 0.038\delta(E - 4.66) + 0.029\delta(E - 4.62) + \\ 0.024\delta(E - 4.57) + 0.29\delta(E - 4.53) + 0.3\delta(E - 3.78) + 0.057\delta(E - 2.79) + 0.041\delta(E - 2.76)$$

From mostly here: <https://core.ac.uk/download/pdf/14696698.pdf>

here: <https://pubs.acs.org/doi/epdf/10.1021/nl403576c>

and here: <https://chemistry-europe.onlinelibrary.wiley.com/doi/full/10.1002/chem.202200972>

3.1 Dipole Moments (μ):

- **Ground State (trans-azobenzene):**

- Magnitude: ≈ 0 Debye
- Direction: No net dipole moment (symmetrical)
- Electric Field Interaction: Negligible
- $\mu_{trans} = \mathbf{0}$

- **Excited State (cis-azobenzene):**

- Magnitude: ≈ 3 Debye
- Direction: Along N=N bond axis, positive towards N atoms
- Electric Field Interaction: Strong, dependent on field orientation
- $\mu_{cis} \approx 1.00 \times 10^{-29} \text{ C} \cdot \text{m} \hat{\mathbf{x}}$

3.2 Transition Dipole Moments (μ_{mn}):

- **S0 \rightarrow S1 ($n\pi^*$):**

- Magnitude: $\approx 0.71 ea_0$
- Direction: Perpendicular to molecular plane
- Electric Field Interaction: Induced by field perpendicular to plane
- $0.71e \cdot a_0 \cdot (1.60218 \cdot 10^{-19} \text{ C} / e) \cdot (5.29177 \cdot 10^{-11} \text{ m} / a_0) \cdot 6.02 \cdot 10^{-30} \text{ C} \cdot \text{m} \\ m$
- $\mu_{S0 \rightarrow S1} \approx 6.02 \times 10^{-30} \text{ C} \cdot \text{m} \hat{\mathbf{z}}$

- **S0 \rightarrow S2 ($\pi\pi^*$):**

- Magnitude: $\approx 2.88 ea_0$
- Direction: In-plane, along long axis of conjugated system

- Electric Field Interaction: Induced by field parallel to long axis
- $2.88e \cdot a_0 \cdot (1.60218 \cdot 10^{-19} C / e) \cdot (5.29177 \cdot 10^{-11} m / a_0) 2.44 \cdot 10^{-29} C \cdot m$
- $\mu_{S_0 \rightarrow S_2} \approx 2.44 \times 10^{-29} \text{ C} \cdot \text{m} \hat{\mathbf{x}}$

3.3 Electric Field (E):

- **Plasmonic Fields:** Highly localized, variable in magnitude/direction
- **E-Field :** $E \sim 10^7 \text{ V/m}$