Supporting Information: Floquet Analysis for Vibronically Modulated Electron Tunneling

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Pathway Analysis

The individual rates appearing in Eq. (23) of the main text may be decomposed into vibronic pathways as indicated in Figure 4.\textsuperscript{1–3} The presence of IR driving introduces new vibronic pathways to the final states. IR driving allows vibrational transitions without vibronic interactions, i.e. by exciting the oscillator.

The use of Green’s functions to determine rate channel contributions through Eqs. (30)-(34) is elaborated in Figure 4 (main text). In Figure 4, the system begins in state $|\psi_D 1\rangle$, the electron deexcites the oscillator as it passes through the upper bridge ($|\psi_U 1\rangle \Rightarrow |\psi_U 0\rangle$), and the electron finally reaches the acceptor which is $\hbar \omega_0$ above the donor energy. For the case $\alpha_A = \alpha_D + \hbar \omega_0$ in Figure 3, the mechanism shown in Figure 0.1 dominates the ET rate, and is given by Eq. (0.1).

Figure 0.1: Physical mechanism for $k_{D1 \rightarrow A0}$ channel, i.e. lowest order pathway to reach A0 from D1. Terms in $k_{GR}$ appear in blue.

$$k_{GR}^{D1 \rightarrow A0} \approx \frac{2\pi}{\hbar} \left| \frac{t_{DU}}{[\alpha_D + 3\hbar \omega_0/2] - [\alpha_U + 3\hbar \omega_0/2]} \gamma \frac{t_{UA}}{[\alpha_D + 3\hbar \omega_0/2] - [\alpha_U + \hbar \omega_0/2]} \right|^2 \times (\pi \frac{\hbar}{\gamma})^{-1} \quad (0.1)$$

Classical Kinetics Analog

By considering only two paths, we can build a kinetic model of the system in question. In the limit of fast relaxation on the acceptor ($t_r << \hbar/|T_{DA}|$), this kinetic model provides the same ET rate
behavior as the full Floquet treatment and validates the use of Eqs. (21) - (27) of the main text. The kinetic model (Figure 0.2) is:

$$
[DA]_1 \xrightleftharpoons[k^{-1}_{ET}]{k^1_{ET}} [D^+A^-]_1 \rightarrow [DA*]_0 \xrightarrow[k^0_{ET,B}]{k^0_{ET}} [D^+A^-]_0 \xrightarrow[k^0_{ET,B}]{k^0_{ET}} [DA]_0,
$$

(0.2)

$$
\frac{d[DA*]_0}{dt} = -k^0_{ET}[DA*]_0 - k^1_{ET}[DA*]_0 + k^0_{ET,B}[D^+A^-]_0 + k^1_{ET,B}[D^+A^-]_1,
$$

(0.3)

$$
\frac{d[D^+A^-]_0}{dt} = k^0_{ET}[DA*]_0 - k^0_{ET,B}[D^+A^-]_0 - k_R[D^+A^-]_0,
$$

(0.4)

$$
\frac{d[D^+A^-]_1}{dt} = k^1_{ET}[DA*]_0 - k^1_{ET,B}[D^+A^-]_1 - k_R[D^+A^-]_1.
$$

(0.5)

In Eq. (0.2) and Eq. (0.5), the subscript 0(1) indicates an oscillator in the ground (first excited) state. $k^0_{ET,B}$ is a back ET rate for channel n. $[DA*]_0$ is the concentration of the excited DBA system that is capable of ET, $[D^+A^-]_n$ is the concentration of the charge separated DBA system in oscillator state n, and $[DA]$ is the concentration of relaxed DBA system that can no longer undergo ET.

Setting the initial conditions $[DA*]_0 = 1$ and all other concentrations equal to 0, the system of equations was solved to find the time-dependent species concentrations. In analogy with Eqs (21)-(23) of the main text, ET probabilities through separate channels and average lifetimes were calculated by setting all $k_{ET}$ rates to 0 in Eq. (0.4) and Eq. (0.5), i.e., for $k_R >> k^1_{ET}, k^0_{ET,B}, k^1_{ET,B}, k^0_{ET,B}$, and identifying concentrations with probabilities.
\[ P(t; t_0)_{Di \rightarrow Af} \rightarrow [D^+A^-]_f(t), \quad (0.6) \]

\[ k_{Di \rightarrow Af} \rightarrow \frac{\int_{t_0}^{\infty} t[D^+A^-]_f(t) dt}{\sum_f \int_{t_0}^{\infty} t[D^+A^-]_f(t) dt} \approx k_{ET}^f \left( 1 - \frac{k_{ET}^{0}k_{ET,B}^{0} + k_{ET}^{1}k_{ET,B}^{1}}{k_{ET}^{0} + k_{ET}^{1}} \right). \quad (0.7) \]

Here \( f \) is 1 or 0, depending on which channel is being considered. In the limit \( k_R \gg k_{ET}^{1}, k_{ET}^{0} \), Eq. (0.7) recovers the rate \( k_{ET}^f \), as expected.

**Quantum Analog**

A simple quantum analog of the classical kinetic system may also be constructed and used to calculate ET rates (Figure 0.3).

![Figure 0.3: Pathway depiction of the quantum analog to the kinetic model.](image)

The pathways shown in Figure 0.3 may be further developed by constructing a Hamiltonian representation of the same system as shown in Eq. (0.8). Identifying the diagonal energies with \( |\psi_D 0\rangle, |\psi_A 0\rangle \) and \( |\psi_A 1\rangle \) respectively, we may build the quantum analog of the kinetic scheme just considered. \( T_{D0,A0} \) and \( T_{D0,A1} \) may be assumed to be perturbatively small compared to the energy differences between vibronic states and \( \hbar / t_r \). The effective coupling between initial state \( |\psi_D 0\rangle \) and final states \( |\psi_A 0\rangle \) and \( |\psi_A 1\rangle \) are \( T_{D0,A0} \) and \( T_{D0,A1} \), respectively.
\[ H = \begin{bmatrix} \alpha_D + \hbar \omega_0 / 2 & T_{D0,A0} & T_{D0,A1} \\ T_{D0,A0} & \alpha_A + \hbar \omega_0 / 2 - i\hbar / t_r & 0 \\ T_{D0,A1} & 0 & \alpha_A + (3\hbar \omega_0 / 2) - i\hbar / t_r \end{bmatrix} \] (0.8)

A propagator and transition probabilities can be constructed from this Hamiltonian.

\[
P(t; t_0)_{D0\rightarrow Af} = \left| \langle \psi_A f | \exp(-i:\hat{H}t / \hbar) | \psi_D 0 \rangle \right|^2
\] (0.9)

Finally, a rate is determined in the limit of fast relaxation, i.e \( \hbar / t_r >> T_{D0,A0}, T_{Dl,A1} \)

\[
k_{D0\rightarrow Af} \rightarrow \frac{\int_0^\infty \left| \langle \psi_A f | \exp(-i:\hat{H}t / \hbar) | \psi_D 0 \rangle \right|^2 dt}{\sum_n \int_0^\infty t \left| \langle \psi_A n | \exp(-i:\hat{H}t / \hbar) | \psi_D 0 \rangle \right|^2 dt} \approx \frac{2\pi}{\hbar} T_{D0,Af}^2 \frac{\hbar / t_r}{\pi[\left( \hbar / t_r \right)^2 + \delta^2]} (0.10)
\]

In Eq. (0.10) \( \delta \) is the energy difference between the initial and final states. Eq. (0.10) recovers the familiar golden rule expression, Eq. (29) of the main text, including the form for the density of states \( \rho_{if} \).

**References**


Xiao D.; Skourtis, S. S.; Rubtsov, I.; Beratan, D. N. *Nano Lett.* **2009**, *9*, 1818-1823