

Supplementary Information

Surface Crossing and Energy Flow in Many-Dimensional Quantum systems

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A. Franck Condon factor for a displaced oscillator

The eigenstates for a shifted harmonic oscillator with Hamiltonian

$$\tilde{H}_s = (b^\dagger - \alpha)(b - \alpha)$$

Can be expressed in terms of the spatial displacement operator:

$$|\alpha; n\rangle = D(\alpha)|n\rangle$$

$$D(\alpha) = e^{\alpha(\hat{b}^\dagger - \hat{b})}$$

The $|\alpha; n\rangle$ can be expressed in terms of eigenstates of the unshifted harmonic oscillator $|n\rangle$:

$$|\alpha; n\rangle = \frac{1}{\sqrt{n!}} (\hat{b}^\dagger - \alpha)^n |\alpha; 0\rangle$$

$$|\alpha; 0\rangle = D(\alpha)|0\rangle = e^{-\alpha^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle$$

The Franck-Condon factor $\langle n' | \alpha; n \rangle$ can be expressed using associated Laguerre polynomials and has following expression⁵ (assuming $n \leq m$):

$$\langle n' | \alpha; n \rangle = \sqrt{\frac{n!}{n'!}} \alpha^{n'-n} e^{-\frac{1}{2}\alpha^2} L_n^{(n'-n)}(\alpha^2)$$

B. Numerical calculation of the quantum survival probability $P(t)$

To quantify energy delocalization, we computed the survival probability $P(t) = |\langle t=0|t\rangle|^2$ of initial zero order states $|t=0\rangle$ for small and large values of a and V_3 . The example in Figure S1a illustrates an initial state where surface crossing alone would not be sufficient to delocalize the state to $\sigma < 0.01$, but there is a sufficiently large value of a that allows for higher order vibrational couplings that lead to delocalization. In Figure S1b, the initial state will undergo some delocalization via electronic coupling alone, but this is further enhanced by increased higher order anharmonicity. In Figure S1c, we see that increasing cubic coupling is insufficient to delocalize the states below $\sigma = 0.01$ (on the time scale shown), whereas in Figure S1d, the stronger cubic coupling is enough to bring σ well below 0.01. Figure S4 shows the resulting effect on the dilution factor.

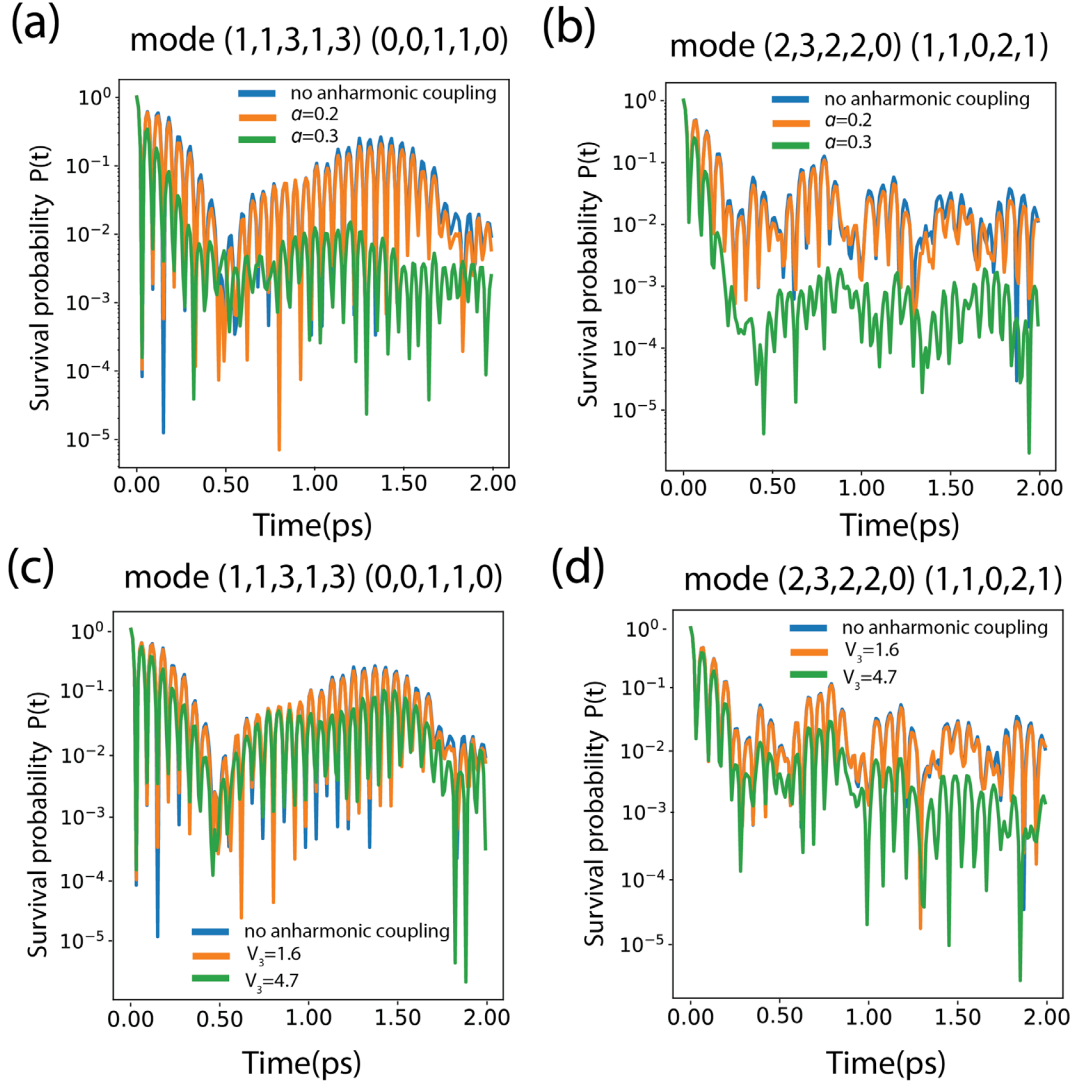


Figure S1. Dependence of vibrational energy flow on the scaling parameter a and the anharmonic coupling strength V_3 ($V_t = 363 \text{ cm}^{-1}$). Left: state $|1,1,3,1,3\rangle |0,0,1,1,0\rangle$ ($E = 8705 \text{ cm}^{-1}$), which was localized with only $V_t \neq 0$ and no vibrational couplings in Figure 3. Right: state $|2,3,2,2,0\rangle |1,1,0,2,1\rangle$ ($E = 11894 \text{ cm}^{-1}$), which was already delocalized with only $V_t \neq 0$ and no vibrational couplings in Figure 3. (a, b) Blue curve: $V_3=0$. Orange ($a=0.2$) and green ($a=0.3$) curves, $V_3/a^3=300$. The smaller scaling factor $a=0.2$ does not assist the non-adiabatic energy flow, whereas stronger higher order couplings do. (c, d) Blue curve: $V_3=0$. Orange ($V_3 \approx 1.6 \text{ cm}^{-1}$) and green ($V_3 \approx 4.7 \text{ cm}^{-1}$) curves, $a=0.25$. The smaller cubic anharmonicity does not assist the non-adiabatic energy flow, whereas stronger cubic anharmonicity does.

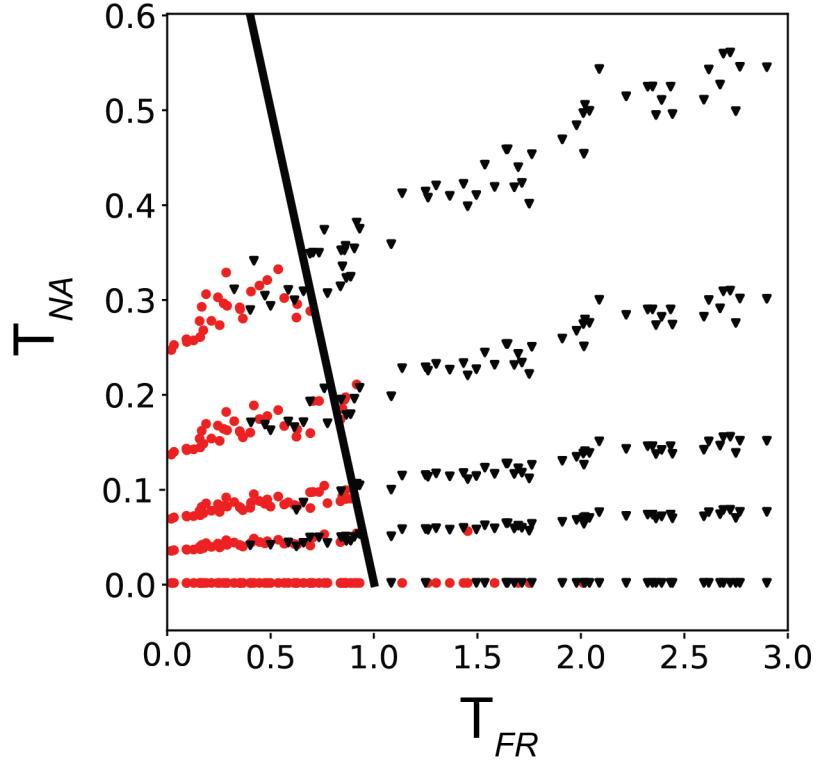


Fig S2. Scatter plot for the dilution factors on the plane of T_{FR} vs. T_{NA} when one monomer has no vibrational excitation, the typical initial condition at low temperature. In this computation, we keep the vibrational couplings the same as in the natural system and vary the nonadiabatic coupling V_t with values [0, 50, 100, 200, 363]. The criterion $\sigma_c = 0.08$ we choose to classify localized and extended states is the square root of the minimum dilution factor on the single surface in our simulation. Here, the red dotted data represents states with dilution factor $\sigma > \sigma_c$, and the black inverted triangle data represents states with dilution factor $\sigma < \sigma_c$. The solid black line is the theoretical prediction $T_{FR} = 1 - T_{NA}$.

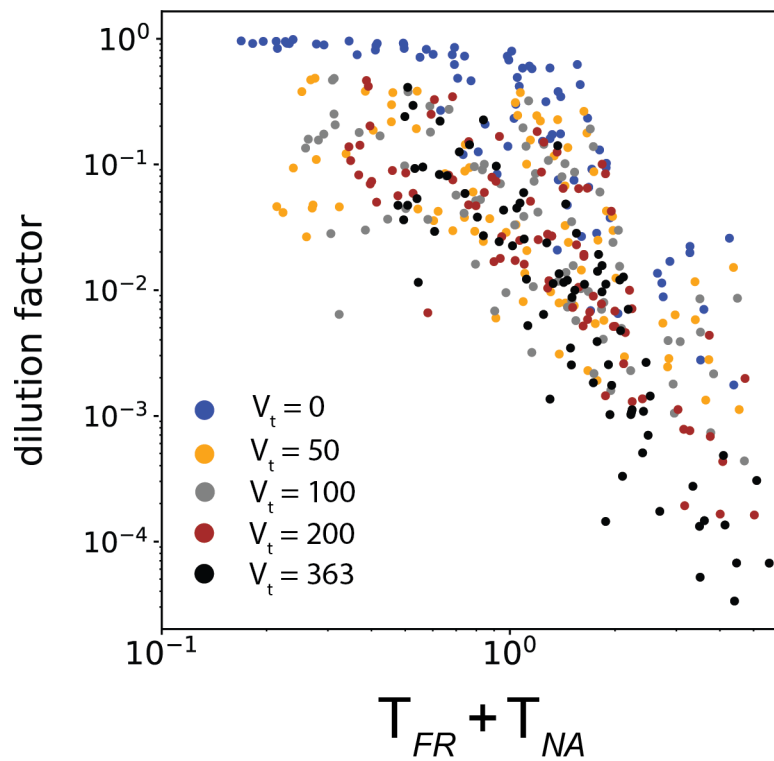


Fig S3. Dilution factor σ vs. $T_{FR} + T_{NA}$ for 80 vibrational states in the two surface systems. We evaluate σ for five values of the nonadiabatic coupling V_t value: 0, 50, 100, 200, and 363 cm^{-1} .

C. Calculation of T_{FR} and T_{NA}

In this section we discuss the procedure to compute the anharmonic transition factor T_{FR} and the nonadiabatic transition factor T_{NA} .

The way to compute T_{FR} is discussed in section 2.3.2 in ref. (37) in the main text, and in section IV.A. of ref. (19) in the main text. This is briefly recapped below. The anharmonic transition factor T_{FR} is:

$$T_{FR} = \sqrt{\frac{2\pi}{3}} \sum_m K_m \langle V_m \rangle D_m(E)$$

Here the number of states coupled to the initial state a distance m away is K_m , and the local density of states at the distance m is $D_m(E)$. The average anharmonic coupling strength is V_m . As already pointed out, the matrix elements coupling states in vibrational state space decrease exponentially with m , below we will include terms $m=3, 4$ to consider cubic and quartic coupling. In multi-dimensional quantum systems, when degrees of freedom N is large enough, we have following estimation (1, 2):

$$K_m = \frac{(2N)^m}{m!}$$

$$D_m \approx (\pi p^{1/2} \omega_{rms})^{-1}$$

$$\langle V_m \rangle \approx V_3 a^m M^{m/2}$$

$$M \approx \frac{E}{N \omega_{rms}}$$

Here ω_{rms} is the root-mean-square of the vibrational frequencies, M is the average number of excited vibrational quanta per mode, V_3 is the cubic Fermi resonance coupling strength and a is the scaling factor for distance in state space, usually in the range of 0.1 to 0.3 for organic molecules.

Below we show how to estimate nonadiabatic transition factor $T_{NA}(E)$:

$$T_{NA}(E) = \sqrt{\frac{2\pi}{3}} K_t \langle V_t^{n',n} \rangle D_L^{NA}(E)$$

Here $V_t^{n',n}$ is nonadiabatic coupling between states n', n on two different surfaces, K_t is nonadiabatic connectivity and $D_L^{NA}(E)$ is the local density of states for nonadiabatic couplings.

We first consider the relation between $\langle V_t^{n',n} \rangle$, nonadiabatic connectivity K_t and Franck Condon factor $\langle n' | \boldsymbol{\alpha}; \mathbf{n} \rangle = \prod_i^N \langle n'_i | \alpha_i; n_i \rangle$. We have the following relations:

$$V_t^{n',n} = V_t \langle n' | \boldsymbol{\alpha}; \mathbf{n} \rangle = V_t \prod_i^N \langle n'_i | \alpha_i; n_i \rangle$$

$$\sum_{n'_i} |\langle n'_i | \alpha_i; n_i \rangle|^2 = 1$$

Assume there are K_i states coupled to initial states through nonadiabatic coupling with average Franck Condon factor $\overline{\langle n'_i | \alpha_i; n_i \rangle}$ along mode i and $K_t = \prod_i^N K_i$. Using normalization conditions for $\langle n'_i | \alpha_i; n_i \rangle$, we have following relation:

$$\langle n' | \boldsymbol{\alpha}; \mathbf{n} \rangle \approx \frac{1}{K_t^{1/2}}$$

We estimate K_t from the Franck Condon factor as:

$$K_t = \prod_i^N K_i$$

$$K_i = \frac{1}{\sum_{m_i=0}^{\infty} |\langle n'_i | \alpha_i; n_i \rangle|^4}$$

This is similar to the estimation of dilution factor for the wave function. Although $D_L^{NA}(E)$ is not the same as the anharmonic local density of states $D_Q(E)$, as long as the ground state energy

difference δE is not large enough to make two potential energy surfaces have very different vibrational coupling structure in the state space, $D_L^{NA}(E)$ can be approximated with a similar formula:

$$D_L^{NA}(E) \approx (\pi\omega_{rms})^{-1}$$

Therefore, we have following estimation for T_{NA} ,

$$\begin{aligned} T_{NA}(E) &= \sqrt{\frac{2\pi}{3}} K_t \langle V_t^{m,n} \rangle D_L^{NA}(E) \\ &\approx \sqrt{\frac{2\pi}{3}} (\pi\omega_{rms})^{-1} V_t (K_t)^{1/2} \end{aligned}$$

To show the validity of our estimates for T_{FR} and T_{NA} , we compare them with the number of locally coupled states, $N_{loc,FR}$ and $N_{loc,NA}$. The anharmonic locally coupled states number is defined as in ref. (13) of the main text. $N_{loc,FR}(i) = \sum_j \frac{1}{1+(\Delta E_{ij}/V_{ij})^2}$ and $N_{loc,NA}$ is defined similarly for the nonadiabatic coupling. $N_{loc,FR}$, $N_{loc,NA}$ indicate the number of states effectively coupled to given vibrational states, either through anharmonic coupling ($N_{loc,FR}$) or nonadiabatic coupling ($N_{loc,NA}$). In ref. (13) of the main text, T_{FR} and $N_{loc,FR}$ are shown to positively correlated with each other.

In Figure S3, we show the correlation between the number of locally coupled states $N_{loc,FR}$, $N_{loc,NA}$ and the transition factor T_{FR}, T_{NA} . We see there is a good correlation between $N_{loc,FR}$ and T_{FR} , and $N_{loc,NA}$ and T_{NA} . $N_{loc,FR}$ and $N_{loc,NA}$ are larger than T_{FR}, T_{NA} because several states have to couple locally before a freely percolating network in state space is formed.

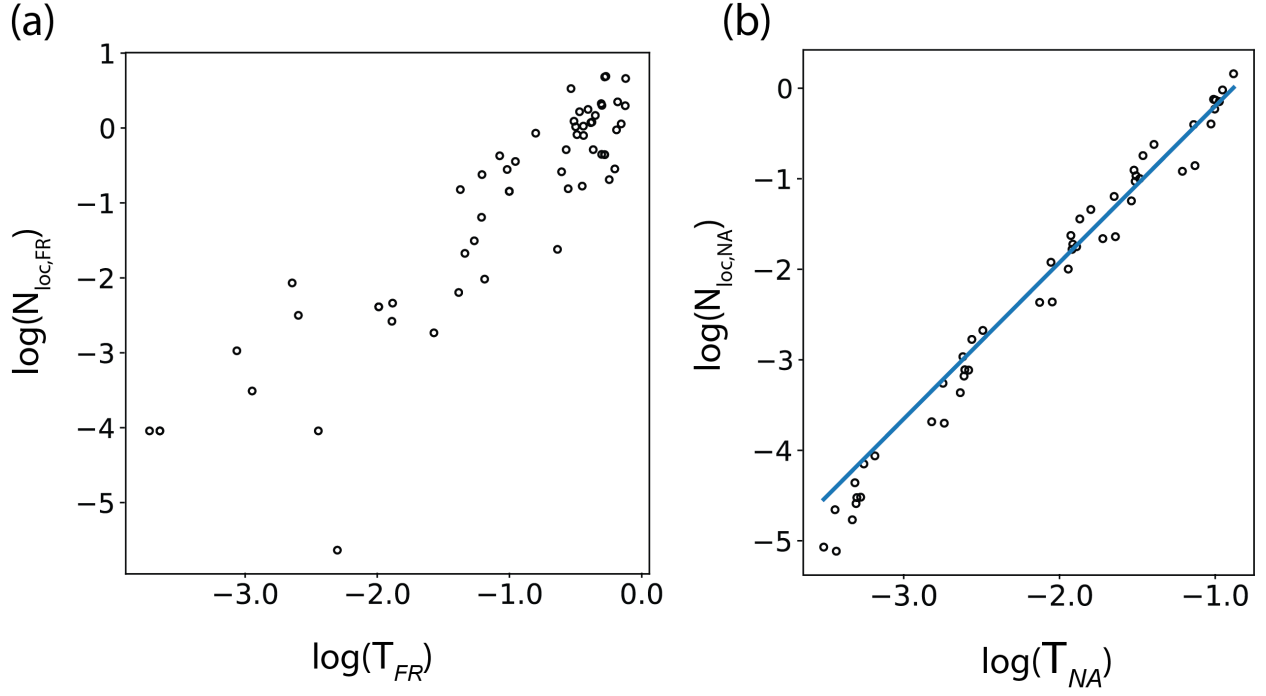


Figure S3. Correlation between locally coupled states number $N_{loc,FR}$, $N_{loc,NA}$ and transition factor T_{FR}, T_{NA} . (a) $\log(T_{FR})$ vs $\log(N_{loc,FR})$ for anharmonic couplings. (b) $\log(T_{NA})$ vs $\log(N_{loc,NA})$ for nonadiabatic couplings. Here for $\log(T_{NA}) > 2.5$, we have linear relation: $\log(N_{loc,NA}) = 1.73 \log(T_{NA}) + 1.53$ by fitting.