

## Supporting information to "Anharmonic vibrations in linear and two-dimensional electronic spectra"

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### 1 Perturbative analysis of wavefunction overlaps for anharmonic vibrations

We use the first order perturbation theory to approximate the level structure of the anharmonic surfaces. We assume the harmonic Hamiltonian  $H_j = \hbar\omega_j \hat{a}_j^\dagger \hat{a}_j$  to be the nonperturbative part of the Hamiltonian with eigenfunctions  $|\psi_n\rangle$ . The perturbation is the cubic term  $V_j^i = \hbar\tilde{\alpha}_j(\hat{a}_j^\dagger + \hat{a}_j)^3$  with  $\tilde{\alpha}_j = \sqrt{\hbar}(2/m\omega_j)^{3/2}\alpha_j$ , where  $j = g, e$ . For the cubic potential the energy corrections vanish to the first order and the frequencies in the spectrum are insignificantly changed

$$E_n^j = (n + 1/2)\omega_j + \frac{1}{\hbar} \langle \psi_n^j | V_j^i | \psi_n^j \rangle = (n + 1/2)\omega_j. \quad (1)$$

Therefore, most of the cubic term effects on the spectrum are due to corrected wavefunctions. Anharmonic vibrational wave functions  $|\Psi_n\rangle$  to first order in  $\alpha$  are obtained by setting

$$|\Psi_n^j\rangle = |\psi_n^j\rangle + \sum_{m \neq n} \frac{\langle \psi_n^j | V^i | \psi_m^j \rangle}{\hbar\omega_j(n-m)} |\psi_m^j\rangle, \quad (2)$$

Anharmonic wavefunctions are further expressed as (with notation  $|\psi_{n<0}\rangle = 0$ )

$$\begin{aligned} |\Psi_n^j\rangle = & |\psi_n^j\rangle + \frac{3\tilde{\alpha}_j n \sqrt{n}}{\omega_j} |\psi_{n-1}^j\rangle \\ & - \frac{3\tilde{\alpha}_j (n+1) \sqrt{n+1}}{\omega_j} |\psi_{n+1}^j\rangle \\ & - \frac{\tilde{\alpha}_j \sqrt{n+3} \sqrt{n+2} \sqrt{n+1}}{3\omega_j} |\psi_{n+3}^j\rangle \\ & + \frac{\tilde{\alpha}_j \sqrt{n-2} \sqrt{n-1} \sqrt{n}}{3\omega_j} |\psi_{n-3}^j\rangle. \end{aligned} \quad (3)$$

The overlap integrals between vibrational levels on electronic excited and ground states are defined as

$$I_{mn} = \int \Psi_m^{(e)*}(x) \Psi_n^{(g)}(x) dx. \quad (4)$$

Here, we are focusing on the two overlap integrals related to first peak of the vibronic progression in absorption and emission spectra given by

$$\begin{aligned} I_{01} &= \int \Psi_0^{(e)*}(x) \Psi_1^{(g)}(x) dx \\ I_{10} &= \int \Psi_1^{(e)*}(x) \Psi_0^{(g)}(x) dx. \end{aligned} \quad (5)$$

To that end we specify equation 3

$$\begin{aligned} |\Psi_0^e\rangle &= |\psi_0^e\rangle - \frac{3\tilde{\alpha}_e}{\omega_e} |\psi_1^e\rangle - \frac{\tilde{\alpha}_e \sqrt{6}}{3\omega_e} |\psi_3^e\rangle \\ |\Psi_1^e\rangle &= |\psi_1^e\rangle + \frac{3\tilde{\alpha}_e}{\omega_e} |\psi_0^e\rangle - \frac{6\sqrt{2}\tilde{\alpha}_e}{\omega_e} |\psi_2^e\rangle - \frac{\tilde{\alpha}_e \sqrt{24}}{3\omega_e} |\psi_4^e\rangle \\ |\Psi_0^g\rangle &= |\psi_0^g\rangle - \frac{3\tilde{\alpha}_g}{\omega_g} |\psi_1^g\rangle - \frac{\tilde{\alpha}_g \sqrt{6}}{3\omega_g} |\psi_3^g\rangle \\ |\Psi_1^g\rangle &= |\psi_1^g\rangle + \frac{3\tilde{\alpha}_g}{\omega_g} |\psi_0^g\rangle - \frac{6\sqrt{2}\tilde{\alpha}_g}{\omega_g} |\psi_2^g\rangle - \frac{\tilde{\alpha}_g \sqrt{24}}{3\omega_g} |\psi_4^g\rangle. \end{aligned} \quad (6)$$

Inserting Eq. (6) into Eq (5), the overlap integrals relevant for the  $0' \rightarrow 1''$  and  $1' \leftarrow 0''$  transitions are found. The overlap integrals  $\int \psi_m^{(e)*}(x) \psi_n^{(g)}(x) dx$  of harmonic system are well known<sup>1</sup>.

The general expressions can be largely simplified when the vibrational frequency is the same in the ground and excited states  $\omega_e = \omega_g = \omega$ . For instance, the harmonic  $e$  and  $g$  eigensystems are just shifted  $\psi_m^{(e)*}(x) = \psi_m^{(g)*}(x-d)$  and the overlaps (denoted as  $v_{mn}$  in the following) satisfies the symmetry rule

$$\int \psi_m^{(e)*}(x) \psi_n^{(g)}(x) dx = \int \psi_m^{(g)*}(x-d) \psi_n^{(g)}(x) dx \equiv v_{mn} = (-1)^{m+n} v_{nm}$$

grounding Eq. (7) of the main text. To the first order in  $\tilde{\alpha}_g$  or  $\tilde{\alpha}_e$  we get

$$I_{01} = v_{01} + \frac{3\tilde{\alpha}_g}{\omega} v_{00} - \frac{6\sqrt{2}\tilde{\alpha}_g}{\omega} v_{02} - \frac{\tilde{\alpha}_g \sqrt{24}}{3\omega} v_{04} - \frac{3\tilde{\alpha}_e}{\omega} v_{11} - \frac{\sqrt{6}\tilde{\alpha}_e}{3\omega} v_{31}, \quad (7)$$

$$I_{10} = -v_{01} + \frac{3\tilde{\alpha}_e}{\omega} v_{00} - \frac{6\sqrt{2}\tilde{\alpha}_e}{\omega} v_{02} - \frac{\tilde{\alpha}_e \sqrt{24}}{3\omega} v_{04} - \frac{3\tilde{\alpha}_g}{\omega} v_{11} - \frac{\sqrt{6}\tilde{\alpha}_g}{3\omega} v_{31}, \quad (8)$$

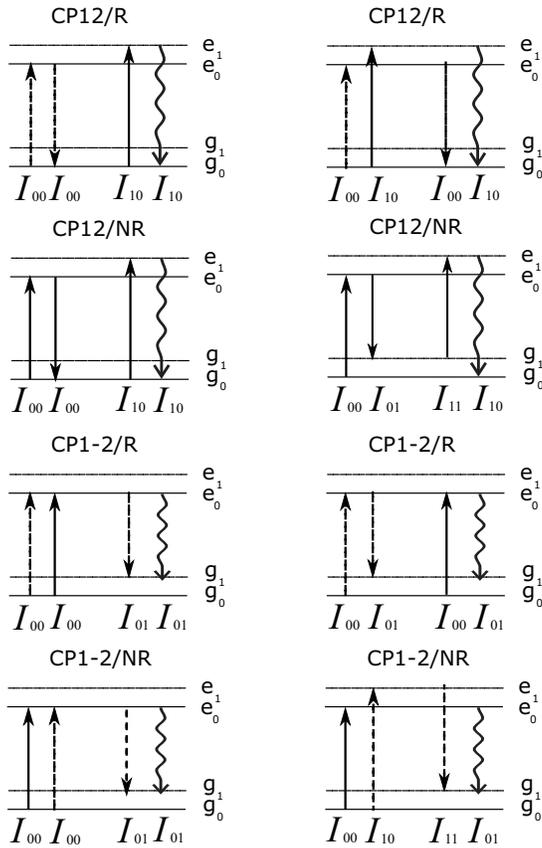
with harmonic FC-factors given by

$$\begin{aligned} v_{01} &= \tilde{d} v_{00}, & v_{02} &= \frac{\tilde{d}^2}{\sqrt{2}} v_{00}, & v_{04} &= \frac{\tilde{d}^4}{2\sqrt{6}} v_{00} \\ v_{11} &= (1 - \tilde{d}^2) v_{00}, & v_{31} &= \frac{-\tilde{d}^4}{\sqrt{6}} v_{00} + \frac{\tilde{d}^2 \sqrt{3}}{\sqrt{2}} v_{00}. \end{aligned} \quad (9)$$

where  $\tilde{d} \equiv d \sqrt{\frac{m\omega}{\hbar}}$ . Inserting Eq. (9) into Eqs. (7) and (8) and expanding to the first order we get for the ratio of interest

$$\frac{I_{01}}{I_{10}} = -1 + \frac{4(\tilde{\alpha}_e + \tilde{\alpha}_g)\tilde{d}}{\omega}$$

what base for Equation (10) of the main text.



**Figure 1** Diagrams for Liouville space pathways contributing to crosspeaks CP12 and CP1-2.  $g$  and  $e$  corresponds to ground and excited state, respectively, and indices denote the vibrational levels in each state.

## 2 Diagrammatic analysis of 2D signal

In this SI part we explain structure of 2D signals at CP12 and CP1-2 cross peaks as given in Eqs (15) and (16) of the main text. We used graphic representation following Ref. 2. Here, the pathways for rephasing (R) and non-rephasing (NR) signals are depicted into vibronic energy ladder diagrams with horizontal lines of vibronic levels. Vertical lines symbolize field-matter interactions: actions of dipole to bra  $\mu^l$  and ket  $\mu^r$  index of density matrix are shown as full and dashed arrows, respectively. The final tracing  $Tr\hat{\mu}$  for resulting signal are wavy arrows. Time of interaction is increased from left to right side of each diagram.

Fig 1 summarize all diagrams forming cross peaks CP12 and CP1-2 up to the second order in displacement  $\propto d^2$ . Thus, transition up to first vibrational excitation (dashed horizontal) are involved. Each vertical line is connected with Franck-Condon overlap factor for transition which represent.

The diagrams are attributed to peaks and signals as follows: First interaction define  $\Omega_1$ , frequency, last define  $\Omega_1$  frequency. Rephasing signals grows from diagrams with opposite coherence is the between the first two and last two interactions, i.e. start with bra interaction (dashed vertical). Applying these rules we have eight diagrams which represent the peaks of interest as in Eq. (15) and (16) of the main text.

## References

- [1] E. Hutchisson, *Phys. Rev.*, 1930, **36**, 410–420.
- [2] D. Lee and A. Albrecht, *Adv. Phys. Chem.*, 2007, **83**, 43–87.