

Optical absorption and emission spectra of molecular crystals

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May 6, 2019

1 Hamiltonian

We assume an infinite 3D crystal in which each molecule has one vibrational and one electronic degree of freedom. Molecules are labeled according to the unit cell they belong to (indicated by \mathbf{n}) and to their position inside the cell (indicated by α). Vibrationally each molecule \mathbf{n}, α has one effective configuration coordinate $Q_{\mathbf{n}, \alpha}$, and the vibrational potential is $V_{\mathbf{n}, \alpha}^{gr} = \hbar\Omega Q_{\mathbf{n}, \alpha}^2$ in the electronic ground state and $V_{\mathbf{n}, \alpha}^{ex} = \hbar\Omega (Q_{\mathbf{n}, \alpha} - \lambda)^2$ in the excited state. We include the interaction between all the molecules of the infinite crystal; the Hamiltonian reads

$$H^{FE} = H_{elec}^{FE} + H^{ph} + H^{FE-ph}, \quad (1)$$

with

$$H_{elec}^{FE} = \hbar\omega \sum_{\mathbf{n}, \alpha} a_{\mathbf{n}, \alpha}^\dagger a_{\mathbf{n}, \alpha} + \sum_{\substack{\mathbf{n}, \alpha, \mathbf{m}, \beta \\ \{\mathbf{n}, \alpha\} \neq \{\mathbf{m}, \beta\}}} J_{\alpha\beta}(\mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{m}}) a_{\mathbf{n}, \alpha}^\dagger a_{\mathbf{m}, \beta}, \quad (2)$$

$$H^{ph} = \hbar\Omega \sum_{\mathbf{n}, \alpha} b_{\mathbf{n}, \alpha}^\dagger b_{\mathbf{n}, \alpha}, \quad (3)$$

$$H^{FE-ph} = \hbar\Omega \sum_{\mathbf{n}, \alpha} a_{\mathbf{n}, \alpha}^\dagger a_{\mathbf{n}, \alpha} [-\lambda (b_{\mathbf{n}, \alpha}^\dagger + b_{\mathbf{n}, \alpha}) + \lambda^2]. \quad (4)$$

2 Multi particle basis functions

The multiparticle basis states are denoted by

$$\begin{aligned} |\mathbf{n}, \alpha; \underline{\nu}\rangle &\equiv \\ &\equiv |\mathbf{n}, \alpha\rangle |\cdots \nu_{\{-1,0,0\};1} \cdots \nu_{\{-1,0,0\};\sigma} \nu_{\mathbf{0};1} \cdots \tilde{\nu}_{\mathbf{0};\alpha} \cdots \nu_{\mathbf{0};\sigma} \nu_{\{1,0,0\};1} \cdots \nu_{\{1,0,0\};\sigma} \cdots\rangle \\ &\equiv a_{\mathbf{n}, \alpha}^\dagger |0^{el}\rangle \times \frac{1}{\sqrt{\nu_{\mathbf{0};\alpha}!}} \left(\tilde{b}_{\mathbf{n}, \alpha}^\dagger \right)^{\nu_{\mathbf{0};\alpha}} |\tilde{0}_{\mathbf{n}, \alpha}\rangle \times \prod_{(\delta\mathbf{n}, \beta) \neq (\mathbf{0}; \alpha)} \frac{1}{\sqrt{\nu_{\delta\mathbf{n}, \beta}!}} \left(b_{\mathbf{n}+\delta\mathbf{n}, \beta}^\dagger \right)^{\nu_{\delta\mathbf{n};\beta}} |0_{\mathbf{n}+\delta\mathbf{n}, \beta}\rangle, \end{aligned} \quad (5)$$

where $\mathbf{n} \equiv \{n_a, n_b, n_c\}$ denotes the crystal vector $\mathbf{r}_{\mathbf{n}} = n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c}$ (the notation $\mathbf{0} = \{0, 0, 0\}$ was also used); $\alpha = 1, \dots, \sigma$ labels the translationally non-equivalent molecules in the unit cell placed at $\mathbf{r}_{\mathbf{n}, \alpha} = \mathbf{r}_{\mathbf{n}} + \mathbf{r}_{\alpha}$, where \mathbf{r}_{α} denotes the position inside the cell. Operators $b_{\mathbf{n}, \alpha}^\dagger$ create a phonon excitation localized on a α molecule in its ground state, while $\tilde{b}_{\mathbf{n}, \alpha}^\dagger = b_{\mathbf{n}, \alpha}^\dagger - \lambda$ create a phonon excitation localized on a α molecule in its excited state.

With the restriction that phonon clouds be localized around the purely electronic excitation we Fourier transform the basis states and we need a single wave vector that describes the delocalization of the electronic excitation surrounded by the phonon cloud:

$$|\mathbf{k}, \alpha; \underline{\nu}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \exp(i\mathbf{k}\mathbf{r}_{\mathbf{n}}) |\mathbf{n}, \alpha; \underline{\nu}\rangle. \quad (6)$$

2.1 Matrix elements in real space

First we compute matrix elements in real space, i.e.

$$\langle \mathbf{n}, \alpha; \underline{\nu} | H^{FE} | \mathbf{m}, \beta; \underline{\mu} \rangle. \quad (7)$$

We separate the Hamiltonian into two terms and obtain respectively

$$\langle \mathbf{n}, \alpha; \underline{\nu} | H^{ph} + H^{FE-ph} | \mathbf{m}, \beta; \underline{\mu} \rangle = \hbar \Omega \delta_{\{\mathbf{n}, \alpha\}, \{\mathbf{m}, \beta\}} \delta_{\underline{\nu}, \underline{\mu}} \sum_{\delta \mathbf{n}, \gamma} \nu_{\delta \mathbf{n}, \gamma} \quad (8)$$

and

$$\langle \mathbf{n}, \alpha; \underline{\nu} | H_{elec}^{FE} | \mathbf{m}, \beta; \underline{\mu} \rangle = \hbar \omega \delta_{\{\mathbf{n}, \alpha\}, \{\mathbf{m}, \beta\}} \delta_{\underline{\nu}, \underline{\mu}} + \quad (9)$$

$$+ J_{\alpha\beta}(\delta \mathbf{r}) S \left(\begin{matrix} \nu_{\mathbf{0}, \alpha} \\ \mu_{\delta \mathbf{r}, \alpha} \end{matrix} \right) S \left(\begin{matrix} \mu_{\mathbf{0}, \beta} \\ \nu_{-\delta \mathbf{r}, \beta} \end{matrix} \right) \prod_{\{\mathbf{r}, \gamma\} \neq \{\mathbf{0}, \alpha\} \neq \{-\delta \mathbf{r}, \beta\}} \langle \nu_{\mathbf{r}, \gamma} | \mu_{\mathbf{r} + \delta \mathbf{r}, \gamma} \rangle, \quad (10)$$

where

$$\delta \mathbf{r} \equiv \mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{m}}, \quad (11)$$

$$J_{\alpha\alpha}(\mathbf{0}) = 0. \quad (12)$$

The symbol $\delta_{\underline{\nu}, \underline{\mu}}$ is different from 0 only if the two phonon clouds are identical and localized on the same molecule. Moreover we have

$$S \left(\begin{matrix} \mu \\ \nu \end{matrix} \right) \equiv \left\langle \frac{1}{\sqrt{\mu!}} (b^\dagger)^\mu 0 \left| \frac{1}{\sqrt{\nu!}} (\tilde{b}^\dagger)^\nu 0 \right. \right\rangle = \quad (13)$$

$$= \frac{\exp(-\lambda^2/2)}{\sqrt{\mu! \nu!}} \sum_{i=0}^{\min(\mu, \nu)} \frac{(-1)^{\nu-i} \lambda^{\mu+\nu-2i} \mu! \nu!}{i! (\mu-i)! (\nu-i)!} \quad (14)$$

and

$$\langle \nu_{\mathbf{r}, \gamma} | \mu_{\mathbf{r} + \delta \mathbf{r}, \gamma} \rangle = \delta_{\nu, \mu} \quad (15)$$

2.2 Matrix elements in k space

We want to compute

$$\langle \mathbf{k}, \alpha; \underline{\nu} | H^{FE} | \mathbf{k}', \beta; \underline{\mu} \rangle \quad (16)$$

Using the results of the previous section and equation (6) we find

$$\langle \mathbf{k}, \alpha; \underline{\nu} | H^{ph} + H^{FE-ph} | \mathbf{k}', \beta; \underline{\mu} \rangle = \hbar \Omega \delta_{\{\mathbf{k}, \alpha\}, \{\mathbf{k}', \beta\}} \delta_{\underline{\nu}, \underline{\mu}} \sum_{\delta \mathbf{n}, \gamma} \nu_{\delta \mathbf{n}, \gamma} \quad (17)$$

and

$$\begin{aligned} \langle \mathbf{k}, \alpha; \underline{\nu} | H_{elec}^{FE} | \mathbf{k}', \beta; \underline{\mu} \rangle &= \hbar \omega \delta_{\{\mathbf{k}, \alpha\}, \{\mathbf{k}', \beta\}} \delta_{\underline{\nu}, \underline{\mu}} + \\ &+ \delta_{\mathbf{k}, \mathbf{k}'} \sum_{\delta \mathbf{r}} J_{\alpha\beta}(\delta \mathbf{r}) \exp(i \mathbf{k} \delta \mathbf{r}) S \left(\begin{matrix} \nu_{\mathbf{0}, \alpha} \\ \mu_{\delta \mathbf{r}, \alpha} \end{matrix} \right) S \left(\begin{matrix} \mu_{\mathbf{0}, \beta} \\ \nu_{-\delta \mathbf{r}, \beta} \end{matrix} \right) \prod_{\{\mathbf{r}, \gamma\} \neq \{\mathbf{0}, \alpha\} \neq \{-\delta \mathbf{r}, \beta\}} \langle \nu_{\mathbf{r}, \gamma} | \mu_{\mathbf{r} + \delta \mathbf{r}, \gamma} \rangle, \end{aligned} \quad (18)$$

where

$$J_{\alpha\alpha}(\mathbf{0}) = 0. \quad (19)$$

3 Multi-phonon basis set

3.1 Real space (phonon cloud)

We start with a basis set made by one-, two-, etc. particle states in real space. We include two intramolecular phonon modes: one low energy mode (lp) described by the multi-phonon basis set, and a second high energy mode (hp) included within a vibronic approximation. In our one-particle (**zero phonon**) states the electronic excitation and $\tilde{\mu}$ high energy vibrations are localized on molecule α in the crystal cell $\mathbf{n} = (n_1, n_2, n_3)$ at position $\mathbf{r}_{n,\alpha}$; they are indicated as

$$|\mathbf{n}, \alpha, \tilde{\mu}\rangle = |\mathbf{n}, \alpha\rangle_e \otimes |\mathbf{n}, \alpha, \tilde{\mu}\rangle_{hp} \equiv a_{\mathbf{n}, \alpha, \tilde{\mu}}^\dagger |0\rangle. \quad (20)$$

In our two-particle (**one phonon**) states the electronic excitation and the high energy vibrations are localized on molecule α in the crystal cell \mathbf{n} at position $\mathbf{r}_{n,\alpha}$, while a single low energy vibration is localized on a different molecule β in the crystal cell \mathbf{m} at position $\mathbf{r}_{m,\beta}$; they are indicated as

$$|\mathbf{n}, \alpha, \tilde{\mu}; \mathbf{m}, \beta\rangle = |\mathbf{n}, \alpha\rangle_e \otimes |\mathbf{n}, \alpha, \tilde{\mu}\rangle_{hp} \otimes |\mathbf{m}, \beta\rangle_{lp}. \quad (21)$$

In our three-particle (**two phonons**) states the electronic excitation and the high energy vibrations are localized on molecule α in the crystal cell \mathbf{n} at position $\mathbf{r}_{n,\alpha}$, while a single low energy vibration is localized on a different molecule β_1 in the crystal cell \mathbf{m}_1 at position \mathbf{r}_{m_1,β_1} and another single low energy vibration is localized on a different molecule β_2 in the crystal cell \mathbf{m}_2 at position \mathbf{r}_{m_2,β_2} ; they are indicated as

$$|\mathbf{n}, \alpha, \tilde{\mu}; \mathbf{m}_1, \beta_1; \mathbf{m}_2, \beta_2\rangle = |\mathbf{n}, \alpha\rangle_e \otimes |\mathbf{n}, \alpha, \tilde{\mu}\rangle_{hp} \otimes |\mathbf{m}_1, \beta_1\rangle_{lp} \otimes |\mathbf{m}_2, \beta_2\rangle_{lp}. \quad (22)$$

In the same way we can define **p-phonon** states. The Hamiltonian in real space reads

$$H^{\text{two-modes}} = H_{elec}^{FE} + H^{ph} + H^{FE-ph}, \quad (23)$$

with

$$H_{elec}^{FE} = (\hbar\omega + \tilde{\mu}\hbar\Omega_{hp}) \sum_{\mathbf{n}, \alpha, \tilde{\mu}} a_{\mathbf{n}, \alpha, \tilde{\mu}}^\dagger a_{\mathbf{n}, \alpha, \tilde{\mu}} + \sum_{\substack{\mathbf{n}, \alpha, \mathbf{m}, \beta, \tilde{\mu} \\ \{\mathbf{n}, \alpha\} \neq \{\mathbf{m}, \beta\}}} S^2 \left(\begin{matrix} \tilde{\mu} \\ 0 \end{matrix} \right) J_{\alpha\beta}(\mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{m}}) a_{\mathbf{n}, \alpha, \tilde{\mu}}^\dagger a_{\mathbf{m}, \beta, \tilde{\mu}}, \quad (24)$$

$$H^{ph} = \hbar\Omega \sum_{\mathbf{n}, \alpha} b_{\mathbf{n}, \alpha}^\dagger b_{\mathbf{n}, \alpha}, \quad (25)$$

$$H^{FE-ph} = \hbar\Omega \sum_{\mathbf{n}, \alpha} a_{\mathbf{n}, \alpha}^\dagger a_{\mathbf{n}, \alpha} [-\lambda (b_{\mathbf{n}, \alpha}^\dagger + b_{\mathbf{n}, \alpha}) + \lambda^2]. \quad (26)$$

where we used the same notation as in section 1 for the low energy mode and we added the high energy phonon term.

3.2 Wave vector space

3.2.1 States

In strong EP coupling regime is useful to turn to Fourier space and use BO basis functions made of products of Bloch combinations of both electronic and phononic parts:

$$|\mathbf{k}, \alpha, \tilde{\mu}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \exp(i\mathbf{k}\mathbf{r}_{n,\alpha}) |\mathbf{n}, \alpha, \tilde{\mu}\rangle \equiv a_{\mathbf{k}, \alpha, \tilde{\mu}}^\dagger |0\rangle; \quad (27)$$

$$|\mathbf{k}, \alpha, \tilde{\mu}; \mathbf{q}, \beta\rangle = \frac{1}{N} \sum_{\mathbf{n}, \mathbf{m}} \exp(i\mathbf{k}\mathbf{r}_{n,\alpha} + i\mathbf{q}\mathbf{r}_{m,\beta}) |\mathbf{n}, \alpha, \tilde{\mu}\rangle b_{\mathbf{m}, \beta}^\dagger |0\rangle_{lp} = a_{\mathbf{k}, \alpha, \tilde{\mu}}^\dagger b_{\mathbf{q}, \beta}^\dagger |0\rangle, \quad (28)$$

where

$$b_{\mathbf{q},\beta}^\dagger \equiv \frac{1}{\sqrt{N}} \sum_{\mathbf{m}} \exp(i\mathbf{q}\mathbf{r}_{m,\beta}) b_{\mathbf{m},\beta}^\dagger; \quad (29)$$

$$\begin{aligned} |\mathbf{k}, \alpha, \tilde{\mu}; \mathbf{q}_1, \beta_1; \mathbf{q}_2, \beta_2\rangle &= \frac{1}{N\sqrt{N}} \sum_{\mathbf{n}, \mathbf{m}_1, \mathbf{m}_2} \exp(i\mathbf{k}\mathbf{r}_{n,\alpha} + i\mathbf{q}_1\mathbf{r}_{m_1,\beta_1} + i\mathbf{q}_2\mathbf{r}_{m_2,\beta_2}) |\mathbf{n}, \alpha, \tilde{\mu}\rangle b_{\mathbf{m}_2,\beta_2}^\dagger b_{\mathbf{m}_1,\beta_1}^\dagger |0\rangle_{lp} \\ &= a_{\mathbf{k},\alpha,\tilde{\mu}}^\dagger b_{\mathbf{q}_2,\beta_2}^\dagger b_{\mathbf{q}_1,\beta_1}^\dagger |0\rangle, \end{aligned} \quad (30)$$

with the appropriate normalization factors: $\sqrt{2}^{-1}$ if $\mathbf{q}_1 = \mathbf{q}_2$ and $\beta_1 = \beta_2$, 1 else;

$$\begin{aligned} |\mathbf{k}, \alpha, \tilde{\mu}; \mathbf{q}_1, \beta_1; \mathbf{q}_2, \beta_2; \mathbf{q}_3, \beta_3\rangle &= \\ &= \frac{1}{N^2} \sum_{\mathbf{n}, \mathbf{m}_1, \mathbf{m}_2, \mathbf{m}_3} \exp(i\mathbf{k}\mathbf{r}_{n,\alpha} + i\mathbf{q}_1\mathbf{r}_{m_1,\beta_1} + i\mathbf{q}_2\mathbf{r}_{m_2,\beta_2} + i\mathbf{q}_3\mathbf{r}_{m_3,\beta_3}) |\mathbf{n}, \alpha, \tilde{\mu}\rangle b_{\mathbf{m}_3,\beta_3}^\dagger b_{\mathbf{m}_2,\beta_2}^\dagger b_{\mathbf{m}_1,\beta_1}^\dagger |0\rangle_{lp} \\ &= a_{\mathbf{k},\alpha,\tilde{\mu}}^\dagger b_{\mathbf{q}_3,\beta_3}^\dagger b_{\mathbf{q}_2,\beta_2}^\dagger b_{\mathbf{q}_1,\beta_1}^\dagger |0\rangle, \end{aligned} \quad (31)$$

with the appropriate normalization factors: $\sqrt{6}^{-1}$ if all three phonons are the same, $\sqrt{2}^{-1}$ if there are two equal phonons, 1 else.

In the case of lattice with N cells and σ molecules per cell we have:

$$\text{number of 0 phonon states:} \quad \sigma, \quad (32)$$

$$\text{number of 1 phonon states:} \quad N\sigma^2, \quad (33)$$

$$\text{number of 2 phonon states:} \quad \sigma [N \cdot CR_\sigma^2 + \sigma^2 C_N^2], \quad (34)$$

$$\text{number of 3 phonon states:} \quad \sigma [N \cdot CR_\sigma^3 + \sigma \cdot D_N^2 \cdot CR_\sigma^2 + \sigma^3 \cdot C_N^3], \quad (35)$$

where

$$C_n^k = \binom{n}{k} = \frac{n!}{k!(n-k)!} \quad (36)$$

$$CR_n^k = C_{n+k-1}^k = \frac{(n+k-1)!}{k!(n-1)!} \quad (37)$$

$$D_n^k = \frac{n!}{(n-k)!}. \quad (38)$$

3.2.2 Hamiltonian

The Hamiltonian can be written in Fourier space and it reads

$$\begin{aligned} H &= (\hbar\omega + \tilde{\mu}\hbar\Omega_{hp}) \sum_{\mathbf{k},\alpha,\tilde{\mu}} a_{\mathbf{k},\alpha,\tilde{\mu}}^\dagger a_{\mathbf{k},\alpha,\tilde{\mu}} + \sum_{\mathbf{k},\alpha,\beta,\tilde{\mu},\tilde{\mu}'} S \begin{pmatrix} \tilde{\mu} \\ 0 \end{pmatrix} S \begin{pmatrix} \tilde{\mu}' \\ 0 \end{pmatrix} \tilde{J}_{\alpha\beta}(\mathbf{k}) a_{\mathbf{k},\alpha,\tilde{\mu}}^\dagger a_{\mathbf{k},\beta,\tilde{\mu}'} \\ &+ \hbar\Omega \sum_{\mathbf{q},\alpha} b_{\mathbf{q},\alpha}^\dagger b_{\mathbf{q},\alpha} + \lambda^2 \hbar\Omega - \frac{\lambda\hbar\Omega}{\sqrt{N}} \sum_{\mathbf{k},\mathbf{q},\alpha,\tilde{\mu}} \left[b_{\mathbf{q},\alpha}^\dagger a_{\mathbf{k},\alpha,\tilde{\mu}}^\dagger a_{\mathbf{k}+\mathbf{q},\alpha,\tilde{\mu}} + b_{\mathbf{q},\alpha} a_{\mathbf{k},\alpha,\tilde{\mu}}^\dagger a_{\mathbf{k}-\mathbf{q},\alpha,\tilde{\mu}} \right]. \end{aligned} \quad (39)$$

Hamiltonian matrix elements between **0 phonon** states are:

$$\begin{aligned} \langle \mathbf{k}', \alpha', \tilde{\mu}' | H | \mathbf{k}, \alpha, \tilde{\mu} \rangle &= \delta(\mathbf{k} - \mathbf{k}') \delta_{\alpha\alpha'} \delta_{\tilde{\mu}\tilde{\mu}'} [\hbar\omega + \tilde{\mu}\hbar\Omega_{hp} + \lambda^2 \hbar\Omega] \\ &+ \delta(\mathbf{k} - \mathbf{k}') S \begin{pmatrix} \tilde{\mu} \\ 0 \end{pmatrix} S \begin{pmatrix} \tilde{\mu}' \\ 0 \end{pmatrix} \tilde{J}_{\alpha\alpha'}(\mathbf{k}) \end{aligned} \quad (40)$$

where

$$\tilde{J}_{\alpha\alpha'}(\mathbf{k}) = \sum_{\mathbf{n}}' \exp[i\mathbf{k}(\mathbf{r}_{n,\alpha} - \mathbf{r}_{0,\alpha'})] J_{\alpha\alpha'}(\mathbf{r}_{n,\alpha} - \mathbf{r}_{0,\alpha'}), \quad (41)$$

and $\sum_{\mathbf{n}}'$ means that $\{n, \alpha\} \neq \{0, \alpha'\}$.

Coupling between 0- and 1- phonon states is given by:

$$\langle \mathbf{k}', \alpha', \tilde{\mu}' | H | \mathbf{k}, \alpha, \tilde{\mu}; \mathbf{q}, \beta \rangle = -\frac{\lambda \hbar \Omega}{\sqrt{N}} \delta_{\tilde{\mu}\tilde{\mu}'} \delta_{\alpha\alpha'} \delta_{\alpha\beta} \delta(\mathbf{k} + \mathbf{q} - \mathbf{k}'), \quad (42)$$

Hamiltonian matrix elements between **1-phonon states** are:

$$\begin{aligned} \langle \mathbf{k}', \alpha', \tilde{\mu}'; \mathbf{q}', \beta' | H | \mathbf{k}, \alpha, \tilde{\mu}; \mathbf{q}, \beta \rangle &= \delta(\mathbf{k} - \mathbf{k}') \delta(\mathbf{q} - \mathbf{q}') \delta_{\beta\beta'} \{ \delta_{\alpha\alpha'} \delta_{\tilde{\mu}\tilde{\mu}'} [\hbar\omega + \tilde{\mu}\hbar\Omega_{hp} + \hbar\Omega(1 + \lambda^2)] \\ &\quad + S \left(\begin{smallmatrix} \tilde{\mu} \\ 0 \end{smallmatrix} \right) S \left(\begin{smallmatrix} \tilde{\mu}' \\ 0 \end{smallmatrix} \right) \tilde{J}_{\alpha\alpha'}(\mathbf{k}) \}, \end{aligned} \quad (43)$$

Coupling between 1- and 2- phonon states is given by:

$$\begin{aligned} \langle \mathbf{k}', \alpha', \tilde{\mu}'; \mathbf{q}', \beta' | H | \mathbf{k}, \alpha, \tilde{\mu}; \mathbf{q}_1, \beta_1; \mathbf{q}_2, \beta_2 \rangle &= -\frac{\lambda \hbar \Omega}{\sqrt{N}} \delta_{\alpha\alpha'} \delta_{\tilde{\mu}\tilde{\mu}'} [\delta(\mathbf{k} - \mathbf{k}' + \mathbf{q}_2) \delta(\mathbf{q}_1 - \mathbf{q}') \delta_{\alpha\beta_2} \delta_{\beta_1\beta'} \\ &\quad + \delta(\mathbf{k} - \mathbf{k}' + \mathbf{q}_1) \delta(\mathbf{q}_2 - \mathbf{q}') \delta_{\alpha\beta_1} \delta_{\beta_2\beta'}] \left[1 + \delta_{\beta_1\beta_2} \delta(\mathbf{q}_1 - \mathbf{q}_2) \left(\frac{1}{\sqrt{2}} - 1 \right) \right]; \end{aligned} \quad (44)$$

Hamiltonian matrix elements between **2-phonon states** are:

$$\begin{aligned} \langle \mathbf{k}', \alpha', \tilde{\mu}'; \mathbf{q}'_1, \beta'_1; \mathbf{q}'_2, \beta'_2 | H | \mathbf{k}, \alpha, \tilde{\mu}; \mathbf{q}_1, \beta_1; \mathbf{q}_2, \beta_2 \rangle &= \\ \delta(\mathbf{k} - \mathbf{k}') [\delta(\mathbf{q}_1 - \mathbf{q}'_1) \delta(\mathbf{q}_2 - \mathbf{q}'_2) \delta_{\beta_1\beta'_1} \delta_{\beta_2\beta'_2} + \delta(\mathbf{q}_1 - \mathbf{q}'_2) \delta(\mathbf{q}_2 - \mathbf{q}'_1) \delta_{\beta_1\beta'_2} \delta_{\beta_2\beta'_1} - \\ \delta(\mathbf{q}_1 - \mathbf{q}'_1) \delta(\mathbf{q}_2 - \mathbf{q}'_2) \delta_{\beta_1\beta'_1} \delta_{\beta_2\beta'_2} \delta(\mathbf{q}_1 - \mathbf{q}_2) \delta_{\beta_1\beta_2}] \\ \times \left[\delta_{\alpha\alpha'} \delta_{\tilde{\mu}\tilde{\mu}'} [(2 + \lambda^2) \hbar\Omega + \tilde{\mu}\hbar\Omega_{hp} + \hbar\omega] + S \left(\begin{smallmatrix} \tilde{\mu} \\ 0 \end{smallmatrix} \right) S \left(\begin{smallmatrix} \tilde{\mu}' \\ 0 \end{smallmatrix} \right) \tilde{J}_{\alpha\alpha'}(\mathbf{k}) \right]. \end{aligned} \quad (45)$$

Coupling between 2- and 3- phonon states is given by:

$$\begin{aligned} \langle \mathbf{k}', \alpha', \tilde{\mu}'; \mathbf{q}'_1, \beta'_1; \mathbf{q}'_2, \beta'_2 | H | \mathbf{k}, \alpha, \tilde{\mu}; \mathbf{q}_1, \beta_1; \mathbf{q}_2, \beta_2; \mathbf{q}_3, \beta_3 \rangle &= \\ -\frac{\lambda \hbar \Omega}{\sqrt{N}} \delta_{\alpha\alpha'} \delta_{\tilde{\mu}\tilde{\mu}'} [& \\ +\delta(\mathbf{k} + \mathbf{q}_1 - \mathbf{k}') \delta(\mathbf{q}_2 - \mathbf{q}'_1) \delta(\mathbf{q}_3 - \mathbf{q}'_2) \delta_{\alpha\beta_1} \delta_{\beta_2\beta'_1} \delta_{\beta_3\beta'_2} & \\ +\delta(\mathbf{k} + \mathbf{q}_1 - \mathbf{k}') \delta(\mathbf{q}_3 - \mathbf{q}'_1) \delta(\mathbf{q}_2 - \mathbf{q}'_2) \delta_{\alpha\beta_1} \delta_{\beta_3\beta'_1} \delta_{\beta_2\beta'_2} & \\ +\delta(\mathbf{k} + \mathbf{q}_2 - \mathbf{k}') \delta(\mathbf{q}_1 - \mathbf{q}'_1) \delta(\mathbf{q}_3 - \mathbf{q}'_2) \delta_{\alpha\beta_2} \delta_{\beta_1\beta'_1} \delta_{\beta_3\beta'_2} & \\ +\delta(\mathbf{k} + \mathbf{q}_2 - \mathbf{k}') \delta(\mathbf{q}_3 - \mathbf{q}'_1) \delta(\mathbf{q}_1 - \mathbf{q}'_2) \delta_{\alpha\beta_2} \delta_{\beta_3\beta'_1} \delta_{\beta_1\beta'_2} & \\ +\delta(\mathbf{k} + \mathbf{q}_3 - \mathbf{k}') \delta(\mathbf{q}_1 - \mathbf{q}'_1) \delta(\mathbf{q}_2 - \mathbf{q}'_2) \delta_{\alpha\beta_3} \delta_{\beta_1\beta'_1} \delta_{\beta_2\beta'_2} & \\ +\delta(\mathbf{k} + \mathbf{q}_3 - \mathbf{k}') \delta(\mathbf{q}_2 - \mathbf{q}'_1) \delta(\mathbf{q}_1 - \mathbf{q}'_2) \delta_{\alpha\beta_3} \delta_{\beta_2\beta'_1} \delta_{\beta_1\beta'_2}] \times & \\ \times \left[1 + \left(\frac{1}{\sqrt{2}} - 1 \right) \delta(\mathbf{q}'_1 - \mathbf{q}'_2) \delta_{\beta'_1\beta'_2} \right] \times & \\ \times \left[1 + \left(\frac{1}{\sqrt{2}} - 1 \right) \delta(\mathbf{q}_1 - \mathbf{q}_2) \delta_{\beta_1\beta_2} + \left(\frac{1}{\sqrt{2}} - 1 \right) \delta(\mathbf{q}_1 - \mathbf{q}_3) \delta_{\beta_1\beta_3} + \left(\frac{1}{\sqrt{2}} - 1 \right) \delta(\mathbf{q}_2 - \mathbf{q}_3) \delta_{\beta_2\beta_3} \right. & \\ \left. + \left(2 - \frac{3}{\sqrt{2}} + \frac{1}{\sqrt{6}} \right) \delta(\mathbf{q}_1 - \mathbf{q}_2) \delta_{\beta_1\beta_2} \delta(\mathbf{q}_2 - \mathbf{q}_3) \delta_{\beta_2\beta_3} \right] & \end{aligned} \quad (46)$$

Hamiltonian matrix elements between ordered (also the molecule part) **3-phonon states** are:

$$\begin{aligned} \langle \mathbf{k}', \alpha', \tilde{\mu}'; \mathbf{q}'_1, \beta'_1; \mathbf{q}'_2, \beta'_2; \mathbf{q}'_3, \beta'_3 | H | \mathbf{k}, \alpha, \tilde{\mu}; \mathbf{q}_1, \beta_1; \mathbf{q}_2, \beta_2; \mathbf{q}_3, \beta_3 \rangle &= \\ \delta(\mathbf{k} - \mathbf{k}') \delta(\mathbf{q}_1 - \mathbf{q}'_1) \delta(\mathbf{q}_2 - \mathbf{q}'_2) \delta(\mathbf{q}_3 - \mathbf{q}'_3) \delta_{\beta_1\beta'_1} \delta_{\beta_2\beta'_2} \delta_{\beta_3\beta'_3} & \\ \times \left[\delta_{\alpha\alpha'} \delta_{\tilde{\mu}\tilde{\mu}'} [(3 + \lambda^2) \hbar\Omega + \tilde{\mu}\hbar\Omega_{hp} + \hbar\omega] + S \left(\begin{smallmatrix} \tilde{\mu} \\ 0 \end{smallmatrix} \right) S \left(\begin{smallmatrix} \tilde{\mu}' \\ 0 \end{smallmatrix} \right) \tilde{J}_{\alpha\alpha'}(\mathbf{k}) \right]. & \end{aligned} \quad (47)$$

We can also treat the $\mathbf{q} = 0$ phonon exactly and write the Hamiltonian as

$$\begin{aligned}
H = & (\hbar\omega + \tilde{\mu}\hbar\Omega_{hp}) \sum_{\mathbf{k}, \alpha, \tilde{\mu}} a_{\mathbf{k}, \alpha, \tilde{\mu}}^\dagger a_{\mathbf{k}, \alpha, \tilde{\mu}} + \sum_{\mathbf{k}, \alpha, \beta, \tilde{\mu}, \tilde{\mu}'} S \begin{pmatrix} \tilde{\mu} \\ 0 \end{pmatrix} S \begin{pmatrix} \tilde{\mu}' \\ 0 \end{pmatrix} \tilde{J}_{\alpha\beta}(\mathbf{k}) a_{\mathbf{k}, \alpha, \tilde{\mu}}^\dagger a_{\mathbf{k}, \beta, \tilde{\mu}'} \\
& + \hbar\Omega \sum_{\alpha} \left[\tilde{b}_{0, \alpha}^\dagger \tilde{b}_{0, \alpha} + \sum_{\mathbf{q} \neq 0} b_{\mathbf{q}, \alpha}^\dagger b_{\mathbf{q}, \alpha} \right] + \left(1 - \frac{1}{N} \right) \lambda^2 \hbar\Omega \\
& - \frac{\lambda \hbar\Omega}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{q} \neq 0, \alpha, \tilde{\mu}} \left[b_{\mathbf{q}, \alpha}^\dagger a_{\mathbf{k}, \alpha, \tilde{\mu}}^\dagger a_{\mathbf{k}+\mathbf{q}, \alpha, \tilde{\mu}} + b_{\mathbf{q}, \alpha} a_{\mathbf{k}, \alpha, \tilde{\mu}}^\dagger a_{\mathbf{k}-\mathbf{q}, \alpha, \tilde{\mu}} \right],
\end{aligned} \tag{48}$$

where

$$\tilde{b}_{0, \alpha} \equiv b_{0, \alpha} - \frac{\lambda}{\sqrt{N}}. \tag{49}$$

4 Emission

4.1 General definitions

Emission polarized along direction \mathbf{u} is given by

$$S_{\mathbf{u}}(\hbar\omega) = R(T) \frac{1}{Z} \sum_{\mathbf{k}, dc, n} e^{-\frac{E_{\mathbf{k}, dc, n} - E_{LBE}}{k_B T}} S_{\mathbf{u}}^{(\mathbf{k}, dc, n)}(\hbar\omega), \tag{50}$$

where the partition function is

$$Z \equiv \sum_{\mathbf{k}, dc, n} e^{-\frac{E_{\mathbf{k}, dc, n} - E_{LBE}}{k_B T}} \tag{51}$$

$$S_{\mathbf{u}}^{(\mathbf{k}, dc, n)}(\hbar\omega) = \sum_{\nu_t=0,1,\dots} I_{\mathbf{u}}^{0-\nu_t}(\mathbf{k}, dc, n) \left[\frac{E_{\mathbf{k}, dc, n} - \nu_t \hbar\omega_0}{E_{LBE}} \right]^3 \frac{W_e(\hbar\omega - E_{\mathbf{k}, dc, n} + \nu_t \hbar\omega_0)}{W_e(0)} \tag{52}$$

$$I_{\mathbf{u}}^{0-\nu_t}(\mathbf{k}, dc, n) = \sum_{\{\nu_{\mathbf{n}, \alpha}\}}' \left| \langle \psi_{\mathbf{k}, dc, n} | \hat{\mathbf{D}} \cdot \mathbf{u} \prod_{\mathbf{n}, \alpha} |g_{\mathbf{n}, \alpha}, \nu_{\mathbf{n}, \alpha}\rangle \right|^2, \tag{53}$$

$$\hat{\mathbf{D}} = \sum_{\mathbf{n}, \alpha} \mathbf{d}_{\alpha} |\mathbf{n}, \alpha\rangle \langle g| + h.c. \tag{54}$$

$$R(T) = \frac{P}{\gamma_r + \gamma_{nr}(T)} \tag{55}$$

4.2 Weak electronic coupling: two-particle approximation

Conditions: $W \ll \hbar\omega_0$ and $k_B T \ll \hbar\omega_0$. We assume that the emitting states are only the σ lowest energy states in each Davydov subspace. We now consider a multi particle basis set containing one- and two-particle states. The eigenstates are written as

$$\psi_{\mathbf{k}, dc, n=0} = \sum_{\alpha, \underline{\mu}} c_{\alpha, \underline{\mu}}(\mathbf{k}, dc) |\mathbf{k}, \alpha, \underline{\mu}\rangle = \sum_{\alpha, \underline{\mu}, \mathbf{n}} c_{\alpha, \underline{\mu}}(\mathbf{k}, dc) \frac{e^{-i\mathbf{k}\rho_{\alpha}}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} |\mathbf{n}, \alpha, \underline{\mu}\rangle \tag{56}$$

$$|\mathbf{k}, \alpha, \underline{\mu}\rangle \equiv \frac{e^{-i\mathbf{k}\rho_{\alpha}}}{\sqrt{N}} \sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} |\mathbf{n}, \alpha, \underline{\mu}\rangle. \tag{57}$$

Following Spano we write

$$I_{\mathbf{u}}^{0-\nu_t}(\mathbf{k}, dc, n) = \delta_{\nu_t,0} I_{\mathbf{u}}^{(0)}(\mathbf{k}, dc, n) + (1 - \delta_{\nu_t,0}) \left\{ I_{\mathbf{u}}^{(1)}(\nu_t; \mathbf{k}, dc, n) \right. \quad (58)$$

$$\left. + \sum_{\nu_1=1}^{\nu_t-1} I_{\mathbf{u}}^{(2)}(\nu_1, \nu_t - 1; \mathbf{k}, dc, n) \right\}, \quad (59)$$

where $I_{\mathbf{u}}^{(p)}$ is the line strength corresponding to emission to ground electronic states with a total of ν_t quanta spread over p molecules. The 0-0 emission line only contains terms due to one-particle states

$$I_{\mathbf{u}}^{(0)}(\mathbf{k}, dc, n) = \left| \langle \psi_{\mathbf{k}, dc, n} | \hat{\mathbf{D}} \cdot \mathbf{u} | 0 \rangle \right|^2 = \left| \langle \psi_{\mathbf{k}, dc, n} | \hat{\mathbf{D}} | 0 \rangle \cdot \mathbf{u} \right|^2 \quad (60)$$

$$= \left| \sum_{\alpha, \tilde{\mu}, \mathbf{n}} \sum_{\mathbf{m}, \beta} c_{\alpha, \tilde{\mu}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_{\alpha}}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} \langle \mathbf{n}, \alpha | \mathbf{m}, \beta \rangle_{\text{el}} \langle \tilde{\mu} | 0 \rangle_{\text{ph}} \mathbf{d}_{\beta} \cdot \mathbf{u} \right|^2 \quad (61)$$

$$= \left| \sum_{\alpha, \tilde{\mu}, \mathbf{n}} c_{\alpha, \tilde{\mu}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_{\alpha}}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} S_{\tilde{\mu}0} \mathbf{d}_{\alpha} \cdot \mathbf{u} \right|^2 \quad (62)$$

$$= \delta(\mathbf{k}) \left| \sum_{\alpha, \tilde{\mu}} c_{\alpha, \tilde{\mu}}(\mathbf{k}, dc, n) \sqrt{N} e^{-i\mathbf{k}\rho_{\alpha}} S_{\tilde{\mu}0} \mathbf{d}_{\alpha} \cdot \mathbf{u} \right|^2 \quad (63)$$

$$= N \delta(\mathbf{k}) \left| \sum_{\alpha, \tilde{\mu}} c_{\alpha, \tilde{\mu}}(\mathbf{k} = 0, dc, n) S_{\tilde{\mu}0} \mathbf{d}_{\alpha} \cdot \mathbf{u} \right|^2 \quad (64)$$

$$(65)$$

where we used the relation

$$\sum_{\mathbf{n}} \frac{1}{N} e^{i\mathbf{k}\mathbf{n}} = \delta(\mathbf{k}). \quad (66)$$

Now we give the expression for $I_{\mathbf{u}}^{(1)}(\nu_t; \mathbf{k}, dc, n)$, which consider emission ending on states $|g; \nu_t, \mathbf{l}, \gamma\rangle \equiv |g\rangle_{\text{el}} |\nu_t, \gamma\rangle_{\text{ph}}$ in which all molecules are in their electronic ground state and there are ν_t vibrational quanta on molecule (\mathbf{l}, γ) . Here we have an additional contribution due to two-particle states. The phonon cloud in this case is indicated for convenience as $\underline{\mu} \equiv \{\tilde{\mu}; \nu, \mathbf{p}, \sigma\}$, where $\tilde{\mu}$ indicates the number of phonons on the (electronically) excited molecule and ν indicates the number of phonons in the (electronic) ground state molecule residing at the relative position (\mathbf{p}, σ) with respect to the (electronically) excited molecule.

$$\begin{aligned} I_{\mathbf{u}}^{(1)}(\nu_t; \mathbf{k}, dc, n) &= \quad (67) \\ &= \sum_{\mathbf{l}, \gamma} \left| \langle \psi_{\mathbf{k}, dc, n} | \hat{\mathbf{D}} \cdot \mathbf{u} | g; \mathbf{l}, \gamma, \nu_t \rangle \right|^2 \\ &= \sum_{\mathbf{l}, \gamma} \left| \sum_{\mathbf{n}, \alpha, \underline{\mu}, \nu, \mathbf{p}, \sigma, \mathbf{m}, \beta} c_{\alpha, \underline{\mu}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_{\alpha}}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} \langle \mathbf{n}, \alpha | \mathbf{m}, \beta \rangle_{\text{el}} \langle \mathbf{n}, \alpha, \tilde{\mu}; \mathbf{n} + \mathbf{p}, \sigma, \nu | \mathbf{l}, \gamma, \nu_t \rangle_{\text{ph}} \mathbf{d}_{\beta} \cdot \mathbf{u} \right|^2 \\ &= \sum_{\mathbf{l}, \gamma} \left| \sum_{\tilde{\mu}} c_{\gamma, \tilde{\mu}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_{\gamma}}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{l}} S_{\tilde{\mu}\nu_t} \mathbf{d}_{\gamma} \cdot \mathbf{u} + \sum_{\mathbf{p}, \alpha, \tilde{\mu}} c_{\alpha, \{\tilde{\mu}, \mathbf{p}, \gamma, \nu_t\}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_{\alpha}}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{l}} e^{-i\mathbf{k}\mathbf{p}} S_{\tilde{\mu}0} \mathbf{d}_{\alpha} \cdot \mathbf{u} \right|^2 \\ &= \sum_{\gamma} \left| \sum_{\tilde{\mu}} c_{\gamma, \tilde{\mu}}(\mathbf{k}, dc, n) e^{-i\mathbf{k}\rho_{\gamma}} S_{\tilde{\mu}\nu_t} \mathbf{d}_{\gamma} \cdot \mathbf{u} + \sum_{\mathbf{p}, \alpha, \tilde{\mu}} c_{\alpha, \{\tilde{\mu}, \mathbf{p}, \gamma, \nu_t\}}(\mathbf{k}, dc, n) e^{-i\mathbf{k}\rho_{\alpha}} e^{-i\mathbf{k}\mathbf{p}} S_{\tilde{\mu}0} \mathbf{d}_{\alpha} \cdot \mathbf{u} \right|^2 \end{aligned}$$

where the first term is due to one-particle states and the second to two-particle states. We made use of the relation

$$\langle \mathbf{n}, \alpha, \tilde{\mu}; \mathbf{n} + \mathbf{p}, \sigma, \nu | \mathbf{l}, \gamma, \nu_t \rangle_{\text{ph}} = \delta_{\mathbf{n}, \mathbf{l}} \delta_{\alpha \gamma} \delta_{\nu 0} S_{\tilde{\mu} \nu_t} + \delta_{\mathbf{n} + \mathbf{p}, \mathbf{l}} \delta_{\sigma \gamma} \delta_{\nu \nu_t} S_{\tilde{\mu} 0} (1 - \delta_{\nu 0}) \quad (68)$$

$$\begin{aligned} I_{\mathbf{u}}^{(2)}(\nu_1, \nu_2; \mathbf{k}, dc, n) &= \\ &= \sum_{\mathbf{l}, \gamma, \mathbf{j}, \xi} \left| \langle \psi_{\mathbf{k}, dc, n} | \hat{\mathbf{D}} \cdot \mathbf{u} | g; \mathbf{l}, \gamma, \nu_1; \mathbf{j}, \xi, \nu_2 \rangle \right|^2 \\ &= \sum_{\mathbf{l}, \gamma, \mathbf{j}, \xi} \left| \sum_{\mathbf{n}, \alpha, \tilde{\mu}, \nu, \mathbf{p}, \sigma} \sum_{\mathbf{m}, \beta} c_{\alpha, \tilde{\mu}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} \langle \mathbf{n}, \alpha | \mathbf{m}, \beta \rangle_{\text{el}} \langle \mathbf{n}, \alpha, \tilde{\mu}; \mathbf{n} + \mathbf{p}, \sigma, \nu | \mathbf{l}, \gamma, \nu_1; \mathbf{j}, \xi, \nu_2 \rangle_{\text{ph}} \mathbf{d}_\beta \cdot \mathbf{u} \right|^2 \\ &= \sum_{\mathbf{l}, \gamma, \mathbf{j}, \xi} \left| \sum_{\tilde{\mu}} c_{\gamma, \{\tilde{\mu}, \mathbf{j}-\mathbf{l}, \xi, \nu_2\}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\gamma}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{l}} S_{\tilde{\mu} \nu_1} \mathbf{d}_\gamma \cdot \mathbf{u} + \sum_{\tilde{\mu}} c_{\xi, \{\tilde{\mu}, \mathbf{l}-\mathbf{j}, \gamma, \nu_1\}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\xi}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{j}} S_{\tilde{\mu} \nu_2} \mathbf{d}_\xi \cdot \mathbf{u} \right|^2 \\ &= \sum_{\gamma, \mathbf{r}, \xi} \left| \sum_{\tilde{\mu}} c_{\gamma, \{\tilde{\mu}, \mathbf{j}-\mathbf{l}, \xi, \nu_2\}}(\mathbf{k}, dc, n) e^{-i\mathbf{k}\rho_\gamma} S_{\tilde{\mu} \nu_1} \mathbf{d}_\gamma \cdot \mathbf{u} + \sum_{\tilde{\mu}} c_{\xi, \{\tilde{\mu}, \mathbf{l}-\mathbf{j}, \gamma, \nu_1\}}(\mathbf{k}, dc, n) e^{-i\mathbf{k}\rho_\xi} e^{i\mathbf{k}\mathbf{r}} S_{\tilde{\mu} \nu_2} \mathbf{d}_\xi \cdot \mathbf{u} \right|^2 \end{aligned} \quad (69)$$

where all terms are due to two-particle states. We defined

$$\mathbf{r} \equiv \mathbf{j} - \mathbf{l} \quad (70)$$

and made use of the relation

$$\langle \mathbf{n}, \alpha, \tilde{\mu}; \mathbf{n} + \mathbf{p}, \sigma, \nu | \mathbf{l}, \gamma, \nu_1; \mathbf{j}, \xi, \nu_2 \rangle_{\text{ph}} = \delta_{\mathbf{n}, \mathbf{l}} \delta_{\alpha \gamma} \delta_{\mathbf{n} + \mathbf{p}, \mathbf{j}} \delta_{\sigma, \xi} \delta_{\nu \nu_2} S_{\tilde{\mu} \nu_1} + \delta_{\mathbf{n}, \mathbf{j}} \delta_{\alpha \xi} \delta_{\mathbf{n} + \mathbf{p}, \mathbf{l}} \delta_{\sigma, \gamma} \delta_{\nu \nu_1} S_{\tilde{\mu} \nu_2} \quad (71)$$

4.3 Strong electronic coupling

Conditions: $W \gg \hbar\omega_0$ and $k_B T \ll \hbar\omega_0$. We assume that the single emitting state is the lowest energy at each \mathbf{k} and we expand it to the first order perturbation theory. The Hamiltonian is

$$H = H_0 + H_1, \quad (72)$$

where

$$H_0 = \hbar\omega_{0-0} + D + \sum_{\mathbf{k}, \alpha, \beta} \tilde{J}_{\alpha\beta}(\mathbf{k}) |\mathbf{k}, \alpha, \tilde{\mu}\rangle \langle \mathbf{k}, \beta, \tilde{\nu}| + \hbar\omega_0 \sum_{\mathbf{q}, \alpha} b_{\mathbf{q}, \alpha}^\dagger b_{\mathbf{q}, \alpha} + \lambda_0^2 \hbar\omega_0, \quad (73)$$

is the unperturbed Hamiltonian, which can be easily diagonalized and

$$H_1 = \frac{\lambda_0 \hbar\omega_0}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{q}, \alpha} [b_{\mathbf{q}, \alpha}^\dagger |\mathbf{k}, \alpha\rangle \langle \mathbf{k} + \mathbf{q}, \alpha| + b_{\mathbf{q}, \alpha} |\mathbf{k}, \alpha\rangle \langle \mathbf{k} - \mathbf{q}, \alpha|], \quad (74)$$

is the perturbation. Eigenstates of H_0 consist of a product of a pure exciton part and a pure phonon part. To zero order, the lowest energy exciton with wave vector \mathbf{k} contains no phonons

$$\psi_{\mathbf{k}, dc=\text{Lowest}}^{(0)} \equiv \psi_{\mathbf{k}}^{(0)} = |\mathbf{k}, L\rangle \otimes |0\rangle_{ph} = \sum_{\alpha} c_{\alpha}(\mathbf{k}, L) |\mathbf{k}, \alpha\rangle \otimes |0\rangle_{ph} = \sum_{\alpha, \mathbf{n}} c_{\alpha}(\mathbf{k}, L) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} |\mathbf{n}, \alpha\rangle \otimes |0\rangle_{ph}, \quad (75)$$

where $|0\rangle_{ph}$ is the vacuum phonon state and

$$|\mathbf{k}, \alpha\rangle \equiv \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} \sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} |\mathbf{n}, \alpha\rangle. \quad (76)$$

Perturbation couples $\psi_{\mathbf{k}}^{(0)}$ with all the one phonon states with total wave vector \mathbf{k}

$$\psi_{\mathbf{q},dc,\beta}^{1ph,\mathbf{k}} = |\mathbf{q}, dc\rangle \otimes b_{\mathbf{k}-\mathbf{q},\beta}^\dagger |0\rangle_{ph} = \sum_{\alpha} c_{\alpha}(\mathbf{q}, dc) |\mathbf{q}, \alpha\rangle \otimes b_{\mathbf{k}-\mathbf{q},\beta}^\dagger |0\rangle_{ph} \quad (77)$$

$$= \sum_{\alpha, \mathbf{n}} c_{\alpha}(\mathbf{q}, dc) \frac{e^{-i\mathbf{q}\rho_{\alpha}}}{\sqrt{N}} e^{i\mathbf{q}\mathbf{n}} |\mathbf{n}, \alpha\rangle \otimes b_{\mathbf{k}-\mathbf{q},\beta}^\dagger |0\rangle_{ph} \quad (78)$$

$$= \sum_{\alpha, \mathbf{n}} c_{\alpha}(\mathbf{q}, dc) \frac{e^{-i\mathbf{q}\rho_{\alpha}}}{\sqrt{N}} e^{i\mathbf{q}\mathbf{n}} |\mathbf{n}, \alpha\rangle \otimes \sum_{\mathbf{m}} \frac{e^{i(\mathbf{k}-\mathbf{q})\mathbf{m}}}{\sqrt{N}} b_{\mathbf{m},\beta}^\dagger |0\rangle_{ph}. \quad (79)$$

$$\langle \psi_{\mathbf{k}}^{(0)} | H_1 | \psi_{\mathbf{q},dc,\beta}^{1ph,\mathbf{k}} \rangle = \sum_{\alpha, \gamma} c_{\alpha}^*(\mathbf{k}, L) c_{\gamma}(\mathbf{q}, dc) \langle \mathbf{k}, \alpha | \otimes \langle 0 |_{ph} H_1 | \mathbf{q}, \gamma \rangle \otimes b_{\mathbf{k}-\mathbf{q},\beta}^\dagger |0\rangle_{ph} \quad (80)$$

$$= \frac{\lambda_0 \hbar \omega_0}{\sqrt{N}} \sum_{\gamma} c_{\beta}^*(\mathbf{k}, L) c_{\gamma}(\mathbf{q}, dc) \langle \mathbf{k}, \beta | \otimes \langle 0 |_{ph} \left[\sum_{\mathbf{k}', \mathbf{q}', \alpha'} b_{\mathbf{q}', \alpha'} |\mathbf{k}', \alpha'\rangle \langle \mathbf{k}' - \mathbf{q}', \alpha' | \right] |\mathbf{q}, \gamma\rangle \otimes b_{\mathbf{k}-\mathbf{q},\beta}^\dagger |0\rangle_{ph} \quad (81)$$

$$= \frac{\lambda_0 \hbar \omega_0}{\sqrt{N}} c_{\beta}^*(\mathbf{k}, L) c_{\beta}(\mathbf{q}, dc) \quad (82)$$

$$\psi_{\mathbf{k}}^{(1)} = \sum_{\mathbf{q}, dc, \beta} \frac{\langle \psi_{\mathbf{q},dc,\beta}^{1ph,\mathbf{k}} | H_1 | \psi_{\mathbf{k}}^{(0)} \rangle}{J_{\mathbf{k},L} - (J_{\mathbf{q},dc} + \hbar \omega_0)} |\psi_{\mathbf{q},dc,\beta}^{1ph,\mathbf{k}}\rangle \quad (83)$$

$$= \frac{\lambda_0 \hbar \omega_0}{\sqrt{N}} \sum_{\mathbf{q}, dc, \beta} \frac{c_{\beta}(\mathbf{k}, L) c_{\beta}^*(\mathbf{q}, dc)}{J_{\mathbf{k},L} - (J_{\mathbf{q},dc} + \hbar \omega_0)} |\psi_{\mathbf{q},dc,\beta}^{1ph,\mathbf{k}}\rangle \quad (84)$$

$$= \frac{\lambda_0 \hbar \omega_0}{\sqrt{N}} \sum_{\mathbf{q}, dc, \beta} \frac{c_{\beta}(\mathbf{k}, L) c_{\beta}^*(\mathbf{q}, dc)}{J_{\mathbf{k},L} - (J_{\mathbf{q},dc} + \hbar \omega_0)} |\mathbf{q}, dc\rangle \otimes b_{\mathbf{k}-\mathbf{q},\beta}^\dagger |0\rangle_{ph} \quad (85)$$

To the first order the emitting state is therefore

$$\psi_{\mathbf{k}} = \psi_{\mathbf{k}}^{(0)} + \psi_{\mathbf{k}}^{(1)}. \quad (86)$$

Emission to the ground state can only proceed from $\psi_{\mathbf{k}}^{(0)}$ so we can write

$$I_{\mathbf{u}}^{0-0}(\mathbf{k}) = \left| \langle \psi_{\mathbf{k}} | \hat{\mathbf{D}} \cdot \mathbf{u} | 0 \rangle \right|^2 = \left| \langle \psi_{\mathbf{k}}^{(0)} | \hat{\mathbf{D}} | 0 \rangle \cdot \mathbf{u} \right|^2 \quad (87)$$

$$= \left| \langle \mathbf{k}, L | \hat{\mathbf{D}} | 0 \rangle_{el} \cdot \mathbf{u} \right|^2 = \delta(\mathbf{k}) \left| \langle \mathbf{k} = 0, L | \hat{\mathbf{D}} | 0 \rangle_{el} \cdot \mathbf{u} \right|^2 \quad (88)$$

$$= \delta(\mathbf{k}) \left| \sum_{\alpha, \mathbf{n}} c_{\alpha}(\mathbf{k} = 0, L) \frac{1}{\sqrt{N}} \langle \mathbf{n}, \alpha | \hat{\mathbf{D}} | 0 \rangle_{el} \cdot \mathbf{u} \right|^2 = \delta(\mathbf{k}) \left| \sum_{\alpha, \mathbf{n}} c_{\alpha}(\mathbf{k} = 0, L) \frac{1}{\sqrt{N}} \mathbf{d}_{\alpha} \cdot \mathbf{u} \right|^2 \quad (89)$$

$$= N \delta(\mathbf{k}) \left| \sum_{\alpha} c_{\alpha}(0, L) \mathbf{d}_{\alpha} \cdot \mathbf{u} \right|^2 = N \delta(\mathbf{k}) |\mathbf{d}_L \cdot \mathbf{u}|^2, \quad (90)$$

where we defined

$$\mathbf{d}_{dc} \equiv \sum_{\alpha} c_{\alpha}(0, dc) \mathbf{d}_{\alpha}. \quad (91)$$

Emission to one phonon states can only proceed from $\psi_{\mathbf{k}}^{(1)}$ so we can write

$$I_{\mathbf{u}}^{0-1}(\mathbf{k}) = \sum_{\mathbf{l}, \gamma} \left| \langle g; \mathbf{l}, \gamma | \hat{\mathbf{D}} \cdot \mathbf{u} | \psi_{\mathbf{k}}^{(1)} \rangle \right|^2 \quad (92)$$

$$= \frac{\lambda_0^2 (\hbar \omega_0)^2}{N} \sum_{\mathbf{l}, \gamma} \left| \sum_{\mathbf{q}, dc, \beta} \frac{c_{\beta}(\mathbf{k}, L) c_{\beta}^*(\mathbf{q}, dc)}{J_{\mathbf{k}, L} - (J_{\mathbf{q}, dc} + \hbar \omega_0)} \langle 0 | \hat{\mathbf{D}} \cdot \mathbf{u} | \mathbf{q}, dc \rangle_{el} \langle g; \mathbf{l}, \gamma | b_{\mathbf{k}-\mathbf{q}, \beta}^{\dagger} | 0 \rangle_{ph} \right|^2 \quad (93)$$

$$= \frac{\lambda_0^2 (\hbar \omega_0)^2}{N} \sum_{\mathbf{l}, \gamma} \left| \sum_{\mathbf{q}, dc, \beta} \frac{c_{\beta}(\mathbf{k}, L) c_{\beta}^*(\mathbf{q}, dc)}{J_{\mathbf{k}, L} - (J_{\mathbf{q}, dc} + \hbar \omega_0)} \langle 0 | \hat{\mathbf{D}} \cdot \mathbf{u} | \mathbf{q}, dc \rangle_{el} \delta_{\gamma \beta} \frac{e^{i(\mathbf{k}-\mathbf{q})\mathbf{l}}}{\sqrt{N}} \right|^2 \quad (94)$$

$$= \frac{\lambda_0^2 (\hbar \omega_0)^2}{N} \sum_{\mathbf{l}, \gamma} \left| \sum_{dc} \frac{c_{\gamma}(\mathbf{k}, L) c_{\gamma}^*(\mathbf{q} = 0, dc)}{J_{\mathbf{k}, L} - (J_{\mathbf{q}=0, dc} + \hbar \omega_0)} \langle 0 | \hat{\mathbf{D}} \cdot \mathbf{u} | \mathbf{q} = 0, dc \rangle_{el} \frac{e^{i\mathbf{k}\mathbf{l}}}{\sqrt{N}} \right|^2 \quad (95)$$

$$= \lambda_0^2 (\hbar \omega_0)^2 \sum_{\gamma} \left| \sum_{dc} \frac{c_{\gamma}(\mathbf{k}, L) c_{\gamma}^*(0, dc)}{J_{\mathbf{k}, L} - (J_{0, dc} + \hbar \omega_0)} \langle 0 | \hat{\mathbf{D}} \cdot \mathbf{u} | 0, dc \rangle_{el} \frac{1}{\sqrt{N}} \right|^2 \quad (96)$$

$$= \lambda_0^2 (\hbar \omega_0)^2 \sum_{\gamma} \left| \sum_{dc} \frac{c_{\gamma}(\mathbf{k}, L) c_{\gamma}^*(0, dc)}{J_{\mathbf{k}, L} - (J_{0, dc} + \hbar \omega_0)} \mathbf{d}_{dc} \cdot \mathbf{u} \right|^2. \quad (97)$$

In the above derivation we made use of the relations

$$\langle g; \mathbf{l}, \gamma | b_{\mathbf{k}-\mathbf{q}, \beta}^{\dagger} | 0 \rangle_{ph} = \delta_{\gamma \beta} \frac{e^{i(\mathbf{k}-\mathbf{q})\mathbf{l}}}{\sqrt{N}}. \quad (98)$$

$$\langle 0 | \hat{\mathbf{D}} \cdot \mathbf{u} | 0, dc \rangle_{el} = \langle 0 | \hat{\mathbf{D}} \cdot \mathbf{u} \sum_{\alpha, \mathbf{n}} c_{\alpha}(0, dc) \frac{1}{\sqrt{N}} | \mathbf{n}, \alpha \rangle_{el} \quad (99)$$

$$= \sqrt{N} \sum_{\alpha} c_{\alpha}(0, dc) \mathbf{d}_{\alpha} \cdot \mathbf{u} = \sqrt{N} \mathbf{d}_{dc} \cdot \mathbf{u} \quad (100)$$

Appendix A. Harmonic oscillator

Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 \quad (101)$$

Eigenfunctions

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} \exp \left(-\frac{m\omega x^2}{2\hbar} \right) H_n \left(\sqrt{\frac{m\omega}{\hbar}} x \right) \quad (102)$$

with eigenenergies $E_n = \hbar \omega (n + 1/2)$. We can introduce creation and destruction operators

$$a = \sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{i}{m\omega} p \right) \quad (103)$$

$$a^{\dagger} = \sqrt{\frac{m\omega}{2\hbar}} \left(x - \frac{i}{m\omega} p \right) \quad (104)$$

which operate on the eigenfunctions as

$$a |\psi_n\rangle = \sqrt{n} |\psi_{n-1}\rangle \quad (105)$$

$$a^{\dagger} |\psi_n\rangle = \sqrt{n+1} |\psi_{n+1}\rangle \quad (106)$$

so that Hamiltonian reads $H = \hbar\omega(a^\dagger a + 1/2)$ with $[a, a^\dagger] = 1$. If we measure energy in units of $\hbar\omega$ and lengths in units of $\sqrt{\frac{2\hbar}{m\omega}}$ the Hamiltonian reads

$$H = -\frac{1}{4} \frac{\partial^2}{\partial Q^2} + Q^2 \quad (107)$$

and eigenfunctions become

$$\psi_n(Q) = \frac{1}{\sqrt{2^n n!}} (\pi/2)^{-1/4} \exp(-Q^2) H_n(\sqrt{2}Q). \quad (108)$$

A harmonic oscillator displaced by λ in "natural" coordinates has Hamiltonian

$$H = -\frac{1}{4} \frac{\partial^2}{\partial Q^2} + (Q - \lambda)^2 \quad (109)$$

and eigenfunctions

$$\psi_{n,\lambda}(Q) = \frac{1}{\sqrt{2^n n!}} (\pi/2)^{-1/4} \exp(-(Q - \lambda)^2) H_n(\sqrt{2}(Q - \lambda)). \quad (110)$$

Overlaps between these functions are usually defined as

$$S_{\mu\nu} = \langle \psi_{\mu,0} | \psi_{\nu,\lambda} \rangle \quad (111)$$

Franck-Condon factors are then given by

$$S_{0\nu}^2 = \langle \psi_{0,0} | \psi_{\nu,\lambda} \rangle^2 = \frac{\exp(-\lambda^2) \lambda^{2\nu}}{\nu!} \quad (112)$$

A Huang-Rhys factor has also been defined as $S = \lambda^2$.

Appendix B. Ewald summation for sub-dipoles

The position of a sub-dipole is given by $\mathbf{r}_{\mathbf{n},\alpha}^i$ where \mathbf{n} denotes the unit cell, α the molecule and i the sub-dipole. In particular we can write $\mathbf{r}_{\mathbf{n},\alpha}^i = \mathbf{n} + \rho_\alpha + \delta\rho_\alpha^i$, and we also introduce the symbols $\delta\mathbf{r} = \delta\rho_\alpha^i - \delta\rho_\beta^j$ and $\mathbf{R} = \mathbf{r}_{\mathbf{0},\alpha}^i - \mathbf{r}_{\mathbf{n},\beta}^j$. We now consider the value of $\tilde{L}_{\alpha,\beta}(\mathbf{k})$ and we obtain

$$\tilde{L}_{\alpha,\beta}(\mathbf{k}) = \sum_{\mathbf{n}}' \sum_{i,j=1}^{N_s} M_{\mathbf{0}\alpha i, \mathbf{n}\beta j} e^{i\mathbf{k}\mathbf{r}_{\mathbf{n}}} \equiv \frac{1}{N_s^2} \sum_{i,j=1}^{N_s} (A + B + C) \quad (113)$$

where N_s is the number of sub-dipoles, $M_{\mathbf{0}\alpha i, \mathbf{n}\beta j}$ is the dipole-dipole interaction between sub-dipoles and $\mathbf{r}_{\mathbf{n}} = \mathbf{n} + \rho_\alpha - \rho_\beta$.

$$\begin{aligned} A &= \frac{4\pi}{v} \sum_{\mathbf{K}} \frac{[(\mathbf{K} + \mathbf{k}) \cdot \mathbf{d}_\alpha][(\mathbf{K} + \mathbf{k}) \cdot \mathbf{d}_\beta]}{(\mathbf{K} + \mathbf{k})^2} \exp\left[-\frac{(\mathbf{K} + \mathbf{k})^2}{4\eta^2}\right] \\ &\times \exp[-i\mathbf{K}(\rho_\alpha - \rho_\beta)] \exp[-i(\mathbf{K} + \mathbf{k}) \cdot \delta\mathbf{r}] \end{aligned} \quad (114)$$

where \mathbf{d} is the full dipole of each molecule.

$$\begin{aligned} B &= \sum_{\mathbf{n}}' e^{i\mathbf{k}\mathbf{r}_{\mathbf{n}}} \left\{ \left[\frac{\mathbf{d}_\alpha \mathbf{d}_\beta - 3(\mathbf{d}_\alpha \hat{\mathbf{R}})(\mathbf{d}_\beta \hat{\mathbf{R}})}{R^3} \right] \left[\text{erfc}(\eta R) + \frac{2\eta R}{\sqrt{\pi}} \exp(-\eta^2 R^2) \right] \right. \\ &\quad \left. - 3(\mathbf{d}_\alpha \hat{\mathbf{R}})(\mathbf{d}_\beta \hat{\mathbf{R}}) \left[\frac{4\eta^3}{3\sqrt{\pi}} \exp(-\eta^2 R^2) \right] \right\} \\ C &= -\delta_{\alpha\beta} \left\{ \delta_{ij} \mathbf{d}_\alpha \mathbf{d}_\beta \frac{4\eta^3}{3\sqrt{\pi}} + (1 - \delta_{ij}) \left\{ \left[\frac{\mathbf{d}_\alpha \mathbf{d}_\beta - 3(\mathbf{d}_\alpha \hat{\delta\mathbf{r}})(\mathbf{d}_\beta \hat{\delta\mathbf{r}})}{\delta r^3} \right] \right. \right. \\ &\quad \left. \times \left[1 - \text{erfc}(\eta \delta r) - \frac{2\eta \delta r}{\sqrt{\pi}} \exp(-\eta^2 \delta r^2) \right] + 3(\mathbf{d}_\alpha \hat{\delta\mathbf{r}})(\mathbf{d}_\beta \hat{\delta\mathbf{r}}) \left[\frac{4\eta^3}{3\sqrt{\pi}} \exp(-\eta^2 \delta r^2) \right] \right\} \end{aligned}$$

Appendix C. Dielectric tensor

The dielectric tensor can be obtained from the computed excitonic states from the following formula

$$\epsilon_{ij}(\omega) = \epsilon_{\infty}\delta_{ij} + \frac{2}{\epsilon_0 v \hbar} \sum_n \frac{(\mathbf{d}_n)_i (\mathbf{d}_n)_j \omega_n}{\omega_n^2 - \omega^2 - i\gamma\omega}, \quad (115)$$

where v is the cell volume, $\hbar\omega_n$ and \mathbf{d}_n are the energy and transition dipole of the n -th state respectively; γ is a damping factor which can also depend on the frequency ω . We recall that there is an extra factor 2 due to the spin degeneracy, which is appropriate to excitonic singlet states, which must be included in the dipole moment value \mathbf{d}_n . The above expression corresponds to an oscillator strength of

$$f_n = \frac{2m\omega_n \mathbf{d}_n^2}{e^2 \hbar}, \quad (116)$$

for each excitonic transition, where again the extra factor 2 must be included in the dipole moment value \mathbf{d}_n and it is appropriate to excitonic singlet states. This can be seen by comparing the above expression for ϵ with its general form:

$$\epsilon = \epsilon_b + \sum_n \frac{f_n \omega_p^2}{\omega_n^2 - \omega^2}, \quad (117)$$

where we neglected damping, ϵ_b is a background dielectric constant and

$$\omega_p^2 = \frac{e^2}{vm\epsilon_0}. \quad (118)$$

If dipoles are expressed in Debyes, energies in eV and lengths in Å, formula (115) reduces to

$$\epsilon_{ij}(\omega) = \epsilon_{\infty}\delta_{ij} + \frac{8\pi}{1.602v} \sum_n \frac{(\mathbf{d}_n)_i (\mathbf{d}_n)_j E_n}{E_n^2 - E^2 - i\Gamma E}, \quad (119)$$

where $E_n = \hbar\omega_n$, $E = \hbar\omega$ and $\Gamma = \hbar\gamma$. We obtained the above coefficient by using the following constants and conversions

$$\epsilon_0 = 8.8541 \times 10^{-12} C^2 m^{-2} N^{-1} \quad (120)$$

$$1D = 3.336 \times 10^{-30} Cm = e10^{-20}m \quad (121)$$

$$1eV = 1.602 \times 10^{-19} J \quad (122)$$

$$\hbar c = 1.97327 \times 10^{-7} m \cdot eV \quad (123)$$

$$mc^2 = 0.511 \times 10^6 eV \quad (124)$$

The above formulas are equivalent to the gaussian units expression

$$\epsilon_{ij}(\omega) = \epsilon_{\infty}\delta_{ij} + \frac{8\pi}{v\hbar} \sum_n \frac{(\mathbf{d}_n)_i (\mathbf{d}_n)_j \omega_n}{\omega_n^2 - \omega^2 - i\gamma\omega}, \quad (125)$$

where dipoles are in statC · cm, energies in erg, lengths in cm and statC = cm \sqrt{dyn} . We recall that gaussian units expressions can be obtained substituting each SI charge q with $q\sqrt{4\pi\epsilon_0}$.

We finally note that the oscillator strength indicated by Gaussian is $f_n^{(Gaussian)} = f_n/3$ and gives a dipole moment in Debyes of

$$|\mathbf{d}_n| = \sqrt{\frac{3}{2} 175.8 \frac{f_n^{(Gaussian)}}{E_n}} = 16.239 \sqrt{\frac{f_n^{(Gaussian)}}{E_n}}, \quad (126)$$

where E_n is expressed in eV.

5 Appendix D. Weak electronic coupling: vibronic approximation

Conditions: $W \ll \hbar\omega_0$ and $k_B T \ll \hbar\omega_0$. We assume that the emitting states are only the σ lowest energy vibronic states in each Davydov subspace. Vibronic states are one-particle states that can be written as

$$\psi_{\mathbf{k},dc,n=0} = \sum_{\alpha,\tilde{\mu}} c_{\alpha,\tilde{\mu}}(\mathbf{k},dc) |\mathbf{k}, \alpha, \tilde{\mu}\rangle = \sum_{\alpha,\tilde{\mu},\mathbf{n}} c_{\alpha,\tilde{\mu}}(\mathbf{k},dc) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} |\mathbf{n}, \alpha, \tilde{\mu}\rangle \quad (127)$$

$$|\mathbf{k}, \alpha, \tilde{\mu}\rangle \equiv \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} \sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} |\mathbf{n}, \alpha, \tilde{\mu}\rangle, \quad (128)$$

$$I_{\mathbf{u}}^{0-0}(\mathbf{k}, dc, 0) = \left| \langle \psi_{\mathbf{k},dc,0} | \hat{\mathbf{D}} \cdot \mathbf{u} | 0 \rangle \right|^2 = \left| \langle \psi_{\mathbf{k},dc,0} | \hat{\mathbf{D}} | 0 \rangle \cdot \mathbf{u} \right|^2 \quad (129)$$

$$= \left| \sum_{\alpha,\tilde{\mu},\mathbf{n}} \sum_{\mathbf{m},\beta} c_{\alpha,\tilde{\mu}}(\mathbf{k},dc) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} \langle \mathbf{n}, \alpha | \mathbf{m}, \beta \rangle \langle \tilde{\mu} | 0 \rangle \mathbf{d}_\beta \cdot \mathbf{u} \right|^2 \quad (130)$$

$$= \left| \sum_{\alpha,\tilde{\mu},\mathbf{n}} c_{\alpha,\tilde{\mu}}(\mathbf{k},dc) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} \langle \tilde{\mu} | 0 \rangle \mathbf{d}_\alpha \cdot \mathbf{u} \right|^2 \quad (131)$$

$$= \delta(\mathbf{k}) \left| \sum_{\alpha,\tilde{\mu}} c_{\alpha,\tilde{\mu}}(\mathbf{k},dc) \sqrt{N} e^{-i\mathbf{k}\rho_\alpha} \langle \tilde{\mu} | 0 \rangle \mathbf{d}_\alpha \cdot \mathbf{u} \right|^2 \quad (132)$$

$$= N \delta(\mathbf{k}) \left| \sum_{\alpha,\tilde{\mu}} c_{\alpha,\tilde{\mu}}(\mathbf{k}=0,dc) S_{\tilde{\mu}0} \mathbf{d}_\alpha \cdot \mathbf{u} \right|^2 \quad (133)$$

$$(134)$$

where we used the relation

$$\sum_{\mathbf{n}} \frac{1}{N} e^{i\mathbf{k}\mathbf{n}} = \delta(\mathbf{k}). \quad (135)$$

Now we give the expression for the line strength of the first replica, which ends on states $|g; \mathbf{l}, \gamma\rangle$ in which all molecules are in their electronic ground state and there is one vibrational quantum on molecule (\mathbf{l}, γ) :

$$I_{\mathbf{u}}^{0-1}(\mathbf{k}, dc, n=0) = \sum_{\mathbf{l}, \gamma} \left| \langle \psi_{\mathbf{k}, dc, 0} | \hat{\mathbf{D}} \cdot \mathbf{u} | g; \mathbf{l}, \gamma \rangle \right|^2 \quad (136)$$

$$= \sum_{\mathbf{l}, \gamma} \left| \sum_{\alpha, \tilde{\mu}, \mathbf{n}} \sum_{\mathbf{m}, \beta} c_{\alpha, \tilde{\mu}}(\mathbf{k}, dc) \frac{e^{-i\mathbf{k}\rho_{\alpha}}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} \langle \mathbf{n}, \alpha | \mathbf{m}, \beta \rangle_{el} \langle \tilde{\mu}_{\mathbf{n}, \alpha} | \mathbf{l}, \gamma \rangle_{ph} \mathbf{d}_{\beta} \cdot \mathbf{u} \right|^2 \quad (137)$$

$$= \sum_{\mathbf{l}, \gamma} \left| \sum_{\tilde{\mu}} \sum_{\mathbf{m}, \beta} c_{\gamma, \tilde{\mu}}(\mathbf{k}, dc) \frac{e^{-i\mathbf{k}\rho_{\gamma}}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{l}} \langle \mathbf{l}, \gamma | \mathbf{m}, \beta \rangle_{el} \langle \tilde{\mu} | 1 \rangle_{ph} \mathbf{d}_{\beta} \cdot \mathbf{u} \right|^2 \quad (138)$$

$$= \sum_{\mathbf{l}, \gamma} \left| \sum_{\tilde{\mu}} c_{\gamma, \tilde{\mu}}(\mathbf{k}, dc) \frac{e^{-i\mathbf{k}\rho_{\gamma}}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{l}} S_{\tilde{\mu}1} \mathbf{d}_{\gamma} \cdot \mathbf{u} \right|^2 \quad (139)$$

$$= \frac{1}{N} \sum_{\mathbf{l}, \gamma} \left| \sum_{\tilde{\mu}} c_{\gamma, \tilde{\mu}}(\mathbf{k}, dc) e^{-i\mathbf{k}\rho_{\gamma}} S_{\tilde{\mu}1} \mathbf{d}_{\gamma} \cdot \mathbf{u} \right|^2 \quad (140)$$

$$= \sum_{\gamma} \left| \sum_{\tilde{\mu}} c_{\gamma, \tilde{\mu}}(\mathbf{k}, dc) S_{\tilde{\mu}1} e^{-i\mathbf{k}\rho_{\gamma}} \mathbf{d}_{\gamma} \cdot \mathbf{u} \right|^2 \quad (141)$$