

# Raman scattering with strongly coupled vibron-polaritons

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Strong coupling between cavity photons and molecular vibrations can lead to the formation of vibron-polaritons. In a recent experiment with PVAc molecules in a metal-metal microcavity [A. Shalabney *et al.*, *Ang. Chem. Int. Ed.* **54** 7971 (2015)], such a coupling was observed to enhance the Raman scattering probability by several orders of magnitude. Inspired by this, we theoretically analyze the effect of strong photon-vibron coupling on the Raman scattering amplitude of organic molecules. This problem has recently been addressed in [J. del Pino, J. Feist and F. J. Garcia-Vidal; *J. Phys. Chem. C* **119** 29132 (2015)] using exact numerics for a small number of molecules. In this paper we derive compact analytic results for any number of molecules, also including the ultra-strong coupling regime. Our calculations predict a division of the Raman signal into upper and lower polariton modes, with some enhancement to the lower polariton Raman amplitude due to the mode softening under strong coupling.

## I. INTRODUCTION

Light can be used to probe condensed matter systems, but also, as is increasingly being explored, light can be used to change the material properties of systems. Examples of the latter range from topological Floquet insulators[1–4], where electronic band structure is modified by a drive field, to light induced superconductivity [5–8]. These examples all rely on strong driving, however recently there have been experimental [9–11] and theoretical [12–17] works exploring how similar effects can arise without driving for organic materials strongly coupled to optical microcavities. In some cases, light can be used both to probe the system, as well as to change its properties. This applies particularly when there are multiple optically active transitions, such as infra-red active vibrational modes in addition to optical frequency electronic transitions [18]. This paper studies such a problem in detail.

Organic materials are excellent systems for the exploration of strong matter-light coupling, due to their large electronic oscillator strengths and high binding energies. Most work has focused on strong coupling of light to electronic transitions [19–23] and the resultant formation of two hybrid matter-light excitations, known as exciton-polaritons. The strength of the matter-light coupling can be characterized by the energy splitting between these modes. Strong coupling occurs when this splitting exceeds the linewidth. Ultra-strong coupling occurs when this splitting approaches the bare exciton and photon energies [24]. For organic exciton-polaritons, Rabi splittings of 32% [9], 52% [25], and up to 60% [26] of the bare exciton energy have been demonstrated. In addition to the interest arising from ultra-strong coupling, organic materials are also interesting because of the relatively strong coupling between electronic state and internal mechanical degrees of freedom of organic molecules (rotations and vibrations), leading to the complex interplay between matter-light coupling and internal structure discussed above [9–17]. Of specific relevance to this

paper, it was shown in several recent experiments [27–31] that it is also possible to achieve strong coupling between infra-red microcavities and vibrational modes of molecules, leading to “vibron-polaritons”.

Organic materials where both electronic and vibronic transitions couple to light, as well as coupling to each other, present rich possibilities for manipulating properties of matter with light or matter-light coupling. An example of this was work by Shalabney *et al.* [18] where it was shown experimentally that in an infra-red cavity, forming vibron-polaritons, there were dramatic consequences for the Raman scattering (RS) of optical frequency light. The Raman transition probability to a final vibrationally excited state splits between the vibron-polariton modes (referred to below as lower polariton (LP) and upper polariton (UP)). The most intriguing result of [18] is however that the total Raman cross-section was enhanced by three orders of magnitude when the infra-red cavity was resonant with the vibrational modes. Consequently, a new mechanism for RS enhancement was proposed, which is essentially distinct from other methods of RS enhancement such as stimulated RS [32], surface enhanced RS [33, 34], or the recently proposed enhancement by parametric plasmon-vibron coupling [35].

Motivated by these experiments, the aim of this paper is to analyze the effect of strong photon-vibron coupling on the RS probability. In modeling organic systems, a variety of approaches are possible [14, 36], depending on the scale of the problem to be tackled. In this paper, we are focused on understanding the behavior of the  $N$ -molecule system for arbitrary  $N$ , in order to explore what if any collective enhancement of Raman scattering arises. As such, we consider a simplified model of each molecule, describing only one (harmonic) vibrational mode coupled to the electronic transition. Without further approximation, it is in fact possible to derive exact formulae for Raman transition amplitudes. The results we find could also be generalized to multiple vibrational modes (while retaining a closed form analytic expression), or to non-harmonic modes (but then losing the closed form). Given our aim of exploring the nature of collective enhance-

ment, such modifications of our model are not important.

We should note that theoretical calculations of Raman scattering with strongly coupled vibron-polaritons has recently been addressed by del Pino *et al.* [37], who discussed the general behaviour for  $N$  molecules when treated as three-level systems, and performed exact numerics for a small number of molecules using the same model we use below. Their results suggested there is no collective enhancement of Raman scattering. We confirm and extend these results by presenting analytic results for an arbitrary number of molecules, hence confirming the absence of a collective RS enhancement effect. We do however find that the total Raman amplitude can in principle be significantly enhanced at ultra-strong coupling, by softening of the lower polariton mode, however this requires coupling strengths in excess of those seen in Ref. [18].

The remainder of this paper is organized as follows. We divide our discussion into calculations within the rotating wave approximation (Section II) and beyond the rotating wave approximation (Section III). Section II A defines our notation, by presenting the model we consider, and the matrix elements we must calculate. Section II B derives the explicit form of Raman transition matrix elements as a sum over intermediate states. Crucially, section II C then shows how these sums can be performed analytically, resulting in a relatively compact expression. Using coefficients and energies derived in Sec. II D, section II E presents numerical results, and analytic forms for the far detuned limit. Beyond the rotating wave approximation, Section III A presents an alternate approach to calculating Raman transition matrix elements, and Section III B presents corresponding numerical results. Finally, in section IV we extend the rotating-wave approximation formulae to consider final states with multiple vibron-polaritons, and discuss the relative scaling with system size of the different excitation number sectors. Appendices provide further details of some of the mathematical steps.

## II. WITHIN THE ROTATING WAVE APPROXIMATION

### A. Modeling Raman probabilities

We consider a single mode cavity, containing  $N$  molecules. We represent each molecule by two degrees of freedom: two electronic states (corresponding to HOMO and LUMO) levels, and a single vibrational mode. In this respect the model is similar to the ‘‘Tavis-Cummings-Holstein’’ model used recently [12, 17, 38] to model vibrational dressing of polaritons. However, here we consider the case where it is the molecular vibrations, rather than the electronic transition, which couples to the cavity mode. This model is shown schematically in Fig. 1.

The main simplifying assumption in such a model (the same model as used in Ref. [37]) is the replacement of

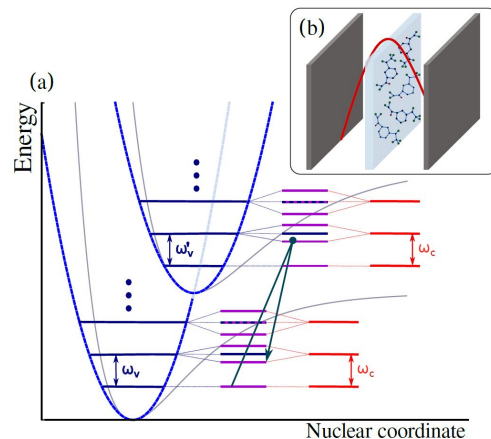


FIG. 1. (a) Schematic illustration of the vibronic energy levels in the two electronic manifold (left) and their hybridization with photon number states (right) to form a ladder of polariton states (middle). (b) Cartoon of molecules placed at the antinode of an optical cavity.

full intramolecular potential by a single harmonic degree of freedom. This is valid in the limit where only a single collective mode dominates the physics, either due to coupling most strongly to the electronic transitions, or due to the resonant cavity coupling predominantly to one mode. From the Raman spectrum seen without strong coupling, this is clearly the relevant regime in Ref.[18]. In this paper we will consider this problem both with and without the rotating wave approximation (RWA). Within the RWA, the Hamiltonian takes the following form:

$$H = \omega_c \hat{a}^\dagger \hat{a} + \sum_n \left( \omega_e \sigma_n^\dagger + \omega_v [\hat{b}_n^\dagger \hat{b}_n + \sqrt{S} (\hat{b}_n^\dagger + \hat{b}_n) \sigma_n^\dagger] + G (\hat{b}_n^\dagger \hat{a} + \hat{b}_n \hat{a}^\dagger) \right). \quad (1)$$

Here  $\hat{a}$  is the annihilation operator for the cavity photon modes with frequency  $\omega_c$ . The Pauli operators  $\sigma_n$  describe transitions of the electronic state of molecule  $n$ , with energy splitting  $\omega_e$ , and we have used the shorthand  $\sigma_n^\dagger = (1 + \sigma_n^z)/2$  for the projector onto the excited state. Finally  $\hat{b}_n$  is the annihilation operator for the vibrational mode of molecule  $n$ , with frequency  $\omega_v$ . The coupling between electronic and vibrational states is parameterized by the Huang–Rhys parameter  $S$ , which describes the relative displacement of the vibrational mode between the electronic ground and excited states. The coupling between cavity photons and vibrational modes is denoted  $G$ .

Using the above Hamiltonian, we are going to calculate the probability of Raman scattering to a polaritonic mode (in the presence of a cavity) and compare it with the Raman scattering probability to the bare vibrational mode without a cavity. In order to study Raman scattering, we consider a weak driving field  $E_{\text{applied}}(t) \sum_n \sigma_n^x$ , which we treat perturbatively. In second order perturbation theory, and using the resonant approximation the

probability of scattering can be written as [39]:

$$P_{0 \rightarrow f_k} = \left| \sum_P \frac{\langle 0 | \hat{V}_1 | P \rangle \langle P | \hat{V}_2 | f_k \rangle}{E_P - E_0 - \omega} \right|^2, \quad (2)$$

where  $\omega$  is the frequency of the applied probe field,  $E_0$  is initial state energy and  $E_P$  the intermediate state energy. The states  $|0\rangle, |P\rangle, |f_k\rangle$  denote initial, intermediate and final states — we have allowed a label  $k$  to distinguish different final states (e.g. upper vs lower polariton excitations). The operators  $\hat{V}_1, \hat{V}_2$  can be written explicitly in terms of coupling between the total dipole operator  $\sum_m \sigma_m^x$  of the molecules and the incident and emitted light. As our aim is ultimately to compare the probabilities for polaritonic and "ordinary" Raman scattering, we can however ignore all constant prefactors. Ignoring also dependence on the polarization of the light we may write the transition probability as:

$$P_{0 \rightarrow f_k} = \gamma |M_k|^2, \quad M_k = \sum_{m,P} \frac{\langle 0 | \sigma_m^- | P \rangle \langle P | \sigma_m^+ | f_k \rangle}{E_P - E_0 - \omega} \quad (3)$$

where  $\gamma$  describes the (constant) electronic matrix elements and density of final photon states,  $m$  labels the specific molecules that is excited, and  $P$  labels the intermediate states. NB, the sum over molecules appears within the modulus squared, so that interference between separate molecules' Raman scattering processes are allowed. Note also that in Eq. (3) there are no cross terms between different molecules, as these vanish due to the assumed initial electronic ground state.

When considering the experimentally measured Raman spectrum, this can be written as corresponding to:

$$P(\nu) \propto \sum_k \delta(\nu - E_k) |M_k|^2 \quad (4)$$

where  $E_k$  is the energy of the final state mode, and  $\nu$  is the measured Stokes shift. This can be important when multiple degenerate modes exist, such that the labeling of final states is arbitrary. In such a case, the measurable quantity is the sum of the probabilities of transitions to the manifold of degenerate final states.

## B. Calculating matrix elements

Calculating the amplitude  $M_k$  in Eq. (3) requires us to find the initial, intermediate and final eigenstates of Eq. (1), and evaluate the matrix elements of  $\sigma_n^\pm$  between these states. Since Eq. (1) is clearly diagonal in electronic state, there are two cases we should consider, the electronic ground state, which we denote  $H_{\text{eff},\downarrow}$  and the state where the  $m^{\text{th}}$  molecule is electronically excited,  $H_{\text{eff},m}$

$$H_{\text{eff},\downarrow} = \omega_c \hat{a}^\dagger \hat{a} + \sum_n \left[ \omega_n \hat{b}_n^\dagger \hat{b}_n + G(\hat{b}_n^\dagger \hat{a} + \hat{b}_n \hat{a}^\dagger) \right] \quad (5)$$

$$H_{\text{eff},m} = H_{\text{eff},\downarrow} + \omega_v \sqrt{S} (\hat{b}_m + \hat{b}_m^\dagger). \quad (6)$$

For the electronic ground state,  $H_{\text{eff},\downarrow}$  can be diagonalized by introducing  $\hat{\xi}_i = v_i \hat{a} + \sum_n U_{n,i} \hat{b}_n$ , which obey the required commutation relations  $[\hat{\xi}_i, \hat{\xi}_j^\dagger] = \delta_{i,j}$ . In this diagonalized basis we may write  $H_{\text{eff},\downarrow} = \sum_i \omega_i \hat{\xi}_i^\dagger \hat{\xi}_i$  where  $\omega_i$  denotes the frequencies of the normal modes. These give us  $N+1$  eigenmodes: 2 polaritonic modes and  $N-1$  degenerate dark modes (which have no photonic part,  $v_i \equiv 0$ ). From the permutation symmetry of the Hamiltonian, it is clear that for the polaritonic modes  $U_{n,i \in LP, UP}$  should be independent of  $n$ , and so orthogonality requires that the dark modes satisfy  $\sum_n U_{n,i \in \text{Dark}} \equiv 0$ .

For the excited state  $H_{\text{eff},m}$ , diagonalization requires an additional linear displacement to remove the linear terms. Since the quadratic terms in Eq. (5,6) are identical, the unitary transformation required is the same for both Hamiltonians. This means one may write  $\hat{\eta}_i = \hat{\xi}_i + \alpha_{m,i}$ , one may use the identity

$$\begin{aligned} H_{\text{eff},m} &= \sum_i \left[ \omega_i \hat{\xi}_i^\dagger \hat{\xi}_i + \omega_i \left( \alpha_{m,i}^* \hat{\xi}_i + \alpha_{m,i} \hat{\xi}_i^\dagger \right) \right] \\ &= \sum_i \omega_i \hat{\eta}_i^\dagger \hat{\eta}_i - \omega_i |\alpha_{m,i}|^2. \end{aligned}$$

to diagonalize the problem. Comparison to Eq. (6) shows that this requires  $\omega_i \alpha_{m,i} = U_{m,i} \omega_v \sqrt{S}$ . Since the explicit form of the  $\omega_i, \alpha_{m,i}$  is not required to deriving the transition probability, we will defer its calculation to section II D. It is however useful to note that from the above, we know that dark states, being purely vibrational will have  $\omega_i = \omega_v$  and obey  $\sum_m \alpha_{m,i} = 0$ .

Using the linear relation between  $\hat{\eta}_i$  and  $\hat{\xi}_i$  given above, one may relate the ground state in the electronic ground state manifold  $|0_\downarrow\rangle = |\downarrow; 0_{LP}, 0_{UP}, 0_1, 0_2, \dots, 0_{N-1}\rangle$  to that in the manifold where the  $m^{\text{th}}$  molecule is excited  $|0_m\rangle = |\uparrow_m; 0_{LP}, 0_{UP}, 0_1, 0_2, \dots, 0_{N-1}\rangle$ . These states are related by:

$$|0_m\rangle = e^{-\sum_i (\alpha_{m,i} \hat{\xi}_i^\dagger - \alpha_{m,i}^* \hat{\xi}_i)} |0_\downarrow\rangle. \quad (7)$$

The matrix elements appearing in Eq. (3) can then be written out using this relation. Let us denote the required overlaps as  $\mathcal{M}_{0,P}^{(m)} \equiv \langle 0 | \sigma_m^- | P \rangle$  and  $\mathcal{M}_{f_k,P}^{(m)} \equiv \langle f_k | \sigma_m^+ | P \rangle$ . If we label the intermediate states  $P$  by the set of occupations  $\{p_i\}$  of each normal mode, this expression becomes:

$$M_k = \sum_{m,\{p_i\}} \frac{\mathcal{M}_{f_k,\{p_i\}}^{(m)*} \mathcal{M}_{0,\{p_i\}}^{(m)}}{\Delta + \sum_i p_i \omega_i} \quad (8)$$

where  $\Delta = \omega_e - \omega$  is the detuning of the probe laser below the electronic transition. Using the displacement relation in Eq. (7), we may see what the overlap between

ground state and intermediate state is given by:

$$\begin{aligned}
\mathcal{M}_{0,\{p_i\}}^{(m)} &\equiv \langle 0_{\downarrow} | \prod_i \frac{\hat{\eta}_i^{\dagger p_i}}{\sqrt{p_i!}} | 0_m \rangle \\
&= \langle 0_{\downarrow} | \prod_i \frac{(\hat{\xi}_i^{\dagger} + \alpha_{m,i}^*)^{p_i}}{\sqrt{p_i!}} e^{-\alpha_{m,i} \hat{\xi}_i^{\dagger} - |\alpha_{m,i}|^2/2} | 0_{\downarrow} \rangle \\
&= \prod_i \frac{\alpha_{m,i}^{* p_i} e^{-|\alpha_{m,i}|^2/2}}{\sqrt{p_i!}}. \tag{9}
\end{aligned}$$

The other matrix element describes the transition from the intermediate state to a given final state. If we consider the final state with a single excitation of mode  $k$ , this can be written as:

$$\mathcal{M}_{f_k,\{p_i\}}^{(m)} = \mathcal{M}_{0,\{p_i\}}^{(m)} \frac{p_k - |\alpha_{m,k}|^2}{\alpha_{m,k}^*}. \tag{10}$$

As discussed in Section IV and Appendix C, this is a special case of the more general formula for a final state with arbitrary occupations of multiple modes in the final state.

Putting the above results together, we find the following expression for the matrix elements for single final-state excitations.

$$M_k = \sum_m \frac{1}{\alpha_{m,k}} \sum_{\{p_i\}} \prod_i \left( e^{-|\alpha_{n,i}|^2} \frac{|\alpha_{n,i}|^{2p_i}}{p_i!} \right) \frac{p_k - |\alpha_{m,k}|^2}{\Delta + \sum_j p_j \epsilon_j}, \tag{11}$$

In the limit of large  $\Delta$ , the denominator can be Taylor expanded, and at leading order the summations can be evaluated. In the next section, we show that this can also be rewritten in a form that makes its evaluation straightforward for all parameter values.

### C. Compact form of matrix elements

In evaluating the sum over  $p_i$  in Eq. (11), the complication is the appearance of  $\sum_j p_j \epsilon_j$  in the denominator. This can be addressed by rewriting the denominator as the integral of an exponential, which then allows all summations of  $p_i$  to be evaluated analytically, as follows:

$$\begin{aligned}
M_k &= \int_0^{\infty} dz e^{-z\Delta} \sum_m \frac{1}{\alpha_{m,k}} \sum_{\{p_i\}} (p_k - |\alpha_{m,k}|^2) \\
&\quad \times \left( \prod_i \frac{(|\alpha_{m,i}|^2 e^{-z\omega_i})^{p_i} e^{-|\alpha_{m,i}|^2}}{p_i!} \right) \\
&= \int_0^{\infty} e^{-z\Delta} \sum_m \frac{(e^{-z\omega_k} - 1)}{\alpha_{m,k}} |\alpha_{m,k}|^2 \prod_i e^{|\alpha_{m,i}|^2 (e^{-z\omega_i} - 1)},
\end{aligned}$$

thus we can write the final expression in the compact form:

$$\begin{aligned}
M_k &= \sum_m \int_0^{\infty} dz e^{-z\Delta} \alpha_{m,k}^* (e^{-z\omega_k} - 1) \\
&\quad \times \exp \left[ - \sum_i |\alpha_{m,i}|^2 (1 - e^{-z\omega_i}) \right]. \tag{12}
\end{aligned}$$

This is one of the central results of this manuscript; we next discuss the analysis of this result, and then consider the generalization beyond the rotating wave approximation.

It can be immediately seen from Eq. (4) that there is no transition to the dark modes, as orthogonality to bright states implies that  $\sum_m \alpha_{m,k} = 0$ ; we discuss this further below. For the remaining bright states,  $\alpha_{m,k}$  is independent of  $m$ , and so the sum over  $m$  appearing in Eq. (12) can be replaced by a factor  $N$ . In the next section, we discuss further details of the behavior of Eq. (12), which rely on the form of  $\omega_i, \alpha_{m,i}$ .

### D. Calculating eigenstates

As noted above,  $H_{\text{eff},\downarrow}$  can be diagonalized by introducing Bosonic operators  $\hat{\xi}_i = v_i \hat{a} + \sum_n U_{n,i} \hat{b}_n$ . This section discusses the coefficients  $v_i, U_{n,i}$  and frequencies  $\omega_i$ , which result.

The eigenstates divide into two classes; two polaritonic modes (involving photons), and  $N - 1$  dark modes for which  $v_i = 0$ . For the polaritonic modes one has:

$$\omega_i \equiv \omega_{1,2} = \frac{\omega_c + \omega_v}{2} \pm \sqrt{\left(\frac{\omega_c - \omega_v}{2}\right)^2 + NG^2}. \tag{13}$$

Enforcing Bosonic commutation relations on  $\hat{\xi}_i$  determines their normalization, so that for the two bright modes one may write:  $U_{n,1} = \sin(\theta)/\sqrt{N}, v_1 = -\cos(\theta)$  and  $U_{n,2} = \cos(\theta)/\sqrt{N}, v_2 = -\sin(\theta)$  where

$$\tan(2\theta) = \frac{G\sqrt{N}}{(\omega_c - \omega_v)/2}. \tag{14}$$

Note that for these modes, the symmetry of the matter-light coupling requires that  $U_{n,i}$  is independent of the molecule label  $n$ .

For the remaining  $N - 1$  dark modes ( $v_i \equiv 0$ ) these are purely vibronic and so  $\omega_i = \omega_v$ . Orthogonality to the bright polaritons demands that  $\sum_n U_{n,i} = 0$ , and normalization imposes the condition  $\sum_n U_{n,i} U_{n,j}^* = \delta_{i,j}$ .

It is clear that the above equations do not uniquely define the dark-state values of  $U_{n,i}$ ; any  $N - 1$  orthonormal modes that are orthogonal to the symmetric mode will suffice. As such, the coefficients

$$\alpha_{m,i} = U_{m,i} \sqrt{S} \frac{\omega_v}{\omega_i} \tag{15}$$

appearing in the observable Raman amplitude in Eq. (12) are not uniquely determined. However, as we discuss next, one can check that the overall result of Eq. (12) is invariant under this freedom.

For all modes, the exponent involves the sum over all modes  $\sum_i |\alpha_{m,i}|^2 (1 - e^{-z\omega_i})$ . Using Eq. (15), the contribution of dark modes to this sum can be seen to be given by  $\sum_{i \in \text{Dark}} |U_{m,i}|^2 = (N-1)/N$ , requiring only the orthonormality and completeness of the coefficients  $U_{m,i}$ . Since the bright modes have coefficients  $\alpha_{m,i}$  that are independent of the molecule label  $m$ , it is clear that the exponent in Eq. (12) does not depend on the molecule label  $m$ . This confirms that the scattering rate into dark modes vanishes because of the condition  $\sum_m \alpha_{m,i \in \text{Dark}} = 0$ , while for the bright modes, the sum over molecules  $m$  can be replaced by a factor  $N$ .

It is worth noting two explicit choices for  $U_{m,i}$  that lead to particularly simple demonstrations of the above results:

*a. Symmetric dark-state basis.* The most obvious choice is to write

$$U_{m,j} = \frac{\exp(i2\pi mj/N)}{\sqrt{N}} \quad (16)$$

where  $j = 1 \dots N-1$  for the dark modes. This clearly satisfies the above expressions as  $|U_{m,j \in \text{Dark}}|^2 = 1$ . This choice has the apparent advantage of treating all molecules equivalently.

*b. Alternate dark-state basis.* An alternate choice is to treat the molecule  $m$  that is electronically excited differently to the others. This then leads to the choice:

$$U_{n,j_0} = \frac{1}{\sqrt{N(N-1)}} \begin{cases} N-1 & n = m \\ -1 & n \neq m \end{cases}, \quad (17)$$

$$U_{n,j \neq j_0} = \frac{1}{\sqrt{N-1}} \begin{cases} 0 & n = m \\ \exp\left(\frac{i2\pi j\tilde{n}}{N-1}\right) & n \neq m \end{cases}.$$

The quantity  $\tilde{n}$  appearing in the last expression is a sequential integer indexing the  $N-1$  molecules excluding molecule  $m$ . Note that there are only  $N-2$  modes  $j \neq j_0$  in the second expression as  $j$  and  $j+N-1$  are equivalent, and  $j=0$  is not orthogonal to the mode  $j_0$ .

The advantage of this choice of basis is that  $U_{m,j \neq j_0} = 0$  means that these terms immediately drop out Eq. (12). i.e., only three modes, two bright and one dark, contribute to the exponent. For these three modes, one can write:

$$\alpha_{m,i} = \sqrt{\frac{S}{N}} \left( \cos \theta \frac{\omega_v}{\omega_{LP}}, \sin \theta \frac{\omega_v}{\omega_{UP}}, \sqrt{N-1} \right), \quad (18)$$

and on resonance, one can further simplify  $\cos \theta = \sin \theta = 1/\sqrt{2}$  and  $\omega_{LP,UP} = \omega_v \mp G\sqrt{N}$ .

## E. Numerical results and large $\Delta$ approximation

In Figure (2) we plot the Raman scattering probability (normalized by the probability in the absence of

matter-light coupling) as a function of the matter-light coupling  $G$ , for the resonant case  $\omega_v = \omega_c$ . For this (and subsequent) figures we choose an unrealistically small value of  $\Delta = \omega_e - \omega$ , so as to exaggerate the effect of matter-light coupling, in order to see how large the effects can be under the best possible circumstances. We discuss below the analytic approximation that arises for  $\Delta \gg G\sqrt{N}, \omega_v, \omega_c$ , a regime often used experimentally. We should also note that the RWA approximation used in this section is only valid only for  $G\sqrt{N} \ll \omega_v, \omega_c$ , so at the largest values of  $G\sqrt{N}$  shown, these results will be modified as discussed below. We can however conclude that, as also found in Ref. [37], within the limit of validity of this approach the total Raman scattering cross-section changes only slightly with matter-light coupling. As one can anticipate from Eq. (18), on resonance the lower polariton has a higher scattering rate due to the larger value of  $\omega_v/\omega_{LP}$ .

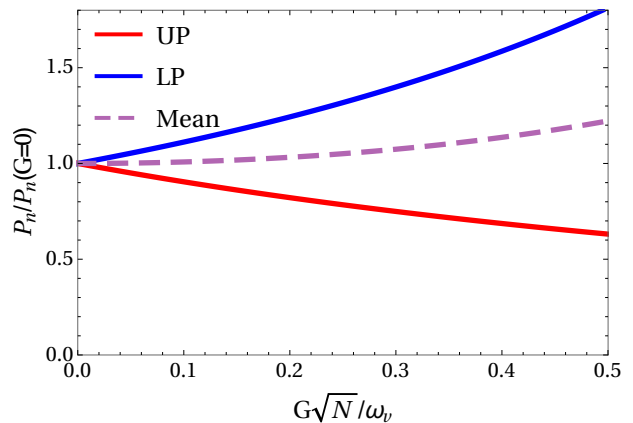


FIG. 2. Transition probability to the upper and lower polariton in the RWA. Plotted for  $\omega_c = \omega_v$ ,  $S = 0.3$ ,  $N = 10^6$  molecules, and  $\Delta = \omega_v$ . Note that, as discussed in the text, such a value of  $\Delta$  is far smaller than experimentally relevant, and thus exaggerates the size of any effect.

A fully analytic result can also be extracted from this expression by considering the limit  $\Delta \gg \omega_c, \omega_v, G\sqrt{N}$ , a limit also discussed in Ref. [37]. In this limit, the integral over  $z$  is dominated by values  $z \ll 1/\Delta$ , for which one may approximate  $1 - e^{-z\omega_i} \simeq z\omega_i$ , giving the result:

$$M_k \approx N\alpha_k\omega_k \left[ \Delta + \sum_j |\alpha_j|^2 \omega_j \right]^{-2}. \quad (19)$$

For the resonant case, if we define  $\zeta = G\sqrt{N}/\omega_v$  we have that  $\omega_{UP,LP} = \omega_v(1 \pm \zeta)$ . Using these expressions and Eq. (18) then gives:

$$M_{k \in LP,UP} \approx \frac{\sqrt{SN/2} \omega_v}{\left[ \Delta + \frac{S}{N} \omega_v \left( N - 1 + \frac{1}{1-\zeta^2} \right) \right]^2}. \quad (20)$$

Due to the  $N$ -dependent term in the denominator, the effect of matter-light coupling, via  $\zeta$ , is in general weak

in this expression, and the upper and lower polariton rates would be equal. However, as  $\zeta \rightarrow 1$ , the expression vanishes, as the denominator diverges. The range of  $\zeta$  for which this divergence manifests itself is set by  $1 > \zeta \gtrsim \zeta_0$ , where  $\zeta_0 \simeq 1 - \frac{1}{2N}$ . However, at such strong coupling the RWA is not valid. We will see below how this divergence behaves beyond the RWA. In summary, for large  $\Delta$ , there is no enhancement of Raman scattering within the RWA, while for small  $\Delta$ , Fig. 2 shows some enhancement.

In Fig. (3) we present the effect of the cavity–vibron detuning  $\delta \equiv (\omega_c - \omega_v)$  on the probability of the Raman scattering. As one might expect, for large detunings the Raman scattering occurs predominantly into the mode with the larger excitonic component. However, equal scattering weights require a negative detuning, as the lower energy of the lower polariton enhance their scattering relative to the upper polariton.

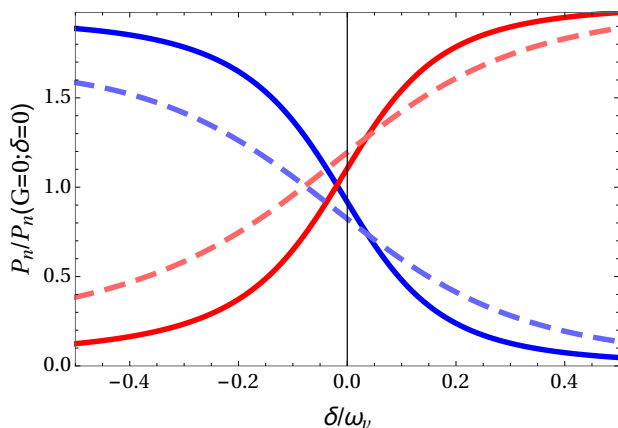


FIG. 3. Transition probability to the LP and UP dependence on the vibron-cavity photon detuning in RWA. Red lines: lower polariton, blue lines: upper polariton. Solid lines correspond to  $G\sqrt{N} = 0.1\omega_v$ , and dashed lines to  $G\sqrt{N} = 0.2\omega_v$ .

### III. ULTRA-STRONG COUPLING & $\omega_v$ DEPENDENCE OF THE ELECTRONIC STATE

As noted earlier, in the ultra-strong coupling regime,  $G\sqrt{N} \gg \omega_v$ , the RWA breaks down and we must modify the Hamiltonian in Eq. (1), by replacing  $G(\hat{b}_n^\dagger \hat{a} + \hat{b}_n \hat{a}^\dagger) \rightarrow G(\hat{b}_n^\dagger + \hat{b}_n)(\hat{a}^\dagger + \hat{a})$ , and by adding the diamagnetic  $\hat{A}^2$  term present in the minimal coupling Hamiltonian [40], i.e.  $\frac{G^2 N}{\omega_v} (\hat{a}^\dagger + \hat{a})^2$ , which prevents spurious ground-state phase transitions [41]. By writing the  $A^2$  term in this expression we implicitly assume the oscillator strength of the vibronic transition is 1, i.e. fully saturating the oscillator strength sum rule. This is a reasonable assumption for a harmonic excitation[40].

Since the Hamiltonian no longer conserves particle number, the intermediate and final eigenstates are no longer Fock states. However, as the problem remains quadratic, it can still be solved analytically, using the po-

sition representation. In the position representation, we may also straightforwardly include an extra effect, missing from Eq. (1), namely the possibility that the vibrational frequency can depend on the electronic state. The resulting Hamiltonian including all these effects takes the form:

$$H = \omega_c \hat{a}^\dagger \hat{a} + \sum_n \left[ \omega_e \sigma_n^\dagger + \omega_v [\hat{b}_n^\dagger \hat{b}_n + \sqrt{S}(\hat{b}_n^\dagger + \hat{b}_n) \sigma_n^\dagger] + G(\hat{b}_n^\dagger + \hat{b}_n)(\hat{a}^\dagger + \hat{a}) + \nu \sigma_n^\dagger (\hat{b}_n^\dagger + \hat{b}_n)^2 + \frac{G^2}{\omega_c} (\hat{a}^\dagger + \hat{a})^2 \right], \quad (21)$$

where the parameter  $\nu$  relates to the frequency difference  $\delta\omega_v$  between ground and excited states via  $\nu = [(\omega_v + \delta\omega_v)^2 - \omega_v^2]/4\omega_v$ .

Before rewriting the Hamiltonian in the position representation, it is convenient first to make a change of basis for the vibrational modes. This change of basis is closely related to the alternate basis for dark state modes introduced in section IID0b. However, in this case, we make the basis change before trying to diagonalize the problem. As seen earlier, when molecule  $m$  is excited, one can choose a basis so that  $N - 2$  of the dark states do not involve any excitation of the mode  $m$ , and thus decouple entirely. In the current context that means we choose to define  $\hat{b}_m \rightarrow \hat{b}$  and  $\sum_{j \neq m} b_j / \sqrt{N-1} \rightarrow \hat{c}$ . When molecule  $m$  is excited, the remaining effective Hamiltonian can be written purely in terms of these operators, as the other  $N - 2$  orthogonal modes decouple. This then allows us to restrict our calculation of matrix elements to three coupled harmonic oscillators. In terms of these operators, we may write:

$$H_{\text{eff},\downarrow} = \omega_c \hat{a}^\dagger \hat{a} + \omega_v (\hat{b}^\dagger \hat{b} + \hat{c}^\dagger \hat{c}) + \frac{G^2 N}{\omega_c} (\hat{a} + \hat{a}^\dagger)^2 + (\hat{a} + \hat{a}^\dagger) (\hat{b} + \hat{b}^\dagger + \sqrt{N-1} (\hat{c} + \hat{c}^\dagger)) \quad (22)$$

$$H_{\text{eff},m} = H_{\text{eff},\downarrow} + \nu (\hat{b} + \hat{b}^\dagger)^2 + \omega_v \sqrt{S} (\hat{b} + \hat{b}^\dagger). \quad (23)$$

This change of basis does however introduce a complication when evaluating the sum over molecules, as the labeling of final states (specifically excitations of modes  $\hat{b}, \hat{c}$ ) are now molecule dependent. This can be addressed by resolving the final state onto a fixed “reference” basis as is discussed further in Appendix A.

#### A. Calculating Matrix Elements

To find the matrix elements between eigenstates of these Hamiltonians, we now switch to the position representation, introducing coordinates  $\hat{x}_i$ , and momentum  $\hat{p}_i$  and (setting  $\hbar = 1$ ) such that:  $\hat{\psi}_i = \sqrt{\omega_i/2}(\hat{x}_i + i\hat{p}_i/\omega_i)$  for the three modes  $\hat{\psi}_i = (\hat{a}, \hat{b}, \hat{c})$ , with  $\omega_i = (\omega_c, \omega_v, \omega_v)$  respectively. This choice of position and momentum operators means that the problem is isotropic in momentum

space, and so we can diagonalize it by solving the classical coupled oscillator problem. We find that both  $H_{\text{eff},\downarrow}$  and  $H_{\text{eff},m}$  can be written as :

$$\hat{H}_{\text{eff},\sigma} = \frac{1}{2} (\mathbf{p}^\dagger \mathbf{p} + \mathbf{x}^\dagger \mathbf{V}_\sigma \mathbf{x} + 2\mathbf{h}_\sigma^\dagger \mathbf{x}), \quad (24)$$

where we take  $\sigma = \downarrow, \uparrow$  for the cases denoted as  $\downarrow$  and  $\uparrow_m$  above. The matrices and vectors appearing here are then  $\mathbf{h}_\downarrow = 0$ ,  $\mathbf{h}_\uparrow = (0, \omega_v \sqrt{2\omega_v S}, 0)^T$  and

$$\mathbf{V}_\downarrow = \begin{pmatrix} \omega_c^2 + 4G^2N & \xi & \xi\sqrt{N-1} \\ \xi & \omega_v^2 & 0 \\ \xi\sqrt{N-1} & 0 & \omega_v^2 \end{pmatrix}$$

$$\mathbf{V}_\uparrow = \mathbf{V}_\downarrow + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 4\varepsilon\nu & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

and we introduced the shorthand  $\xi = 2G\sqrt{\omega_v\omega_c}$ .

We can clearly diagonalize  $\hat{H}_\sigma$  by writing:  $\mathbf{x} = \mathbf{U}_\sigma \mathbf{X}_\sigma - \mathbf{V}_\sigma^{-1} \mathbf{h}_\sigma$  where  $\mathbf{U}_\sigma^\dagger \mathbf{V}_\sigma \mathbf{U}_\sigma \equiv \mathbf{\Omega}_\sigma^2$  is diagonal. Note that  $\mathbf{V}$  is a real symmetric matrix, and so although we write Hermitian conjugates, these are all equivalent to transposes. After diagonalization one finds  $H_{\text{eff},\sigma} = \frac{1}{2} \sum_i (P_{i,\sigma}^2 + \Omega_{i,\sigma}^2 X_{i,\sigma}^2) + \text{const.}$ , thus, one can write eigenfunctions in the position basis as:

$$\Psi_{l_1 l_2 l_3, \sigma}(x_a, x_b, x_c) = \sqrt[4]{\Omega_{i,\sigma} \Omega_{2,\sigma} \Omega_{3,\sigma}} \psi_{l_1} \left( X_{1,\sigma} \sqrt{\Omega_{1,\sigma}} \right) \psi_{l_2} \left( X_{2,\sigma} \sqrt{\Omega_{2,\sigma}} \right) \psi_{l_3} \left( X_{3,\sigma} \sqrt{\Omega_{3,\sigma}} \right), \quad (25)$$

where  $\psi_l(y)$  are the Gauss-Hermite functions

$$\psi_l(y) = \frac{1}{\sqrt{\pi 2^l l!}} H_l(y) e^{-y^2/2},$$

$\Omega_{i\sigma}$  are the diagonal elements of  $\mathbf{\Omega}_\sigma$ , and the components  $X_i$  are related to  $x_i$  by the linear transformation given above.

Now, as in Eq. (3), we need to calculate  $M_k$ , which involves a sum of transition matrix elements over all intermediate states, divided by corresponding energy differences. The transition matrix elements can be written using position basis overlaps of eigenfunctions. Using the wavefunctions introduced above and rewriting the denominator as an integral over  $z$  as before, we get that the matrix element to a final state with mode  $k$  excited is:

$$M_k = N \sqrt{2\Omega_{k,\downarrow}} \prod_i (\Omega_{i,\uparrow} \Omega_{i,\downarrow}) \int_0^\infty ds e^{-s\Delta} \int d^3x d^3x' \prod_i \left[ \sum_{l_i} \psi_{l_i} \left( \sqrt{\Omega_{i,\uparrow}} X_{i,\uparrow} \right) \psi_{l_i} \left( \sqrt{\Omega_{i,\uparrow}} X'_{i,\uparrow} \right) e^{-sl_i \Omega_{i,\uparrow}} \times \psi_0 \left( \sqrt{\Omega_{i,\downarrow}} X_{i,\downarrow} \right) \psi_0 \left( \sqrt{\Omega_{i,\downarrow}} X'_{i,\downarrow} \right) \right] X_{k,\downarrow}. \quad (26)$$

In writing the above, we have used the fact that for bright modes, the sum over molecules is replaced by a factor  $N$ ,

while for dark modes the sum over molecules vanishes (see Appendix A). We have also used the fact that the first-excited Hermite mode is related to the ground state by  $\psi_1(y) = \psi_0(y)\sqrt{2}y$ .

To calculate the coordinate integrals in Eq. (26) we may first note that since  $\mathbf{x}, \mathbf{X}_\sigma$  are all related by unitary transformations, we can change the integration coordinates to  $\mathbf{X}_{i\uparrow}$  with unit Jacobian. The resulting integral then involves known overlaps of Gauss-Hermite functions. For further details, see Appendix B. The result is

$$M_k = 8N \sqrt{2\Omega_{k,\downarrow}} \left[ \mathbf{U}_\downarrow^\dagger \mathbf{U}_\uparrow \right]_{kr} \times \int ds e^{-s\Delta} \prod_i \left( \sqrt{\frac{\Omega_{i,\downarrow} \Omega_{i,\uparrow}}{1 - \exp(-2s\Omega_{i,\uparrow})}} \right) \times \frac{(\mathbf{A}^{-1} \mathbf{q} - \mathbf{l})_r}{\sqrt{\det(\mathbf{A})}} \exp \left[ \frac{1}{2} \mathbf{q}^\dagger \mathbf{A}^{-1} \mathbf{q} - \mathbf{l}^\dagger \mathbf{R} \mathbf{l} \right], \quad (27)$$

where we have introduced the  $6 \times 6$  matrix  $\mathbf{A}$  which naturally comes after computing the six dimensional Gaussian integrals in Eq. (26). This matrix can be written in block form as:

$$\mathbf{A} = \begin{pmatrix} \mathbf{P} + \mathbf{R} & -\mathbf{Q} \\ -\mathbf{Q} & \mathbf{P} + \mathbf{R} \end{pmatrix} \quad (28)$$

where the  $3 \times 3$  blocks are given by  $\mathbf{R} = \mathbf{U}_\uparrow^\dagger \mathbf{U}_\downarrow \mathbf{\Omega}_\downarrow \mathbf{U}_\downarrow^\dagger \mathbf{U}_\uparrow$ ,  $\mathbf{P} = \text{diag} \left( \frac{\Omega_{i,\uparrow}}{\tanh(s\Omega_{i,\uparrow})} \right)$ , and  $\mathbf{Q} = \text{diag} \left( \frac{\Omega_{i,\uparrow}}{\sinh(s\Omega_{i,\uparrow})} \right)$ . The three- and six-component vectors appearing in Eq. (27) are given by  $\mathbf{l} = \mathbf{\Omega}_\uparrow^{-2} \mathbf{U}_\uparrow^\dagger \mathbf{h}_\uparrow$ , and  $\mathbf{q}^\dagger = (\mathbf{l}^\dagger \mathbf{R}, \mathbf{l}^\dagger \mathbf{R})$ . This is as far as we can simplify this expression in the general case, where  $\nu \neq 0$ , but Eq. (27) can nonetheless be evaluated efficiently numerically.

## B. Numerical results and large $\Delta$ approximation

In Figure 4 we compare the behavior with and without electronic-state dependent vibrational frequency. It is clear the inclusion of this term makes only minor changes. It is worth noting that while the detuning  $\nu$  mixes bright and dark states in the excited state manifold, there is no such mixing in the final (electronic ground state manifold). Thus, the effect of  $\nu$  is only to modify the intermediate states appearing in the calculation of the transition amplitude.

On the other hand, as we will discuss next, the correct treatment of the ultra-strong coupling (including the diamagnetic terms) has a significant effect, avoiding features associated with the ground state phase transition.

Since the electronic state dependence of vibrational frequency is unimportant, we may focus on the case  $\nu = 0$ . In this case, Eq. (27) simplifies considerably, as we have  $\mathbf{V}_\uparrow = \mathbf{V}_\downarrow$ , and so consequently  $\mathbf{U}_\uparrow = \mathbf{U}_\downarrow$  and  $\mathbf{\Omega}_\uparrow = \mathbf{\Omega}_\downarrow$ . This then in turn means that  $\mathbf{R} = \mathbf{\Omega}$  becomes diagonal, and so the matrix  $\mathbf{A}$  can be rewritten as three  $2 \times 2$  blocks, and thus inverted in closed form. After some algebra, this

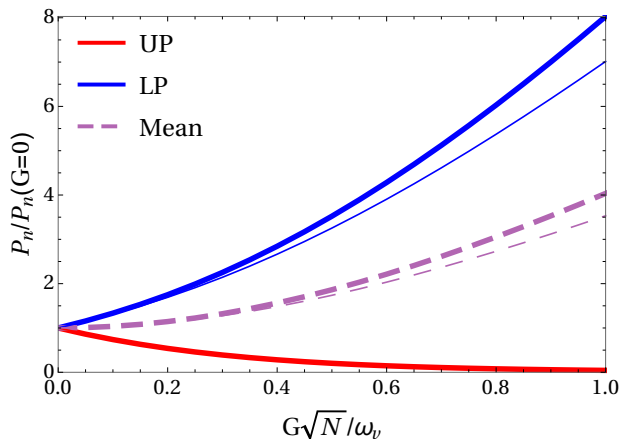


FIG. 4. Transition probability to the upper and lower polariton in beyond the RWA, including  $A^2$  terms. Thick lines plotted for  $\delta\omega_v = 0$ , thin lines to  $\delta\omega_v = -0.5\omega_v$ . Other parameters as for Fig. 2.

leads to an expression of exactly the same form as (12), but with the three coefficients  $\alpha_i$  given by  $\alpha_i = l_i \sqrt{\Omega_i/2}$ . In the resonant case  $\omega_c = \omega_v$  this simplifies further to:

$$\alpha_i = \sqrt{\frac{S}{N}} \left( \frac{1}{\sqrt{2}} \frac{\omega_v^{3/2}}{\omega_{LP}^{3/2}}, \frac{1}{\sqrt{2}} \frac{\omega_v^{3/2}}{\omega_{UP}^{3/2}}, \sqrt{N-1} \right). \quad (29)$$

As discussed in Section II E, the asymptotic behavior at large  $\Delta$  has a simple form. Using Eq. (19) we now have that the large  $\Delta$  asymptote of the resonant case gives

$$M_{k=LP,UP} \approx \frac{\sqrt{\frac{SN}{2}} \frac{\omega_v^3}{\omega_k}}{\left[ \Delta + \frac{S}{N} \omega_v \left( N-1 + \frac{1}{2} \left[ \frac{\omega_v^2}{\omega_{UP}^2} + \frac{\omega_v^2}{\omega_{LP}^2} \right] \right) \right]^2}, \quad (30)$$

Note that in contrast to Eq. (20), the numerator retains a dependence on  $\omega_k$ , due to the extra powers of  $\omega_k$  in the definition of  $\alpha_k$ . Thus, as the lower polariton frequency tends to zero with increasing coupling, the numerator will diverge. This means that beyond the RWA, even for large  $\Delta$ , there is a growth of Raman scattering with  $G$ . This was also seen by del Pino *et al.* [37] for a single molecule. However, at very strong coupling one once again has a divergence of the denominator that is stronger than that of the numerator. Thus the asymptotic limit of strong coupling is in fact for the expression to vanish. This can be seen most clearly by again using  $\zeta = G\sqrt{N}/\omega_v$ . Writing the eigenfrequencies  $\omega_{UP,LP}^2 = \omega_v^2(1 + 2\zeta^2 \pm 2\zeta\sqrt{1+\zeta^2})$  this yields:

$$M_{k=LP,UP} \approx \frac{\sqrt{SN/2} \omega_v \sqrt{\omega_v/\omega_k}}{\left[ \Delta + \frac{S}{N} \omega_v (N + 2\zeta^2) \right]^2}, \quad (31)$$

At large  $\zeta$  one has  $\omega_{LP} \simeq \omega_v/2\zeta$ , making the relatively scaling of numerator and denominator clear. Note however that for  $\zeta^2$  to dominate the denominator would require the (currently unattainable) limit  $G \gg \omega_v$ , i.e. ultra-strong single-molecule coupling.

This expression also shows the crucial role played by the  $A^2$  term at ultra-strong coupling. Unlike the rotating wave approximation, where  $\omega_{LP}$  diverges as  $\zeta \rightarrow 1$ , here the LP energy always remains finite (there is no super-radiance transition [41]), and instead leading to the LP energy vanishing asymptotically at  $\zeta \rightarrow \infty$ . As such, the Raman scattering probability is a smooth function of the coupling strength and neither vanishes nor diverges at any finite coupling strength. One should however note that the assumption  $\omega_{UP} \ll \Delta$  required to make the large  $\Delta$  expansion in Eq. (30,31) will fail in the limit  $\zeta \rightarrow \infty$ . In this limit one must therefore return to using Eq. (12,29).

#### IV. MULTIPLE EXCITATIONS

So far we have determined the Raman transition amplitudes to final states with a single upper or lower polariton. In this section, we discuss how the tractable expressions we derived above for transition matrix elements can also be extended to multiple excitations. Specifically, we consider the RWA expression for the transition amplitude to a state where mode  $i$  has  $q_i$  excitations. Details of the calculation are given in Appendix C. The compact expression for this is given by:

$$M_{\{q_i\}} = \sum_m \int_0^\infty dz e^{-z\Delta} \prod_i (\alpha_{m,i}^*)^{q_i} \frac{(e^{-z\omega_i} - 1)^{q_i}}{\sqrt{q_i!}} \times \exp[-|\alpha_{m,i}|^2(1 - e^{-z\omega_i})]. \quad (32)$$

One can immediately see that if  $q_{i=k} = 1, q_{i \neq k} = 0$ , this reduces to the formula given in Eq. (12).

If we consider the special case where a single mode is multiply occupied, so  $q_{i=LP} = n, q_{i \neq LP} = 0$ , the formula simplifies as all terms are molecule independent and so  $\sum_m \rightarrow N$ . In this case we can see that the transition amplitude to the multiple lower polariton state has a stronger dependence on  $\omega_{LP}$ , increasing as  $\omega_{LP}^{-n}$ , as might be expected from multiplying together the amplitudes for  $n$  excitations. However, the scaling with number of molecules is different: The expression for transition amplitude to  $n$  lower polaritons is proportional to  $N^{1-n/2}$ . i.e., while the Raman transition *probability* to one-excitation final states scales as  $N$ , the transition probability to two-excitation final states does not scale with  $N$ . It is however important to note that within the multiple excitation sector, other final states are possible. For example, a Raman transition to dark modes can now occur: if one considers modes  $k, k'$  using the basis choice of Eq. (16), such that  $k + k' = N$ , then one may see that  $\sum_m \alpha_{k,m} \alpha_{k',m} \neq 0$ . i.e., ‘‘momentum’’ conserving pairs of dark modes become possible. As such, the total transition probability to all two-excitation final states scales as  $N$ , the same scaling as single-excitation final states. However, the two-excitation final states are dominated by the dark state pairs.



## V. CONCLUSION

In this work we analyzed the effect of strong photon-vibron coupling on the Raman scattering intensity, and show that a compact analytic expression can be found for the Raman transition amplitude. As also found in Ref. [37], we find that matter-light coupling leads to a redistribution of the vibronic Raman signal between upper and lower polariton modes (and no scattering into single dark states). At leading order in matter-light coupling, there is no change to the overall scattering amplitude, but changes do occur at higher orders. Under ultra-strong coupling we see significant enhancement of the scattering into the lower polariton due to the mode softening, and suppression of Raman scattering into the upper polariton, so the overall signal goes up. In considering this ultra strong coupling limit, we showed that  $A^2$  terms are essential in preventing (unphysical) divergence of the Raman signal at finite coupling strength. In contrast, we find that electronic-state-dependent vibronic frequency shifts have a negligible effect of the Raman scattering amplitude. We also showed that for Raman scattering to sectors with multiple excitations show a system-size suppression of individual matrix elements, however transitions to states involving multiple dark states now become possible.

## ACKNOWLEDGMENTS

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### Appendix A: Dark modes and three mode description

This appendix addresses a subtle issue about considering transition matrix elements in the ‘‘three mode’’ basis  $\hat{a}, \hat{b}_m \rightarrow \hat{b}, \sum_{j \neq m} b_j / \sqrt{N-1} \rightarrow \hat{c}$  used in writing Eq. (22). The issue is that the set of eigenmodes then used to describe the dark states is dependent on which molecule is excited. Since the overall transition matrix element requires summing over molecules, some care is required to correctly perform this sum and see that dark states still cancel. In contrast the bright states pose no issues, since the bright states are non degenerate, and so uniquely determined independent of basis — the issue with dark states is that degeneracy allows us freedom to choose the set of states, and our three mode basis chooses

a different set of eigenmodes for each molecule.

For the single excitation final state that we consider throughout most of the paper, it is clearest to use a first-quantized Dirac notation to discuss the issue. Our three modes can be considered as the cavity mode  $|\psi_a\rangle = |1; 0, 0, \dots, 0\rangle$ , and the two vibronic modes  $|\psi_b^{(m)}\rangle = |0; \dots, 0, 1, 0, \dots\rangle$ , and  $|\psi_c^{(m)}\rangle = |0; \dots, 1, 0, 1, \dots\rangle / \sqrt{N-1}$  where the non-zero (zero) element in mode b (c) corresponds to the excited molecule  $m$ . In terms of these basis states, the eigenmodes are the two polaritonic states and the dark states are:

$$|LP, UP\rangle = |\psi_a\rangle \pm \frac{1}{\sqrt{N}} \left( |\psi_b^{(m)}\rangle + \sqrt{N-1} |\psi_c^{(m)}\rangle \right),$$

$$|D^{(m)}\rangle = \frac{1}{\sqrt{N}} \left( \sqrt{N-1} |\psi_b^{(m)}\rangle - |\psi_c^{(m)}\rangle \right).$$

In order to correctly sum the contributions of transition amplitudes to the states  $|D^{(m)}\rangle$  for different molecules, we should resolve these states onto a fixed reference state. i.e., we should define a (dark) state  $|X\rangle$  and calculate the transition probability  $P_X \propto |\sum_m \langle X | D^{(m)} \rangle M_{k=D^{(m)}}^{(m)}|^2$  where  $M_k^{(m)}$  is the transition amplitude coming from excitations of molecule  $m$ . This is the correct way to deal with sum over molecules appearing in the Raman transition amplitude.

With this expression, we can indeed show that the total dark state probability vanishes. Suppose we take as our reference  $|X\rangle = |D^{(1)}\rangle$ . The overlaps required then involve the need to use the overlap:

$$\langle D^{(1)} | D^{(m \neq 1)} \rangle = \frac{1}{N} \left( -2 + \frac{N-2}{N-1} \right) = -\frac{1}{N-1}.$$

From our calculation in section III, we find that  $M_{k=D^{(m)}}^{(m)}$  is independent of molecule label  $m$ , so we find that  $P_X \propto |\sum_m \langle X | D^{(m)} \rangle|^2 = 0$ . This demonstrates again that the amplitude for transition to dark modes vanishes, and confirms that we may use such a basis to simplify the calculations, as used in Sec. III.

### Appendix B: Details of non RWA calculation

This appendix provides further details of the steps required to evaluate the sums over modes and Gaussian integrals in Eq. (26). As noted in section III, since the Jacobian for an unitary transformation is 1, we may choose to write the integrals in terms of the variables  $\mathbf{X}_\uparrow, \mathbf{X}'_\uparrow$ . It is convenient to denote  $\mathbf{X} \equiv \mathbf{X}_\uparrow$  in terms of which

$$\mathbf{X}_\downarrow = \mathbf{U}_\downarrow^\dagger \left( \mathbf{U}_\uparrow \mathbf{X} - \mathbf{V}_\uparrow^{-1} \mathbf{h}_\uparrow \right) = \mathbf{U}_\downarrow^\dagger \mathbf{U}_\uparrow (\mathbf{X} - \mathbf{l}), \quad (\text{B1})$$

where we introduced  $\mathbf{l} = \mathbf{U}_\uparrow^\dagger \mathbf{V}_\uparrow^{-1} \mathbf{h}_\uparrow = \mathbf{\Omega}_\uparrow^{-2} \mathbf{U}_\uparrow^\dagger \mathbf{h}_\uparrow$ . A similar set of relations hold for the primed coordinates.

The sum over modes can be evaluated using a version of Mehler's formula [42]:

$$\sum_l \psi_l(\sqrt{\Omega}X) \psi_l(\sqrt{\Omega}X') e^{-s\Omega} = \frac{1}{\sqrt{\pi}} \frac{1}{\sqrt{1-e^{-2s\Omega}}} \exp\left[-\frac{\Omega}{2} \left(\frac{X^2 + X'^2}{\tanh(s\Omega)} - \frac{2XX'}{\sinh(s\Omega)}\right)\right].$$

With this expression Eq. (26) can be reduced to:

$$M_k = \frac{\sqrt{2\Omega_{k,\downarrow}}}{\pi^3} \left[ \mathbf{U}_\downarrow^\dagger \mathbf{U}_\uparrow \right]_{kr} \int ds e^{-s\Delta} \int \prod_i \left( d^3 X_i d^3 X'_i \frac{\sqrt{\Omega_{i,\uparrow}\Omega_{i,\downarrow}}}{\sqrt{1-e^{-2s\Omega_{i,\uparrow}}}} \right) (X_r - l_r) \exp\left[-\frac{1}{2} ((\mathbf{X}-1)^\top \mathbf{R}(\mathbf{X}-1) + (\mathbf{X}'-1)^\top \mathbf{R}(\mathbf{X}'-1)) - \sum_i \frac{\Omega_{i,\uparrow}}{2} \left(\frac{X_i^2 + X_i'^2}{\tanh(s\Omega_{i,\uparrow})} - \frac{2X_i X_i'}{\sinh(s\Omega_{i,\uparrow})}\right)\right] \quad (\text{B2})$$

where we introduced the matrix  $\mathbf{R} \equiv \mathbf{U}_\uparrow^\dagger \mathbf{U}_\downarrow \Omega_\downarrow \mathbf{U}_\downarrow^\dagger \mathbf{U}_\uparrow$ .

Equation (B2) involves a Gaussian integral over the six components  $X_i, X'_i$  which we may define as  $O_r(s)$ , such that

$$M_k = \frac{\sqrt{2\Omega_{k,\downarrow}}}{\pi^3} \left[ \mathbf{U}_\downarrow^\dagger \mathbf{U}_\uparrow \right]_{kr} \times \int ds e^{-s\Delta} \prod_i \left( \sqrt{\frac{\Omega_{i,\uparrow}\Omega_{i,\downarrow}}{1-e^{-2s\Omega_{i,\uparrow}}}} \right) O_r(s),$$

To proceed further, we can notice that  $O_r(s)$  is a 6 dimensional Gaussian integral, and so can be calculated analytically. Defining the six dimensional coordinates:  $\mathbf{z}^\top \equiv (\mathbf{X}^\top, \mathbf{X}'^\top)$  the Gaussian integral  $O_r(s)$  can be written as:

$$O_r(s) = \int d^6 z (z_r - l_r) \exp\left[-\frac{1}{2} \mathbf{z}^\top \mathbf{A} \mathbf{z} + \mathbf{q}^\top \mathbf{z} - c\right],$$

where the matrix  $6 \times 6$  matrix  $\mathbf{A}$  is as given in Eq. (28), the 6 component vector  $\mathbf{q}^\top = (\mathbf{1}^\top \mathbf{R}, \mathbf{1}'^\top \mathbf{R})$ , and the constant  $c = \mathbf{1}^\top \mathbf{R} \mathbf{l}$ . Thus, computing the Gaussian integral over coordinates  $\mathbf{z}$ , we eventually obtain

$$\mathbf{O}_r(s) = \frac{(2\pi)^3 (\mathbf{A}^{-1} \mathbf{q} - \mathbf{l})_r}{\sqrt{\det(\mathbf{A})}} \exp\left[\frac{1}{2} \mathbf{q}^\top \mathbf{A}^{-1} \mathbf{q} - \mathbf{1}^\top \mathbf{R} \mathbf{l}\right],$$

and so derive the final expression Eq. (27).

### Appendix C: Multiple final-state excitations

This appendix provides further details on how to calculate the transition rate to a final state with multiple excitations. For simplicity, we present the result as can be calculated in the rotating wave approximation. In this case, we can use the Fock state basis, as discussed in Sec. II B. If we consider the state in which mode  $i$  has

$q_i$  excitations, we must replace the matrix element between intermediate and final states in Eq. (10) with one describing transitions to a final state specified by the occupations  $\{q_i\}$ . By considering the combinatoric factors associated with the overlap between  $\{p_i\}$  (displaced) excitations in the intermediate state and  $\{q_i\}$  in the final state, one may show that:

$$\mathcal{M}_{\{q_i\},\{p_i\}}^{(m)} = \mathcal{M}_{0,\{p_i\}}^{(m)} \times \prod_i \sqrt{q_i!} \sum_{l_i=q_i-p_i}^{q_i} \frac{(-1)^{l_i}}{l_i!} \frac{|\alpha_{m,i}|^{2l_i}}{\alpha_{m,i}^{*q_i}} \binom{p_i}{q_i - l_i}$$

where the last term is the binomial coefficient. With this result, the Raman transition amplitude  $M_{\{q_k\}}$  can be written using the same exponentiation of denominator as used previously, to give:

$$M_{\{q_i\}} = \int_0^\infty dz e^{-z\Delta} \sum_m \prod_i \sqrt{q_i!} \frac{e^{-|\alpha_{m,i}|^2}}{\alpha_{m,k}^{q_i}} \times \sum_{l_i=0}^{q_i} \sum_{p_i=q_i-l_i}^\infty \frac{(-1)^{l_i} |\alpha_{m,i}|^{2(l_i+p_i)} e^{-p_i z \Omega_i}}{l_i! (p_i - q_i + l_i)! (q_i - l_i)!},$$

where we have swapped the order of summation over  $l_i$  and  $p_i$ . One may then identify the sum over  $p_i$  as being the Taylor expansion of an exponential, to give

$$M_{\{q_i\}} = \int_0^\infty dz e^{-z\Delta} \sum_m \prod_i \sqrt{q_i!} \frac{e^{-|\alpha_{m,i}|^2} (1 - e^{-z\Omega_i})}{\alpha_{m,k}^{q_i}} \times |\alpha_{m,i}|^{2q_i} \sum_{l_i=0}^{q_i} \frac{(-1)^{l_i} e^{-z\Omega_i (q_i - l_i)}}{l_i! (q_i - l_i)!},$$

and then performing the sum over  $l_i$  gives the expression in Eq. (32).

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