UV/vis-to-IR Photonic Down Conversion Mediated by Excited State Vibrational Polaritons

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Abstract

This work proposes a new photophysical phenomenon whereby UV/vis excitation of a molecule involving a Franck-Condon (FC) active vibration yields infrared (IR) emission by strong coupling to an optical cavity. The resulting UV/vis-to-IR photonic down conversion process is mediated by vibrational polaritons in the electronic excited state potential. It is shown that the formation of such excited state vibrational polaritons (ESVP) via UV/vis excitation only occurs with molecules having vibrational modes with both a non-zero FC activity and IR activity in the excited state. Density functional theory calculations are shown to effectively identify a candidate molecule, 1-Pyreneacetic acid (PAA), with this property and the dynamics of ESVP are modeled using the truncated Wigner approximation. Overall, this work presents a new avenue of polariton chemistry where excited state dynamics, driven by photoexcitation, are influenced by the formation of vibrational polaritons. Along with this, the photonic down conversion is potentially useful in both the sensing of excited state vibrations and in quantum transduction schemes.

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1 Introduction

Most light-matter interactions involved in spectroscopy are in the weak coupling regime such that the intramolecular Coulombic fields are significantly stronger than the interacting radiation fields.[1] As such, perturbative theories accurately describe many spectroscopic phenomena.[2] These theories break down in the “strong coupling” regime where light and matter states hybridize, resulting in energy splittings that can be spectroscopically observed.[3] The quanta of such hybrid light-matter states are called “polaritons”, the formation of which is commonly realized by the use of high finesse optical cavities with quantized radiation modes that can be coupled to dipole carrying transitions within states of matter. Polaritons formed between infrared (IR)-active molecular or condensed phase vibrations and an optical cavity are, naturally, called “vibrational polaritons”.

In recent experiments, it has been demonstrated that product selectivity and rates of ground state reactions may be modulated by the formation of vibrational polaritons through coupling an optical cavity to the vibrational coordinate on which a reaction proceeds.[4, 5, 6, 7, 8, 9, 10] Although there has been significant experimental and theoretical work towards understanding such ground state vibrational polaritons and their effect on reactions along with other physiochemical phenomena,[11, 3, 12, 13, 14, 15, 16, 17, 18] analogies on the electronic excited state potential have remained underexplored.[19, 20] Here, we propose a novel photonic down conversion process that results from the formation of excited state vibrational polaritons (ESVP) via UV/vis electronic excitation of a molecule containing a vibrational mode that is coupled to an IR cavity. Under vibronic coupling, the UV/vis excitation of the molecule induces a wavepacket consisting of ESVP, while Rabi oscillations occur between occupied vibrational and photonic states as time evolves. These photons in turn may leak from the cavity, leading to IR light emission.[21]

The UV/vis-to-IR photonic down conversion process proposed in this work has potential applications in quantum information science, where the vibrational wave-packet, formed by a UV/vis excitation of the cavity-embedded molecule, can be directly transduced into a photonic wavepacket through coupling to the optical cavity. Hence, molecules with different vibronic couplings and excited state potential energy surfaces produce different coherences within the photonic wavepacket emitted via the ESVP photonic down conversion process. This could allow for the manipulation of coherent light by molecular design. Furthermore, the UV/vis-to-IR photonic down conversion process implies that an optical cavity can be used to enhance the emission of excited state vibrations, analogous to the Purcell effect in the weak light-matter coupling regime.[22, 23] The effective detection of excited state vibrations through this process would be a powerful measurement tool for identifying vibrational modes induced by electronic transitions—information that has been difficult to obtain experimentally,[24] and that often requires a determination through electronic structure calculations and molecular dynamics simulations.[25] Detection of photonic emission from vibrations is typically impossible due to their non-radiative relaxation being on the order of picoseconds,[26, 27] which out-competes any non-enhanced emission that occurs on a $> 1 \mu s$ time scale.[28, 29] It was experimentally indicated by Raschke and coworkers that ground state vibrational emission could be enhanced by coupling molecules
to an optical resonator, yielding a 50% decrease in the vibrational dephasing lifetime for poly(methylmethacrylate),[29] although photonic emission from vibrations was not actually observed.

Another potential application of ESVP is in the modulation of photophysical processes that occur via transitions between excited electronic states, and which can be mediated by vibrational coherences. For example, vibrational coherences have been shown to mediate singlet fission in certain molecular systems,[30, 31, 32, 33, 34, 35] promote charge and energy transfer in biological light harvesting systems,[36, 37, 38, 39] as well as drive the photochemical reaction of vision.[40, 41, 42] The hybridization of cavity photons with relevant vibrational modes could modulate such coherences as well as change excited state potential energy surfaces (PES), altering reaction pathways and rates similarly to what has been shown for ground state reactions.

In this work, we utilize the truncated Wigner approximation (TWA)[43] to theoretically predict the time evolution of quantum mechanical observables in a combined cavity-molecule system, either without dissipation or when coupled to dissipative harmonic baths. The TWA is exact for systems governed by linear or quadratic potentials, i.e., systems consisting of harmonic oscillators. Furthermore, the TWA benefits from linear scaling of complexity with increasing number of degrees of freedom (DOF), as opposed to the exponential increase in complexity of the Hilbert space of the system. Therefore, the TWA enables exact modeling of the evolution of polariton wavepackets coupled to baths of harmonic oscillators without requiring a truncated Hilbert space and without tracing out the bath DOF, as is done in standard quantum master equation techniques.[44, 45] We are therefore able to concurrently and explicitly monitor the population transfer into both a radiative and non-radiative bath, giving insights into how different interaction parameters affect photonic emission from ESVP in the presence of non-radiative vibrational relaxation.

2 Results

2.1 Photonic Down Conversion Mechanism

Figure 1 shows a schematic of the ESVP mediated photonic down conversion process. A molecule is positioned inside an optical cavity, initially in its ground electronic state. A mode of the optical cavity is assumed to be near resonant with a spectrally isolated vibrational mode of the molecule. We treat the cavity as transparent to high optical frequencies allowing a UV/vis pulse to promote the molecule into an electronically excited state. We also assume the FC approximation where vibronic coupling is characterized by a linear shift in the excited state nuclear PES, as shown in Figure 1, with $Q_0^{(g)}$ and $Q_0^{(e)}$ being the ground and excited state equilibrium nuclear configurations of the vibrational mode of interest, respectively. Assuming a non-zero Huang-Rhys (HR) factor (vibronic coupling constant), a vibrational wavepacket will be created upon electronic excitation of the molecule. In the absence of the cavity, this wavepacket will have an expected occupation number, $\langle \hat{N}_{vib} \rangle$, equal to the HR factor $S$,[46, 47] and its energy expectation value equals $S\hbar\omega_v$, which is called the reorganization energy,
Figure 1: Schematic of the UV/vis-to-IR photonic down conversion process mediated by ESVP. An impulsive excitation by UV/vis light (blue arrow) creates ESVP due to vibronic interactions of the cavity coupled vibrational mode. The ESVP then leak IR radiation from the cavity (red arrows).

where \( \omega_v \) is the vibrational frequency. When the cavity is present and the excited state vibrational transition dipole moment \( \mu_{IR}^{(e)} \) is non-zero for the cavity resonant vibrational mode, the vibrational wavepacket will comprise a superposition of polariton eigenstates and Rabi oscillations will occur between vibrations and cavity photons as time evolves. Furthermore, given a finite quality factor \( Q \) of the cavity, which is a measure of its radiative energy loss,[48] the cavity photons involved in such ESVP will leak out of the cavity resulting in IR emission that can be detected and/or harnessed.[21] Altogether, these steps constitute a photonic down conversion process where a single incident UV/vis photon is converted into one or more IR photons.

In this work, we only consider dissipation of cavity photons through the cavity mirrors so that \( Q \) is dependent only on the amount of detectable radiative emission. In general, other dissipation pathways should also be accounted for such as absorption by the cavity mirrors and bound mode photoluminescence,[21] which would also decrease \( Q \). Therefore, the results presented herein give an idealized estimate of the amount of photonic down conversion that can occur within a lossy cavity.

2.2 Theoretical Model

We use the Pauli-Fierz Hamiltonian as a basis for constructing a model of the ESVP mediated photonic down conversion process.[49, 50, 51] Accordingly, the cavity-molecule system is described as

\[
\hat{H}_{\text{system}} = \hat{H}_{\text{mol}} + \frac{\hat{p}^2}{2} + \frac{\omega_v^2}{2}(\hat{q} + \hat{A} \cdot \hat{\mu})^2,
\]  

(1)
where $\hat{p}$ and $\hat{q}$ are the cavity mode momentum and position operators, respectively, and $\omega_c$ is the frequency of the cavity mode. Moreover, $A = \sqrt{2/\hbar \omega_c A_0 \epsilon_c}$, where $A_0 = \sqrt{\hbar/2\omega_c \epsilon} V$ is the amplitude of the cavity mode vector potential, with $\epsilon$ being the effective permittivity of the cavity and $V$ being the cavity mode volume, and $\epsilon_c$ is the cavity mode polarization unit vector. Lastly, $\hat{\mu}$ is the molecular dipole operator and $\hat{H}_{\text{mol}}$ describes the molecule. We express $\hat{H}_{\text{system}}$ in the molecular diabatic basis at the ground state equilibrium, that is, the basis of electronic eigenstates, $|\alpha\rangle$, that satisfy

$$
\hat{H}_{\text{mol}}^{\text{el}}(Q^{(g)}_0)|\alpha\rangle = E_\alpha(Q^{(g)}_0)|\alpha\rangle. \tag{2}
$$

Here, $\hat{H}_{\text{mol}}^{\text{el}}(Q^{(g)}_0)$ is the component of $\hat{H}_{\text{mol}}$ containing a dependence on the electronic DOF, parameterized by $Q$, which is taken to be fixed at $Q = Q^{(g)}_0$. We truncate this basis to only include the ground and a single excited diabatic state denoted as $|g\rangle$ and $|e\rangle$, respectively. In this basis, $\hat{H}_{\text{mol}}$, including a single harmonic vibrational mode, can be written as

$$
\hat{H}_{\text{mol}} = \frac{\hat{P}^2}{2} + \frac{1}{2}\omega^2 v \hat{Q}^2 + \left(E_{\text{vert}} - \omega^2 v Q^{(e)}_0 \hat{Q}\right)|e\rangle\langle e|, \tag{3}
$$

where $\hat{P}$ and $\hat{Q}$ are the mass-weighted momentum and position operators of the vibrational mode, respectively, $E_{\text{vert}} = \hbar \Omega_{e,g} + S \hbar \omega_v$ is the energy of the vertical transition from the ground to excited electronic PES at the point of the ground state nuclear equilibrium configuration (the FC point) with $\Omega_{e,g}$ being the transition frequency between the ground and excited electronic states at their respective nuclear equilibrium position. Furthermore, in Eq. (3) we have taken the ground state nuclear equilibrium configuration to be at the origin so that $Q^{(g)}_0 = 0$, and it is assumed that there is no coupling between diabatic states. We have also assumed that the vibrational frequency is independent of electronic state.

Eq. (1) and Eq. (3) effectively describe a system of coupled harmonic oscillators: the vibrational mode and the cavity, which are coupled through an interaction of the cavity field with the molecular dipole. Expanding the quadratic term in Eq. (1) gives

$$
\hat{H}_{\text{system}} = \hat{H}_{\text{mol}} + \hat{H}_{\text{cav}} + \hat{H}_{\text{int}}, \tag{4}
$$

where

$$
\hat{H}_{\text{cav}} = \frac{\hat{p}^2}{2} + \frac{\omega_c^2}{2}\hat{q}^2 \tag{5}
$$

and

$$
\hat{H}_{\text{int}} = \omega_c^2 \hat{\mu} \cdot \hat{\mu} \hat{q} + \frac{\omega_c^2}{2}(\hat{\mu} \cdot \hat{\mu})^2. \tag{6}
$$

As is commonly done with Jaynes-Cummings like models,[21, 52, 13] we ignore the 2nd term of $\hat{H}_{\text{int}}$, which is the dipole self energy, reserving a survey of its effects to a follow up study (as it may become significant in ultra strong coupling[51]).

Once $\hat{H}_{\text{system}}$ is expressed in the diabatic basis, each element of the dipole operator in this basis is expanded to the first order with respect to $\hat{Q}$ about the ground state nuclear
equilibrium position \((Q_0^{(g)} = 0)\) in order to account for linear coupling between the cavity and the vibrational mode. This gives rise to two cavity-vibration interaction terms,

\[ \hat{H}_{\text{int}} = \hat{H}_{\text{PFS}} + \hat{H}_{\text{cav-vib}}, \]

where

\[ \hat{H}_{\text{PFS}} = \omega_c^2 A \cdot \mu_0^e \hat{q}, \]

and where

\[ \hat{H}_{\text{cav-vib}} = \omega_c^2 A \cdot \mu_e' \hat{Q} \hat{q}. \]

Here, \(\mu_0^e\) is the permanent dipole moment of the excited state at \(Q_0^{(g)}\) and \(\mu_e'\) is the derivative of the nuclear dipole with respect to \(Q\) (see “Methods”). The term \(\hat{H}_{\text{PFS}}\) polarizes the bare cavity Fock states (hence, denoted PFS for polarizes Fock states),[53] and its effect on the ESVP mediated down conversion process is discussed in section 3 of the SI. However, the term \(\hat{H}_{\text{cav-vib}}\) is the dominant interaction term and mixes cavity and vibrational DOF. Therefore, we only consider \(\hat{H}_{\text{system}} = \hat{H}_{\text{mol}} + \hat{H}_{\text{cav}} + \hat{H}_{\text{cav-vib}}\).

For the application of the TWA we keep \(\hat{H}_{\text{system}}\) in terms of phase space operators; nonetheless, we believe it valuable to connect our model with the coupling constant \((g)\) used in Jaynes-Cummings like models.[21, 52, 13] This is done by substituting \(\hat{Q} = \sqrt{\frac{\hbar}{2\omega_v}} (\hat{b} + \hat{b}^\dagger)\) and \(\hat{q} = \sqrt{\frac{\hbar}{2\omega_c}} (\hat{a} + \hat{a}^\dagger)\) into Eq. (9), as well as taking the rotating wave approximation (RWA), giving rise to the expression

\[ g = \omega_c A_0 \epsilon_c \cdot \mu_{\text{IR}}^{(e)}, \]

where

\[ \mu_{\text{IR}}^{(e)} = \mu_e' \sqrt{\frac{\hbar}{2\omega_v}} \]

is the vibrational transition dipole moment, which can be found through electronic structure calculations or from experimental IR spectra.[54, 55].

\[ g = \omega_c A_0 \epsilon_c \cdot \mu_{\text{IR}}^{(e)}, \]

2.3 Relevant Molecular Parameters

Using the model Hamiltonian described in section 2.2, we determine the relevant molecular properties that are required for the photonic down conversion to occur through ESVP. This is achieved by monitoring the cavity photon occupancy \(\langle \hat{N}_{\text{cav}} \rangle\), which is representative of the amount of photons that can be harnessed as IR emission if the cavity is leaky (finite \(Q\)). Rather than representing the Hilbert space by a truncated basis of cavity photon and vibrational modes, we apply the TWA to arrive at an exact analytical expression for \(\langle \hat{N}_{\text{cav}} \rangle\) (see SI section 2 for more details). Note that the RWA is not invoked here. To apply the TWA, we rotate \(\hat{H}_{\text{system}}\) into a basis of two uncoupled oscillators called the polariton normal mode basis (see Figure 2 and “Methods”). Due to the displacement of the excited state PES, upon a vertical excitation of the molecule both the upper and lower polariton
Figure 2: Pictorial representation of the normal mode decomposition for an optical cavity coupled to a molecular vibration. The cavity and vibration harmonic oscillators are depicted as springs. The cavity, with position coordinate $q$, and vibration, with position coordinate $Q$, are coupled by $G$. The cavity and vibrational coordinates are then rotated into a coordinate system of two uncoupled oscillators called the polariton basis, with coordinates $R_-$ and $R_+$. The cavity and vibrational coordinates are displaced along their respective coordinates, as depicted in Figure 2. This displacement of excited state polariton oscillators creates a non-equilibrium initial condition that drives the dynamics. At finite temperature the resulting photon occupancy, following the UV/vis excitation, is given by

$$
\langle \hat{N}_{\text{cav}}(t) \rangle = \frac{S}{2(C^2 + 1)} \left[ \frac{1}{2\omega_c} \left( \frac{\sin(\Omega_- t)}{\Omega_-} - \frac{\sin(\Omega_+ t)}{\Omega_+} \right)^2 
+ 2\omega_c \left( \frac{\sin^2(\Omega_- t/2)}{\Omega_-^2} - \frac{\sin^2(\Omega_+ t/2)}{\Omega_+^2} \right)^2 \right] + N_\beta,
$$

where $C = \frac{\omega_v^2 - \omega_c^2}{4\pi \sqrt{\omega_v \omega_c}}$, and where the polariton frequencies are given by $\Omega_{\pm} = \sqrt{A \pm B}$ with $A = \frac{1}{2}(\omega_v^2 + \omega_c^2)$ and $B = \frac{1}{2} \sqrt{(\omega_v^2 - \omega_c^2)^2 + 16\pi^2 \omega_v \omega_c}$. The effect of finite temperature is captured by $N_\beta = \frac{1}{4} \sum_\gamma \left( c_{\gamma} c_{\gamma}^\dagger \left( \frac{\Omega_+}{\omega_c} + \frac{\omega_c}{\Omega_+} \right) \coth(\beta \hbar \Omega_+/2) \right) - \frac{1}{2}$, which describes the thermal distribution of vibrational polaritons on the electronic ground state, before electronic excitation of the molecule, where $\gamma$ denotes the upper ($\gamma = +$) or lower ($\gamma = -$) polariton mode, $\beta$ is the inverse temperature, and $c_{\gamma} c_{\gamma}^\dagger$ is the projection of the cavity mode onto the $\gamma$ polariton mode. In the following analysis, we take the zero temperature limit ($\beta \to \infty$) and assume the cavity to be in perfect resonance with the vibration so that $\omega_c = \omega_v$, yielding
\[c^{(\gamma)}_c = 1/\sqrt{2}\] for \(\gamma = +\) and \(\gamma = -\). This results in \(N_{\beta} = \frac{1}{8} \sum_{\gamma} \left( \frac{\Omega_{\gamma}}{\omega_c} + \frac{\omega_c}{\Omega_{\gamma}} \right) - \frac{1}{2}\). For weak coupling, where \(\Omega_{\gamma} \approx \omega_c = \omega_v\), it is apparent that \(N_{\beta} \approx 0\). But, larger coupling strengths result in \(N_{\beta} > 0\), which is concurrent with the breakdown of the RWA. In that case, the polaritonic ground state within the RWA, which has no photons or vibrational quanta, mixes with the state containing a single cavity photon and single vibration, and therefore, even at zero temperature there will be a non-zero number of cavity photons if the coupling is large.

A key result from Eq. (12) is that \(\langle \hat{N}_{\text{cav}}(t) \rangle\) is proportional to \(S\). This can be understood by considering that \(S\) is proportional to the squared displacement of the excited state PES. If the displacement is zero, all FC factors will be zero indicating that no vibrational transitions will be induced upon the UV/vis excitation. Increasing \(S\) increases the displacement, and consequentially, the number of vibrational quanta created upon electronic excitation. Given a non-zero \(g\) value, these vibrational quanta will be converted into cavity photons.

Figure 3: (a) Time evolution of the cavity photon occupancy, \(\langle \hat{N}_{\text{cav}} \rangle\), for a single intramolecular vibration coupled to a cavity following an electronic excitation of the molecule, for different values of \(g\) and for a fixed HR factor \((S = 0.75)\). (b) The maximum value of the \(\langle \hat{N}_{\text{cav}} \rangle\) time trace (Max\{\(\langle \hat{N}_{\text{cav}} \rangle\)\}) as a function of both \(g\) and \(S\). The white dashed line represents \(S = 0.75\), with each point on the line corresponding to the \(S\) and \(g\) values used for the traces in (a). The cavity frequency was set in resonance with the vibration: \(\omega_c = \omega_v = 1600\ \text{cm}^{-1}\).
Figure 3a shows the time evolution of \( \langle \hat{N}_{\text{cav}} \rangle \) given by Eq. (12) for a cavity mode in perfect resonance with the vibrational mode, i.e., \( \omega_c = \omega_v = 7.3 \text{ mHa or } 1600 \text{ cm}^{-1} \). Results are shown for five evenly spaced \( g \) values between 0 and 0.9 mHa. At time zero, \( \langle \hat{N}_{\text{cav}} \rangle = 0 \) for all values of \( g \) since the UV/vis excitation acts exclusively on the electronic DOF, inducing vibrations in the excited state. This vibrational wavepacket has zero projection onto the cavity mode at time zero and is not an eigenstate of \( \hat{H}_{\text{system}} \). As time evolves, Rabi oscillations occur as the wavepacket gains a non-zero projection onto the cavity mode giving rise to the \( \langle \hat{N}_{\text{cav}} \rangle \) traces observed. The multi-oscillatory behavior observed in the \( \langle \hat{N}_{\text{cav}} \rangle \) traces is due to interference between the contributing polariton frequencies. It can be seen that as \( g \) increases so does the maximum value \( \langle \hat{N}_{\text{cav}} \rangle \) can have (Max\{\langle \hat{N}_{\text{cav}} \rangle \}). For small \( g \) values, Max\{\langle \hat{N}_{\text{cav}} \rangle \} is approximately equal to the expected number of vibrational quanta produced upon electronic excitation, \( S \). However, the energy stored in the cavity-vibration coupling will also contribute to \( \langle \hat{N}_{\text{cav}} \rangle \), and as \( g \) becomes less negligible in comparison to the cavity and vibration energies, \( \langle \hat{N}_{\text{cav}} \rangle \) will become noticeably greater than \( S \), as observed in Figure 3a.

Figure 3b shows a heat map of Max\{\langle \hat{N}_{\text{cav}} \rangle \} as a function of \( g \) and \( S \). From this, it is clear that maximizing both \( g \) and \( S \) will lead to the largest Max\{\langle \hat{N}_{\text{cav}} \rangle \} value. Accordingly, a molecule that has a vibrational mode with a significant \( \mu_{IR}^{(e)} \) value, and hence a large \( g \) value (see Eq. (10)), along with having significant vibronic coupling, i.e., large \( S \), will make a good candidate for use in ESVP mediated photonic down conversion.

### 2.4 Radiative and Non-Radiative Dissipation of ESVP

So far our analysis has assumed the molecule and cavity to be fully isolated, apart from their mutual coupling, without including emission from the cavity, which is an integral step of the ESVP mediated photonic down conversion process. Moreover, practical implementations of this process will suffer from non-radiative relaxation of the intramolecular vibration. It is therefore necessary to consider photonic emission and non-radiative dissipation from the cavity-vibration system. To this end, we are interested in how the photonic emission can be maximized throughout the parameter space of the system. It is evident that a large \( S \) value will increase the probability of photonic down conversion as this will produce more excited state vibrational quanta. Other parameters, however, such as the non-radiative relaxation rate, the cavity-vibration coupling, and the cavity emission rate (related to \( Q \)) have a non-trivial relationship to the percentage of incoming UV/vis photons converted to emitted IR photons.

To study the influence of these parameters on the photonic down conversion process, we add two harmonic baths to our model: 1) a bath representing an external electromagnetic field that accounts for cavity emission, and 2) a bath of (solvent) phonon modes that account for non-radiative vibrational relaxation. Accordingly, the total system-bath Hamiltonian is given by

\[
H_{\text{total}} = H_{\text{system}} + \sum_{i=1}^{E+B} \left( \frac{\hat{p}_i^2}{2} + \frac{\omega_i^2 \hat{q}_i^2}{2} \right) + \sum_{i=1}^{E} \kappa_i \hat{r}_i \hat{q} + \sum_{i=E+1}^{E+B} \chi_i \hat{r}_i \hat{Q},
\]

(13)
where \( \hat{r}_i \) is the position operator for the \( 1 \leq i \leq E \) external field modes and \( E < i \leq E + B \) non-radiative bath modes, \( \kappa_i \) is the coupling constant between the \( i \)th external field mode and the cavity, and \( \chi_i \) is the coupling constant between the \( i \)th non-radiative bath mode and the vibration. It should be noted that, from Eq. (26) and Eq. (31) in “Methods”,

\[
\kappa_i = \sqrt{\frac{\omega_i}{2\pi Q D_E}},
\]

where \( D_E \) is the density of states of the external electromagnetic field, chosen to be constant as a function of \( \omega_i \).\(^{[56]} \) Hence, the cavity-external field coupling, \( \kappa_i \), and \( Q \) are inversely related. This is an intuitive result because as \( Q \) decreases, cavity photons are expected to dissipate more efficiently due to a stronger coupling of the cavity to the external field.

The schematic in Figure 4a represents the total Hamiltonian given in Eq. (13). All components of the ensemble are comprised of harmonic oscillators and the red arrows show the coupling between components. Following a similar procedure as was done for the calculation of \( \langle \hat{N}_{\text{cav}} \rangle \) in the isolated cavity-vibration case, we used the TWA to explicitly describe the time evolution of the system, non-radiative bath, and external field. This time, normal modes of the \( \hat{H}_{\text{total}} \) Hessian matrix were determined. The time evolution was monitored by means of the occupation numbers of the different components.

Figures 4b-d show the resulting occupation numbers following a UV/vis excitation of the molecule for different \( Q \) values and for a fixed \( g \) value of 0.04 mHa. These data show that by changing \( Q \), regimes with quantitatively different behaviors are obtained. For the relatively small value \( Q = 9 \) (Figure 4b), the cavity occupancy is significantly dampened due the strong coupling to the external field. Therefore, the cavity dissipation lifetime is shorter than the Rabi oscillation period. It can also be seen that the non-radiative relaxation (green) outcompetes photonic emission (orange) for this case. For the value \( Q = 100 \) (Figure 4c), short lived Rabi-oscillations are observed. The presence of Rabi-oscillations are indicative of strong coupling between the cavity and the molecular vibrational mode. In this case, the photonic emission outcompetes the non-radiative relaxation. For the value \( Q = 1600 \) (Figure 4d), longer-lived Rabi-oscillations are observed between the cavity and the molecular vibration mode. In this case, similar to the \( Q = 9 \) case, the non-radiative relaxation outcompetes the photonic emission. The change in dynamic behavior with \( Q \) observed in Figures 4b-d are the result of \( Q \) affecting the cavity decay lifetime (contingent on both the radiative and non-radiative dissipation rates) relative to \( g \). The strong coupling regime, indicated by the presence of Rabi-oscillations between the cavity and vibration as well as peak splitting in the emission spectrum, occurs when the cavity decay lifetime is long compared to the cavity-vibration Rabi oscillation period.\(^{[57]} \)

Figure 4e shows a heat map of the percentage of vibrations induced by the UV/vis excitation converted to photonic emission (% emission) as a function of \( g \) and \( Q \). The % emission is calculated as the ratio of external field photons at equilibrium normalized to the initial number of vibrations created by the UV/vis excitation, given by \( S \), that is,

\[
\text{% emission} = \frac{1}{S} \sum_{i}^{E} \langle \hat{N}_{\text{ext}}(t_{\text{eq}}) \rangle.
\]
Here, $\hat{N}_{\text{ext}}^i$ is the $i$th external field occupation number operator and $t_{eq}$ is the time at which equilibrium is reached, here taken to be $t_{eq} = 18$ ps, which suffices for all values of $g$ and $\mathcal{Q}$ used. By using this definition the % emission is independent of $S$. For example, the results in Figure 4e were computed with $S = 0.5$ but would be identical for any $S$ value used. Determining the net amount of photons produced in the photonic down conversion process simply requires multiplying the % emission by $S$.

Figure 4f shows slices of the % emission heat map along $\mathcal{Q}$ for different $g$ values given by the dashed lines in Figure 4e. The labeled points in 4f indicate the related dynamics in Figure 4b-d that give rise to those % emission values. It can be seen from Figure 4f that

Figure 4: (a) Schematic showing the total Hamiltonian, $\hat{H}_{\text{total}}$, including the cavity-molecule system, the non-radiative bath modes, and the external-field modes that constitute emission. (b-d) Dynamics of different occupation numbers for different quality factor values ($\mathcal{Q}$) at $g = 0.04$ mHa: Black = cavity photons; blue = intramolecular vibrations; orange = external field photons; green = non-radiative bath. (e) A heat map of the % emission of IR photons as a function of $g$ and $\mathcal{Q}^{1/2}$, where % emission is evaluated at 18 ps. (f) % emission as a function of $\mathcal{Q}^{1/2}$ evaluated at different $g$ values. These traces correspond to % emission along the dashed lines in (e). The labeled points along the $g = 0.04$ mHa trace correspond to the $\mathcal{Q}$ and $g$ values of the dynamics shown in (b-d). The cavity frequency was set in resonance with the vibration: $\omega_c = \omega_v = 1600$ cm$^{-1}$.
the % emission increases with $g$ for all values of $Q$, which indicates that increasing $g$ will always increase the photonic down conversion yield. Furthermore, all traces in Figure 4 have a maximum along $Q$, which we denote as $Q_{\text{max}}^\text{max}$. This is due to the competition between radiative and non-radiative decay. For $Q$ values larger than $Q_{\text{max}}^\text{max}$, the probability of cavity photons leaking from the cavity into the external field becomes small enough that non-radiative dissipation outcompetes emission. On the other hand, for $Q$ values smaller than $Q_{\text{max}}^\text{max}$, the cavity mode is coupled strong enough to the external field modes that it begins to decouple to the vibration, and again, non-radiative dissipation outcompetes emission. In fact, in the limit where $Q$ becomes very small, the cavity mode mixes into the external field to the extent that the system effectively becomes a vibration interacting with a free-space electromagnetic field, and radiative emission from the vibration is not expected due to the fast non-radiative relaxation.

$Q_{\text{max}}^\text{max}$ should be applicable for any polariton system where the matter component has a non-radiative relaxation pathway, implying that a finite cavity $Q$ value is needed to maximize the photonic emission from such systems. This motivates cavity design principles for measuring and utilizing ESVP mediated photonic down conversion, as well as for any system that uses an optical resonator to enhance emission.

2.5 Calculation of Relevant Parameters for Pyrene and PAA

The identification of molecules that allow for the formation of ESVP through a UV/vis excitation is critical for all potential applications of the ESVP mediated photonic down conversion process. Following the results of Figures 3 and 4, molecules must contain vibrational modes that are both FC active (i.e., having non-zero HR factor) and IR active within the excited state for the ESVP photonic down conversion to occur. According to the rule of mutual exclusion, such modes exist only in molecules lacking inversion symmetry (vide infra). Furthermore, the extent to which the photonic down conversion process can occur in non-centrosymmetric molecules is dependent on the strength of their vibronic couplings and excited state IR activity. This section focuses on extracting these molecular properties in specific molecules while making a connection to our theoretical model.

We have performed DFT and time-dependent-DFT (TD-DFT) calculations for two molecules: one with and one without inversion symmetry. Figure 5 shows results for both pyrene and 1-pyreneacetic acid (PAA), which are rigid chromophores with clear vibronic progressions due to vibronic coupling. Pyrene is centrosymmetric and should not have vibrational modes that are both IR and Raman active in accordance with the rule of mutual exclusion.[58] This is relevant as Raman activity implies FC activity. In centrosymmetric molecules, all electronic states contain an inversion symmetry such that electronically exciting them will only induce symmetric vibrations, meaning the excited state PES is displaced only along these symmetric modes. This displacement allows ground state vibrational overtones to be reached in the second order Raman process making them Raman active.[59] Importantly, since only symmetric modes are induced upon electric excitation, which are IR inactive, no ESVP should form in centrosymmetric molecules through UV/vis excitation. PAA, on the other hand, has a carboxylic acid functional group that breaks the inversion symmetry of
Figure 5: DFT calculations of the vibronic couplings and excited state IR dipoles for pyrene and 1-pyreneacetic acid (PAA). Calculated absorption spectra for (a) pyrene and (b) PAA were performed at different temperatures (red = 300 K; blue = 0.1 K) and with different standard deviations (σ) for the Gaussian distribution of electronic energies taken to represent inhomogeneous broadening (red = 200 cm\(^{-1}\); blue = 10 cm\(^{-1}\)). Experimental spectra (black) were taken in cyclohexane for pyrene and toluene for PAA at room temperature (\(\sim 293 \) K). Calculated HR factors \((S)\) and excited state IR dipole moments \((\mu_{IR}^{(e)})\) for vibrational modes of (c) pyrene and (d) PAA are plotted as a function of the wavenumber of each mode. \(\mu_{IR}^{(e)}\) is plotted “on top of” the \(S\) values, and are only shown for modes with \(S > 0\), while its value is indicated above each bar.

the pyrene moiety and should contain IR and FC active vibrational modes. By comparing these two molecules we can test whether simple violations of the rule of mutual exclusion can serve to design molecules for ESVP mediated photonic down conversion.

In order to determine the accuracy of the calculations, absorption spectra were calculated and compared to experimental spectra (Figure 5a and 5b). These spectra were calculated using the TWA as detailed in other work,\(^1\)[60] and are exact within the FC and harmonic approximation. Results were calculated at finite temperature by taking a Boltzmann population on the ground state vibrations and also include inhomogeneous broadening due to a Gaussian distribution (\(\sigma\) denoting the standard deviation) of the electronic transition energy. At room temperature, calculated spectra (red) with \(\sigma = 200 \) cm\(^{-1}\) show excellent qualitative agreement with the experimental spectra (black) indicating that the calculations capture the correct vibronic couplings and normal modes within the molecules. The calculated spectra at 0.1 K and \(\sigma = 10 \) cm\(^{-1}\) remove the majority of the inhomogenous broadening as well as broadening due to transitions from hot ground state vibrations that occur at room tempera-
tude. This gives “the skeleton” of the vibronic progression with peaks corresponding only to transitions from ground vibrational states on the electronic ground state. A renormalization of the DFT-calculated electronic transition energy was applied for our calculations to match the experimental data.

Figure 5c and 5d show $S$ (blue) and $\mu_{IR}^{(e)}$ (green) for the different vibrational modes as a function of each mode’s wavenumber for both pyrene and PAA. Although both molecules contain many modes with non-zero $\mu_{IR}^{(e)}$ values, we only show $\mu_{IR}^{(e)}$ for modes with non-zero $S$ values as these are the only vibrational modes that are excited by electronic transitions. $S$ values are calculated for ground state vibrations and $\mu_{IR}^{(e)}$ values are calculated for excited state normal modes. Because Duschinsky rotations can occur, the overlap squared of each ground state mode with each excited state mode was taken in order to match them. In both molecules, there was generally minimal mixing of ground state normal modes in the excited state, validating our application of the FC approximation. Figure 5c shows that each FC active vibrational mode has a zero $\mu_{IR}^{(e)}$ value for pyrene, in accordance with the rule of mutual exclusion. On the other hand, Figure 5d shows that each FC active vibrational mode in PAA has a non-zero $\mu_{IR}^{(e)}$ value due to the broken inversion symmetry of the pyrene moiety. Therefore, an optical cavity may be tuned to one of the FC active vibrational modes of PAA shown in Figure 5d—a good choice being the highest frequency mode at 1680 cm$^{-1}$—and upon UV/vis excitation of the PAA molecule, ESVP would form.

The results from the DFT calculations presented here can be connected to the theoretical model presented in sections 2.3 and 2.4 through the calculated $S$ and $g$ values. However, for a single molecule coupled to a cavity mode, $g$ is typically very small when compared to values required for the UV/vis-to-IR photonic down conversion process. For example, for the mode at 1680 cm$^{-1}$, $\mu_{IR}^{(e)} = 0.57$ Debye, which corresponds to a $g$ value of $1.8 \times 10^{-6}$ mHa. This is assuming a cavity volume of $V = 1.06 \times 10^{-16}$ m$^3$ using $V = \lambda^3/2$, where $\lambda$ is the wavelength of the cavity mode. Comparing this $g$ value with Figure 4e, there would be negligible photonic down conversion for all $Q$ values. The small $g$ value and photonic down conversion yield are due to having only a single molecule coupled to the cavity. Experimental vibrational-polariton measurements rely on an ensemble of molecules to be coupled to a cavity mode, and the Rabi splittings observed correspond to larger coupling strengths than would be expected from each individual molecule.[62] This is referred to as collective strong coupling for which it is known that the Rabi-splitting increases with the square root of the number of cavity coupled molecules ($N$).[13, 63] As a rough estimate, an effective $g$ value that scales with $\sqrt{N}$ can, therefore, be considered. Using the concentration of molecules present in the optical cavity and knowing the molecule’s absorption cross section, one could estimate the number of excited molecules within the cavity and calculate an effective coupling strength from the DFT results. This would allow the % emission from photonic down conversion of the molecule to be determined as a function of the $Q$. It should be noted, however, that collective strong coupling remains underexplored, especially in the presence of multiple quanta such as involved in the ESVP mediated photonic down conversion process, the topic of which we reserve for future work.
3 Discussion

In this work, a novel UV/vis-to-IR photonic down conversion process is shown to be driven by ESVP for a molecule in an optical cavity. Accordingly, a UV/vis excitation of the molecule induces vibrational polaritons on the molecule’s electronic excited state potential. Such ESVP may then leak IR light, resulting in a photonic down conversion that can potentially be exploited for applications in sensing, quantum information, and in the manipulation of photo-induced reactions. The mechanism and relevant molecular parameters that allow for the down conversion process to occur are the HR factor and the excited state IR dipole, which both need to be non-zero. According to the rule of mutual exclusion, this implies that the photonic down conversion process can only occur within molecules lacking inversion symmetry.

By studying the parameter space of the ESVP mediated photonic down conversion while including both radiative and non-radiative dissipation, we determined the optimal parameters to maximize the down conversion yield, facilitating experimental and practical implementations. Due to the inclusion of non-radiative dissipation, the photonic down conversion is maximized at a specific cavity quality factor. With excess quality factors, the probability of cavity photon leakage becomes small and non-radiative processes will out-compete emission. However, with lower than optimal quality factors, the cavity mode becomes highly delocalized through mixing with free-space electromagnetic field modes outside of the cavity inhibiting strong coupling with the molecular vibration. These two limiting behaviors give rise to an intermediate quality factor, $Q^{\text{max}}$, that maximizes the down conversion process.

In the previous subsection, we demonstrated how to use DFT calculations to predict if ESVP will form on a molecule when it is excited with UV/vis light within a cavity. We believe this to be useful for designing molecules that maximize the ESVP mediated photonic down conversion, allowing for applications in quantum information and sensing to be realized. Such DFT calculations can also determine if an optical cavity could be used to modulate a molecule’s excited state dynamics following a UV/vis excitation with ramifications for photo-induced reactions. The importance of the rule of mutual exclusion is emphasized by our evaluation of both pyrene, containing inversion symmetry, and 1-pyreneacetic acid, lacking an inversion symmetry. Our results show that only 1-pyreneacetic acid has both FC active (non-zero HR factor) and excited state IR active vibrational modes, which permit the formation of ESVP.

We note that a potential exception to the requirement of molecular inversion symmetry for the formation of ESVP induced by a UV/vis excitation would be the occurrence of excited state symmetry breaking due to solvent interactions.\cite{64} This results in ground state vibrational modes of different symmetries mixing in the excited state and could allow excited state IR active vibrations to be produced on ground state centrosymmetric molecules following a UV/vis excitation of the molecule. These vibrations could, therefore, couple to a cavity, opening further ways to mediate the photonic down conversion.
4 Methods

4.1 Diabatic Expansion of the Dipole Operator

The dipole operator can be separated into components that depend on electronic and nuclear DOF as

\[ \hat{\mu} = \hat{\mu}_{el} + \hat{\mu}_{nu}. \]  

(16)

When expanding \( \hat{H}_{\text{system}} \) in the diabatic basis, each element of the dipole operator in this basis becomes

\[ \hat{\mu}_{\alpha\beta}(\hat{Q}) = \langle \alpha | \hat{\mu}_{el}|\beta \rangle + \hat{\mu}_{nu}(\hat{Q})\delta_{\alpha\beta}, \]  

(17)

which act on the nuclear Hilbert space of \( \hat{Q} \) and not on the electronic Hilbert space. Note that \( \hat{\mu}_{nu} \) does not act on the diabatic basis states as they do not depend on \( Q \) (see Eq. (2)). The linear expansion of each element of the dipole operator is given by

\[ \hat{\mu}_{\alpha\beta}(\hat{Q}) = \mu_{\alpha\beta}(Q^{(g)}_0) + \frac{\partial \mu_{\alpha\beta}(Q)}{\partial Q}\bigg|_{Q^{(g)}_0} (\hat{Q} - Q^{(g)}_0), \]  

(18)

with the first coefficient being

\[ \mu_{\alpha\beta}(Q^{(g)}_0) = \langle \alpha | \hat{\mu}_{el}|\beta \rangle + \mu_{nu}(Q^{(g)}_0)\delta_{\alpha\beta}, \]  

(19)

where \( \langle \alpha | \hat{\mu}_{el}|\beta \rangle \) is the permanent electric dipole of state \( \alpha \) when \( \alpha = \beta \) and the transition dipole between the states \( \alpha \) and \( \beta \) when \( \alpha \neq \beta \). Further, \( \mu_{nu}(Q^{(g)}_0) \) is the dipole moment of the nuclei at configuration \( Q^{(g)}_0 \). It follows that the second coefficient in Eq. (18) is given by the derivative of the nuclear dipole moment with respect to \( Q \) at configuration \( Q^{(g)}_0 \),

\[ \frac{\partial \mu_{\alpha\beta}(Q)}{\partial Q}\bigg|_{Q^{(g)}_0} = \frac{\partial \mu_{nu}(Q)}{\partial Q}\bigg|_{Q^{(g)}_0} \delta_{\alpha\beta}. \]  

(20)

We ignored coupling between the cavity and the molecule’s electronic DOF as the cavity mode is assumed to be near resonant with the vibrational mode of interest making it significantly off-resonant from the electronic transition. Accordingly, we set elements of the dipole operator where \( \alpha \neq \beta \) to zero. Because of this, the electronic ground and excited state contributions to \( \hat{H}_{\text{system}} \) are uncoupled and can be treated separately. For the purpose of this study, we focused on the excited state contribution where \( \alpha = \beta = e \). To simplify notation we defined

\[ \mu'_e \equiv \frac{\partial \mu_{ee}(Q)}{\partial Q}\bigg|_{Q^{(g)}_0}, \]  

(21)

and

\[ \mu^0_e \equiv \mu_{ee}(Q^{(g)}_0) - \mu'_e Q^{(g)}_0. \]  

(22)

Note that \( \mu^0_e \) is the permanent dipole moment of the excited state at the ground state equilibrium configuration, which was taken to be \( Q^{(g)}_0 = 0 \).
4.2 Polariton Normal Mode Basis

$\hat{H}_{\text{system}}$ can be rotated into a basis of two uncoupled oscillators called the polariton normal mode basis (see Figure 2). This basis is found by determining the eigenvectors of the cavity-vibration Hessian matrix,

$$H = \begin{pmatrix} \omega^2_c & G \\ G^* & \omega^2_v \end{pmatrix}.$$  \hfill (23)

The polariton harmonic oscillators have upper frequency ($\Omega_+$) and lower frequency ($\Omega_-$) given by the square root of the eigenvalues of $H$. The off diagonal element of the Hessian matrix, $G$, is the cavity-vibration bilinear coupling constant given by

$$G = \frac{2}{\hbar} \sqrt{\omega_c \omega_v} g.$$  \hfill (24)

The analytical expression for $\langle \hat{N}_{\text{cav}}(t) \rangle$ was determined by rotating the cavity photon occupancy operator,

$$\hat{N}_{\text{cav}} = \frac{1}{2\hbar \omega_c} (\omega^2_c \hat{q}^2 + \hat{p}^2) - 1/2,$$  \hfill (25)

into the polariton basis by expanding $\hat{q}$ and $\hat{p}$ in terms of polariton phase space operators, $\hat{R}_-$ and $\hat{R}_+$. The Weyl symbol of $\hat{N}_{\text{cav}}$, in the polariton basis, was determined by replacing the polariton phase space operators with phase space variables that can be evolved according to the classical equations of motion for two uncoupled harmonic oscillators. From this, we calculate the expectation value of the time evolved Weyl symbol of $\hat{N}_{\text{cav}}$ acting on the time independent Wigner distribution of the initial position and momentum of the system.[65, 43]

4.3 System-Bath Couplings

An ohmic spectral density was taken for both the non-radiative bath and the external field, $J_E(\omega) = \eta_E \omega$ and $J_B(\omega) = \eta_B \omega$, respectively, where $\eta_E$ ($\eta_B$) is the cavity (vibration) damping constant due to coupling to the external field (non-radiative bath). By taking a large but finite number of non-radiative bath and external field modes (we used 500 modes for each bath), $\hat{H}_{\text{total}}$ approximates the thermodynamic number of bath modes under experimental conditions.[66] In our modeling, we used a constant density of states ($D_B$ for the non-radiative bath; $D_E$ for the external field) and frequency dependent coupling constants,

$$\kappa_i = \sqrt{\frac{\eta_E \omega_i}{D_E}},$$  \hfill (26)

and

$$\chi_i = \sqrt{\frac{\eta_B \omega_i}{D_B}}.$$  \hfill (27)

In all of our calculations, the vibrational damping constant, $\eta_B$, was fixed such that an excited vibration would have a lifetime of 2 ps for $g = 0$, which is typical of condensed-phase molecular vibrations (we study different non-radiative lifetimes in section 5 of the SI).[26, 27]
Furthermore, $\eta_E$ is related to $Q$, which is defined as the ratio of the cavity center frequency to its emission linewidth, $\Delta \omega_c$: \[ Q = \frac{\omega_c}{\Delta \omega_c}. \] \hspace{1cm} (28)

An expression for the emission profile linewidth of an optical cavity coupled to a bath of external field modes can be extracted from the Lindblad master equation as \[ \Delta \omega_c = 2\pi D E |\kappa\omega_c|^2, \] \hspace{1cm} (29)

where $\kappa\omega_c$ is the cavity-external field coupling at the cavity frequency. Substituting equation 29 into equation 28 gives \[ Q = \frac{\omega_c}{2\pi D E |\kappa\omega_c|^2}. \] \hspace{1cm} (30)

Setting $\kappa_i = \kappa\omega_c$ and $\omega_i = \omega_c$ in equation 26 and then comparing the result to equation 30, it follows that \[ \eta_E = \frac{1}{2\pi Q}. \] \hspace{1cm} (31)

It should be noted that the Lindblad equation invokes the RWA and therefore will give inaccurate $Q$ values in the ultrastrong cavity-external field coupling regime.

### 4.4 DFT Calculations of Huang-Rhys Factors and Excited State IR Dipoles

DFT calculations were performed using the Qchem software (version 5.3). All DFT and TD-DFT calculations utilized the B3LYP functional and 6-31+G* basis set. In order to determine $S$ and $\mu IR^{(e)}$ for pyrene and PAA, first the ground state equilibrium geometry was calculated for each molecule in its singlet ground state, followed by a normal mode analysis about this ground state minimum to obtain the intramolecular vibrations, both done via DFT calculations. TD-DFT calculations were then used to determine the forces felt by the nuclei due to the molecule being excited into the first, bright excited singlet state. This force is due to the electron density of the excited state acting on the ground state nuclear configuration, shifting the equilibrium nuclear configuration. Excited state force vectors from the TD-DFT calculations were projected onto the ground state vibrational modes. These forces determine the shift in the excited state PES and were used to calculate HR factors for each vibrational mode. Finally, we performed TD-DFT excited state normal mode analyses at the FC point to calculate the excited state intramolecular vibrations and their corresponding $\mu IR^{(e)}$ values. No description of solvent interactions was included in the computed spectra.

### 5 Acknowledgments

The authors thank Jonathan D. Schultz for the helpful discussions regarding this work. This work was supported as part of the Center for Molecular Quantum Transduction (CMQT), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of
Science, Basic Energy Sciences under Award No. DE-SC0021314. This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. DGE-2234667.

**Declarations**

The authors declare no competing interests.

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