Unraveling excitation energy transfer assisted by collective behaviors of vibrations

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Abstract

We investigate how collective behaviors of vibrations such as cooperativity and interference can enhance energy transfer in a nontrivial way, focusing on an example of a donor–bridge–acceptor trimeric chromophore system coupled to two vibrational degrees of freedom. Employing parameters selected to provide an overall uphill energy transfer from donor to acceptor, we use numerical calculations of dynamics in a coupled exciton–vibration basis, together with perturbation-based analytics and calculation of vibronic spectra, to identify clear spectral features of single- and multi-phonon vibrationally-assisted energy transfer (VAET) dynamics, where the latter include up to six-phonon contributions. We identify signatures of vibrational cooperation and interference that provide enhancement of energy transfer relative to that obtained from VAET with a single vibrational mode. We observe a phononic analogue of two-photon absorption, as well as a novel heteroexcitation mechanism in which a single phonon gives rise to simultaneous excitation of both the trimeric system and the vibrational degrees of freedom. The impacts of vibrations and of the one- and two-phonon VAET processes on the energy transfer are seen to be quite different in the weak and strong site–vibration coupling regimes. In the weak coupling regime, two-phonon processes dominate, whereas in the strong coupling regime up to six-phonon VAET processes can be induced. The VAET features are seen to be enhanced with increasing temperature and site–vibration coupling strength, and are reduced in the presence of dissipation. We analyze the dependence of these phenomena on the explicit form of the chromophore–vibration couplings, with comparison of VAET spectra for local and non-local couplings.

1. Introduction

Recent experimental and theoretical studies of the molecular structures present in biological light harvesting complexes have revealed the delicate interplay of electronic and vibrational degrees of freedom, and how these come together to orchestrate efficient transfer of photoexcitations in such systems [1–8]. Coherent beating patterns in nonlinear spectroscopy signals initially ascribed to long-lived electronic coherence in such systems [9] are now generally agreed to be due to a combination of electronic and vibrational coherence, with a key role played by coupling of the relevant electronic degrees of freedom to long-lived, underdamped vibrational modes of molecules [10–14]. This revelation has brought to light the subtle ways in which vibrational dynamics in molecular complexes can influence electronic and excitonic properties [15–19]. In this work we draw inspiration from these studies of molecular systems and ask whether vibrational degrees of freedom can exert other subtle influences on energy transfer in such complexes. In particular, can the presence of multiple underdamped vibrations in a molecular complex influence energy transfer dynamics in non-trivial ways?
With the recent growth of quantum technologies, controllable artificial quantum simulators have been developed to probe the underlying basic mechanism of the observed long-time coherences [20–22]. In reference [20], an engineered vibrationally assisted energy transfer (VAET) was experimentally demonstrated for an excitonic dimer emulated in a trapped-ion platform. In that work, not only was a one-phonon VAET process signified by a peak at the vibrational frequency being equal to the excitonic transition frequency unambiguously reported, but also unresolved peaks at smaller frequencies were found. It was suggested that the latter were due to multiphonon VAET processes. This provides further motivation for the study of multiphonon VAET processes. In this work we seek to ascertain the extent to which such multiphonon VAET can be resolved, and also the consequences of any collective behavior of the vibrations for excitonic energy transfer processes. Specifically, it is of interest to explore whether cooperative or interference effects might play a role in the vibrationally enhanced energy transfer. In addition, these systems offer the possibility of finding both the phononic analog of the well-known two-photon absorption [23–25], and the inverse phenomenon [26], in which one phonon might simultaneously excite two excitonic transitions, where the latter could be of different frequencies. The latter inverse situation offers a new twist with phonons relative to atoms, namely that in the context of VAET we can ask whether one phonon from a specific vibrational mode can simultaneously cause an excitonic transition and a vibrational transition in a different vibrational mode.

To address these questions, we consider here a donor–bridge–acceptor trimeric chromophore system coupled to two vibrational degrees of freedom. We analyze the dynamics within a single electronic excitation subspace with explicit incorporation of the vibrational states, performing full numerical simulations for the excitation energy transfer probability from donor to acceptor via the bridging chromophore under various conditions. We construct a two-dimensional spectral representation of the VAET probabilities by scanning the frequencies of the two vibrations. These two-dimensional (2D) VAET spectra allow identification of several mechanisms through which the vibrational modes can influence and/or enhance energy transfer. These mechanisms include both single mode VAET, and multi-mode VAET in which the two vibrational modes can cooperate and/or interfere. Detailed assignment of the VAET features is facilitated by calculation of the vibronic states resulting from the coupling of electronic and vibrational degrees of freedom, which shows that a number of the VAET features are correlated with the presence of avoided crossings in the vibronic energy spectra. In the weak site–vibration coupling regime we analyze the dynamical results with a perturbative analysis and use of double-sided Feynman diagrams [27]. For both weak and strong site–vibration coupling regimes we then investigate the dependence of the VAET features on exciton dissipation and vibrational temperature.

The context of this study is quantum emulation of excitonic energy transfer in ion traps and their use in elucidating the dynamic consequences of exciton–vibration coupling for energy transport in molecular excitonic systems. We focus first on the behavior when the vibrations are coupled locally to individual chromophore sites, as in the case of trapped ions coupled to transverse modes. The model trimeric system of primary interest in this work is generalized from a dimeric system studied previously with an experimental ion trap emulator [20] and starts from a Hamiltonian in which individual vibrational modes are coupled to Frenkel excitons on specific sites. We then extend this to study of the energy transfer dynamics induced by Hamiltonian coupling to vibrations that are correlated between sites, which naturally results from coupling to the longitudinal modes of trapped ions.

The trapped ion internal states in an ion trap emulation of molecular chromophores can be regarded as pseudo-chromophores. The ability to select different states and modulate their energies with external fields allows exploration of the effects of different energetic landscapes on energy transfer. However, the Hamiltonian for interaction of such internal ionic states with the external vibrational modes of the trapped ions has some subtle differences from the form of Hamiltonian relevant to studies of excitonic energy transfer in molecular aggregates such as natural light harvesting systems [28] or J-aggregates. We show here that despite these differences, the effective Hamiltonian that results from projection to the single electronic excitation subspace maps onto the standard form for excitonic energy transfer in the presence of vibrations that are correlated between different chromophores. We study the influence of these correlations on the effectiveness of the energy transfer, focusing in particular on the role of vibrations in enabling uphill energy transport in the excitonic degrees of freedom. The role of coherence in overcoming energy barriers has motivated discussion of rectification [29], while the coherent coupling of vibrational degrees of freedom in a quantum bath to an uphill gradient of excitonic states has been demonstrated to allow quantum ratcheting of energy transfer over long distances [30]. Clearly the phenomenon of VAET [20] is a prime enabler for such uphill energy transport. In this work we shall explore in detail the ways in which VAET processes facilitate and enhance energy transport, with particular emphasis on the role of VAET with correlated vibrational modes. We shall find that not only do resonant single phonon processes play a key role, but also non-resonant processes that facilitate and enhance energy transport.
role in enhancing energy transport, but that multi-phonon processes can also be strong facilitators of energy transport.

The remainder of the paper is organized as follows. Section 2 introduces the model of the trimeric chromophore system with excitonic sites coupling locally to individual vibrational modes, e.g. as with a linear array of trapped ions coupled to transverse vibrational modes. In section 3, we summarize the procedure for numerical calculations of the 2D VAET spectra and the perturbation theory for analysis of the excitation energy transfer features. Full details of the latter are presented in the supplementary material (https://stacks.iop.org/NJP/23/073012/mmedia) [31]. Sections 4 and 5 present and analyze results revealing the various VAET signatures in the weak and strong site–vibration coupling regimes, respectively. In section 6, we present the vibronic energy spectrum and discuss the insights this offers for the VAET processes. We also discuss here the effects of the vibrational cross coupling terms induced by restriction to the single-exciton subspace of a Hamiltonian suitable for emulation of excitonic energy transfer with trapped ions. Section 7 presents 2D VAET spectra and analysis for a trimeric system realizable for linear arrays of trapped ions with coupling only to longitudinal vibrational modes, resulting in a Hamiltonian with explicit correlations in the coupling of individual sites to the vibrational modes. Section 8 provides a summary and outlook for observation of the predicted VAET phenomena in trapped ion experiments, together with a discussion of the implications of this VAET study for understanding excitonic energy transfer in molecular systems.

2. The effective model of a trimeric chromophore system

We consider a donor–bridge–acceptor trimeric chromophore system coupled to two undamped vibrations, shown schematically in figure 1(a). The model can be described by the Hamiltonian

$$H_{tr} = H_s + H_v + H_{int},$$

where (setting $\hbar = 1$)

$$H_s = \omega_1 \sigma_z^{(1)} + \omega_2 \sigma_z^{(2)} + \omega_3 \sigma_z^{(3)} + J_{12} \sigma_x^{(1)} \sigma_x^{(2)} + J_{23} \sigma_x^{(2)} \sigma_x^{(3)},$$

$$H_v = \nu_a a^\dagger a + \nu_b b^\dagger b,$$

$$H_{int} = \kappa_a \sigma_z^{(2)} (a + a^\dagger) + \kappa_b \sigma_z^{(3)} (b + b^\dagger).$$

In the electronic Hamiltonian $H_s$, the three sites correspond to the donor, bridge, and acceptor, respectively. Each site is modelled by a two-level system, with $2\omega_i$ the transition frequency between its ground and excited states, $|g_i\rangle$ and $|e_i\rangle$, respectively. The Pauli operators $\sigma_i^{(j)}$ are given by $\sigma_i^{(0)} = |g_i\rangle\langle e_i| + |e_i\rangle\langle g_i|$ and $\sigma_i^{(j)} = |e_i\rangle\langle e_i| - |g_i\rangle\langle g_i|$. $J_{ij}$ is the coupling strength between adjacent $i$th- and $j$th-sites. We assume that the coupling between the first and third sites is vanishingly small. The vibrational mode with creation operator $a^\dagger$ and frequency $\nu_a$ ($\nu_b$) is coupled to the bridge (acceptor) site with coupling strength $\kappa_a$ ($\kappa_b$). In the quantum emulation context, such local coupling of sites to individual vibrations can be realized by coupling to transverse modes of a linear chain of trapped ions, so we denote this Hamiltonian by $H_v$. In addition to these undamped single-mode vibrations coupled to the electronic sites included in the above Hamiltonian, we shall also incorporate dissipation effects by use of non-Hermitian terms in the electronic Hamiltonian. Since the immediate context of this study is the emulation of excitonic energy transfer by trapped ions, the origin of these non-Hermitian terms will be due to optical dephasing or to spontaneous emission, rather than to the dissipation provided by an overdamped vibrational bath as is usual for natural light harvesting systems.

We focus on the excitation energy transfer in a single electronic excitation subspace. An effective Hamiltonian within this subspace is obtained using the subspace projection operator $\Xi \equiv |egg\rangle\langle egg| + |egg\rangle\langle geg|$, using $\hat{H}_{tr} = \Xi H_{tr} \Xi$. Explicitly, we find

$$\hat{H}_{tr} = \tilde{\omega}_1 |1\rangle\langle 1| + \tilde{\omega}_2 |2\rangle\langle 2| + \tilde{\omega}_3 |3\rangle\langle 3| + J_{12} (|1\rangle\langle 2| + |2\rangle\langle 1|) + J_{23} (|2\rangle\langle 3| + |3\rangle\langle 2|)$$

$$+ \kappa_a (a^\dagger a + a + a^\dagger) (|2\rangle\langle 2| - |1\rangle\langle 1| - |3\rangle\langle 3|) + \kappa_b (b^\dagger b + b + b^\dagger) (|3\rangle\langle 3| - |1\rangle\langle 1| - |2\rangle\langle 2|) + \nu_a a^\dagger a + \nu_b b^\dagger b,$$

where $|1\rangle \equiv |egg\rangle$, $|2\rangle \equiv |ggg\rangle$, $|3\rangle \equiv |egg\rangle$. $\omega_1 = \omega_a - \omega_2 - \omega_3, \omega_2 = \omega_1 - \omega_3$, and $\omega_3 = \omega_2 - \omega_1 - \omega_3$. The couplings in the full Hamiltonian are depicted in figure 1(a) and resulting couplings of the effective Hamiltonian in the single excitation subspace are illustrated in figure 1(b). We note that, just as for a dimer [20], assistance from vibrations for energy transport becomes unnecessary when the transition frequencies of three sites are identical, since there are then no energetic differences between spatially
separated sites. Our numerical calculations in this paper will focus on electronically uphill processes, as indicated schematically in figure 1(b).

Two important remarks on the effective model in equation (5) are in order here. First, the counter-rotating terms in the XX-type interaction of equation (2) do not conserve the number of excitations and therefore do not survive the projection into the single electronic excitation manifold (since \( \Xi = \Xi = 0 \)). Second, it is evident that, in addition to the coupling between an electronic site and its directly connected vibrational mode [see equation (4)], the single-excitation effective model of equation (5) contains terms that couple a vibration to excited states of its unconnected sites, as indicated by dashed arrows in light green and blue in figure 1(b). These terms derive from the projection of the \( \sigma_z \) operators through which sites 2 and 3 couple to their individual vibrations, i.e. \( \Xi = |2, 2⟩ - |1, 1⟩ - |3, 3⟩ \) and \( \Xi = |3, 3⟩ - |1, 1⟩ - |2, 2⟩ \).

The Hamiltonian equation (1) differs formally from the common modelling of vibrational coupling of molecular chromophores, for which only coupling to excited electronic states is included, i.e. \( \kappa_\sigma \sigma_z (a' + a) + \kappa_\sigma \sigma_z (b' + b) \) [28]. In the Born–Oppenheimer approximation, the ground electronic state of a molecular system is defined to be at the minimum of all relevant vibrational degrees of freedom and therefore there is no linear coupling to the electronic ground state. For a single chromophore, this coupling will just shift the overall energy of the system and both pictures are used for single vibronic states that mimic correlations between vibrations at different sites in a molecular system [10, 28, 32–37]. In the following sections we shall see that these cross-couplings can give rise to enhanced collective phenomena in VAET. We note that the cross-couplings in equation (5) show both positive correlations between some sites, e.g. between donor and acceptor sites for mode \( \nu_a \), and negative correlations between other sites, e.g. between donor and bridge sites for mode \( \nu_b \). Consequently the overall effect of the correlations is not easily rationalized in terms of arguments for correlated dimers [28].

To illustrate the relevance of this study for understanding of natural photosynthetic systems, table 1 shows typical values for the parameters considered in this work and compares them to the corresponding typical values for the Fenna–Matthews–Olson (FMO) light harvesting complex unit of green sulphur bacteria [38, 39]. The first row shows typical values from the parameter ranges employed in this work and the third row shows corresponding typical values for the FMO system. The second row shows the result of setting our site energies \( \tilde{\omega}_1, \tilde{\omega}_2, \) and \( \tilde{\omega}_3 \) to the natural value and scaling up the other parameters accordingly. It is evident that the range of parameters available in ion trap emulations scales consistently to the natural system, suggesting that analogs of the phenomena observed here might be present also in some natural light harvesting complexes (for more discussion of this, see the supplementary material [31]). Of particular relevance here are systems that have uphill regions in their landscape of Frenkel (site) exciton energies. This includes the FMO monomer complex [38], as well as the purple bacterium Rhodopseudomonas viridis [40] and the CP43 core antenna of photosystem II [41].
3. Excitation energy transfer probability

We calculate the probability of finding an excitation in the acceptor, i.e. the third site, given an initial excitation localized on the donor, i.e. on the first site, as a function of time, \( P_3(t) \). Since there is no direct excitonic transfer from donor to acceptor, in the absence of coupling to vibrations the excitation is transferred via the bridging site. \( P_3(t) \) is given by

\[
P_3(t) = \text{Tr} \left[ |3⟩⟨3| U(t)|1⟩⟨1| ρ_a ρ_b U^† \right].
\]

(6)

Here the unitary time evolution is for the whole system, i.e. \( U(t)|1⟩⟨1| ρ_a ρ_b U^† \), where \( |1⟩⟨1| \), \( ρ_a \), and \( ρ_b \) are initial states of the chromophoric trimer and two vibrational modes, respectively, and \( U = e^{-iH_0t} \) is an evolution operator with \( H_0 \) given by equation (5). Tracing over the vibrational degrees of freedom leads to the reduced excitonic system dynamics and then further taking the quantum average of the site number operator \( |3⟩⟨3| \) gives the population at the acceptor site, \( P_3(t) \). Numerical calculations of the transfer probability in equation (6) are performed assuming thermal initial states for the two vibrations, i.e. \( ρ_a = e^{-iω_a^0a^†a/k_BT_a}/Tr_a[e^{-iω_a^0a^†a/k_BT_a}] \) and \( ρ_b = e^{-iω_b^0b^†b/k_BT_b}/Tr_b[e^{-iω_b^0b^†b/k_BT_b}] \), where \( k_BT_a \) and \( k_BT_b \) are individual temperatures of each vibration. We shall use Max\[P_3(t)|0 ≤ t ≤ t_f \] and \( \int_0^{t_f} P_3(t)dt \), which measure the maximum and accumulated population during a given time period \( t_f \), respectively, as quantitative measures of the excitonic energy transfer efficiency.

In order to assist in interpreting and understanding the results from these numerical calculations, we also develop an analytic perturbation theory approach. Our analytical treatment focuses on a symmetric version of the effective three-level model, namely, \( J_{12} = J_{23} = J \) and \( \tilde{ω}_3 - \tilde{ω}_2 = \tilde{ω}_2 - \tilde{ω}_1 = Δ \) in equation (5). The excitonic Hamiltonian in equation (5) then becomes \( H_0^{(e)} = \sum_{j=1}^3 \lambda_j |e_j⟩⟨e_j| \), with eigenenergies \( \lambda_j = 0, ±Ω \) (\( Ω = \sqrt{2 J^2 + Δ^2} \)) and eigenstates \( |e_j⟩ \).

Transforming to the interaction picture with respect to the free Hamiltonian [i.e. including only \( H_0^{(e)} \) and the vibrational part (i.e. \( H_0^{(v)} = ν_a^0a^†a + ν_b^0b^†b \))] the site–vibration Hamiltonian becomes (see [31])

\[
H_I(t) = \sum_{j,k} \lambda_j A_{jk} [a^† e^{i(Δ_j + ω_a) t} + a e^{i(Δ_j - ω_a) t}] |e_k⟩⟨e_j| + \sum_{j,k} \lambda_k B_{jk} [b^† e^{i(Δ_k + ω_b) t} + b e^{i(Δ_k - ω_b) t}] |e_k⟩⟨e_j|,
\]

(7)

where \( Δ_j = λ_j - λ_k \) is the transition frequency between eigenstates and the forms for the coefficients \( A_{jk}, B_{jk} \) are given in appendix A. We use fourth-order perturbation theory with respect to the site–vibration coupling to expand the evolution operator as

\[
U_I(t) = T e^{-i∫_0^t dtdH_I(t)} ≈ 1 + \sum_{i=1}^4 U_i^{(i)},
\]

(8)

and correspondingly obtain the transition probability

\[
P_3(t) = P_3^{(0)} + P_3^{(1)} + P_3^{(2)},
\]

(9)

with

\[
P_3^{(0)} = \text{Tr}_{a,b} \{ |A^{(0)}⟩⟨A^{(0)}| ρ_a ρ_b \},
\]

\[
P_3^{(1)} = \text{Tr}_{a,b} \{ (|A^{(1)}⟩⟨A^{(1)}| + |A^{(0)}⟩⟨A^{(2)}| + (|A^{(2)}⟩⟨A^{(0)}|) ρ_a ρ_b \},
\]

and

\[
P_3^{(2)} = \text{Tr}_{a,b} \{ (|A^{(2)}⟩⟨A^{(2)}| + |A^{(1)}⟩⟨A^{(3)}| + (|A^{(3)}⟩⟨A^{(1)}| + (|A^{(0)}⟩⟨A^{(4)}| + (|A^{(4)}⟩⟨A^{(0)}|) ρ_a ρ_b \},
\]

Table 1. Comparison of typical parameters for trapped ion emulators used in this work (line 1) with values found in natural photosynthetic systems (line 3). Line 2 shows parameters scaled up from line 1 to the regime for natural systems. Note that the vibrational frequencies on line 1 are for two-photon processes.

| Parameters     | \( \tilde{ω}_1 \) | \( \tilde{ω}_2 \) | \( \tilde{ω}_3 \) | \( J_{12} \) | \( J_{23} \) | \( ν_a \) | \( ν_b \) | \( ν_b \) | \( k_BT_a \) | \( k_BT_b \) |
|----------------|----------------|----------------|----------------|-------------|-------------|-------|-------|-------|-------------|-------------|
| Values (kHz)   | −0.5          | 0              | 0.5            | 1           | 0.1         | 0.5   | 0.5   | 0.5   | 0.1         | 0.1         |
| Scale-up (cm⁻¹) | −138.6        | 138.6          | 27.72          | 27.72       | 144         | 144   | 27.72 | 27.72 | 200         | 200         |
| Natural system (cm⁻¹) | −138.6        | 138.6          | −5.9           | −15.7       | 180         | 180   | 42.2  | 42.2  | 200         | 200         |
where the transition amplitudes are given by $A^{(0)} = \langle 3 | U_0 | 1 \rangle$ and $A^{(1)} = \langle 3 | U_0 U_1^{(1)} | 1 \rangle$, with $U_0 = e^{-iH_0^{(a)}t_1}$.

Unless otherwise stated, in the numerical calculations and perturbative analysis of these in the following two sections, we shall study the maximum probability $\text{Max}[P_5(t)]$ during a given time period $(0 \leq t \leq t_f = 400 \text{ ms})$, for a symmetric trimeric system with $J_{12} = J_{23} = J$ and $\omega_3 - \omega_2 = \omega_2 - \omega_1 = \Delta$ in equation (5), coupled to two vibrations at a temperature larger (by a factor of $\approx 10$) than these energies. This choice of parameters represents an energetically uphill process in the single excitation subspace. We shall present 2D VAET spectra obtained by evaluating $\text{Max}[P_5(t)]$ over the given time period as a function of the two vibrational frequencies $\nu_a$ and $\nu_b$. These frequencies are given in units of the energy difference $\Delta_{31}$ between the eigenstates $|e_3\rangle$ and $|e_1\rangle$ of the electronic Hamiltonian $H_0^{(a)} |e_3\rangle = \lambda_3 |e_3\rangle$. A full description of the perturbative analysis is given together with explicit expressions for the eigenstates of the symmetric model in the supplementary material [31]. The numerical calculations typically employ a vibrational basis of $N = 15$ Fock states, which is sufficient for convergence of the VAET spectra over a broad range of parameters, as described in appendix B.

4. VAET signatures in the weak site–vibration coupling regime

When the site–vibration coupling is weak, e.g. $\kappa_a, \kappa_b < \Delta, J$, the electronic states of the trimeric chromophore system are only weakly perturbed and do not gain substantial vibronic character. In this situation the energy transfer processes are primarily excitonic in origin but assistance by vibrations that are coupled to the excitonic states can be still expected. Figure 2(a) presents a 2D VAET spectrum in this regime and figure 2(b) presents a corresponding schematic diagram summarizing the energy transfer processes responsible for each of the main features of the 2D VAET spectrum. The perturbative analysis of these features is then summarized in figure 3. We now discuss the 2D VAET spectral features, starting with those due to single-mode VAET processes and then proceeding to the multi-mode VAET processes.

4.1. Single-mode VAET

The main features due to single modes in the weak site–vibration coupling regime are represented by the three vertical lines at $\nu_a/\Delta_{31} = 1, 0.5, 0.25$ and the horizontal lines at $\nu_b/\Delta_{31} = 1, 0.5, 0.25$. These signify resonant one-, two-, and four-phonon VAET processes, respectively, assisted by either the vibration $\nu_a$, which is coupled to the bridge site 2 (vertical lines) or the vibration $\nu_b$ which is coupled to the terminal, acceptor site (horizontal lines). For a given number of phonons, e.g. one, two or four, the vertical line is more intense than the corresponding horizontal line, indicating a stronger impact of the bridging vibration $\nu_a$ in assisting the energy transfer.

This can be confirmed by our perturbative analysis as follows. For the resonant one-phonon VAET, perturbative expansion of the transfer probability (see reference [31] for full details) shows that the first order term, which is second order in the interaction Hamiltonian, is proportional to $\alpha^4(W_{31}^{(a)}) W_{31}^{(b)} \sim \nu_a^2 \nu_b^2 |A_{31}^2|$ for transitions along the line $\nu_a/\Delta_{31} = 1$, and to $\alpha^2(W_{31}^{(a)}) W_{31}^{(b)} \sim \nu_a^2 \nu_b^2 |B_{31}^2|$ along the line $\nu_b/\Delta_{31} = 1$. Here $\alpha \sim 1$ for the weak coupling regime and the coefficients $A_{31}, B_{31}$ are given by equations (A5) and (A6) of appendix A, respectively. This VAET process is illustrated schematically by the Feynman diagrams in figure 3(a). Averaging this transfer probability over the thermal distributions of vibrational states for modes $\nu_a$ and $\nu_b$ [31], shows that even under conditions of identical site–vibration couplings ($\kappa_a = \kappa_b$) and identical vibrational temperatures ($k_b T_a = k_b T_b$), there will nevertheless be a higher probability for excitations along the vertical line than along the horizontal line, confirming the stronger impact of the vibration $\nu_a$ that is coupled to the bridge site. This effect is clearly visible in the one-dimensional top and right slices of figure 2(a), where it can be seen that the probability at the one-phonon VAET peak $\nu_a/\Delta_{31} = 1$ (top slice) is almost four times as large as that of the one-phonon VAET $\nu_b/\Delta_{31} = 1$ (right slice). Closer examination of the perturbative couplings shows that this difference arises from the factor of 2 in $A_{31}$ relative to $B_{31}$ (see equations (A5) and (A6)). $A_{31}$ is the matrix element of the electronic coupling to the bridge vibrational mode $\nu_a$, between the lowest excitonic state $|e_1\rangle$ and the highest excitonic state $|e_3\rangle$ [31], i.e. $A_{31} = \langle e_3 | [(2) |2\rangle - |1\rangle |1\rangle - |3\rangle |3\rangle |e_1\rangle$. $B_{31}$ is the corresponding matrix element of the terminal vibrational mode, i.e. $B_{31} = \langle e_3 | [(3\rangle |3\rangle - |1\rangle |1\rangle - |2\rangle |2\rangle |e_1\rangle$. For the symmetric Hamiltonian, we have $\langle e_1 |1\rangle |e_3\rangle = -\langle e_2 |2\rangle |e_3\rangle = f^2/2\Omega^2$ and $\langle e_3 |3\rangle |e_3\rangle = f^2/\Omega^2$, resulting in a larger value for $A_{31}$, the coupling to the bridge vibrational mode.

When either vibrational frequency, $\nu_a$ or $\nu_b$, is equal to half or an exact transition frequency, the transition from $|e_1\rangle$ to $|e_3\rangle$ is still accessible but only via the intermediate state $|e_2\rangle$. The excitonic transition is then accompanied by an absorption of two phonons. This single-mode two-phonon VAET appears in figure 2(a) at the vertical line $\nu_a/\Delta_{31} = 0.5$ and at the horizontal line $\nu_b/\Delta_{31} = 0.5$. We denote these...
Figure 2. (a) 2D VAET spectrum of a symmetric trimeric chromophore system coupled to two non-interacting vibrations in the weak site–vibration coupling regime $\kappa_a = \kappa_b = 0.01 \text{kHz}$. The maximum transfer probability $\text{Max}[P_3(t)]$ is taken during a time period $t \in [0, 400] \text{ ms}$. $\Delta_{ij}$ is the energy difference between eigenstates $|e_i⟩$ and $|e_j⟩$ of the electronic part in equation (5) with $\{\tilde{\omega}_1, \tilde{\omega}_2, \tilde{\omega}_3, J_{12}, J_{23}\} = \{-0.5, 0, 0.5, 0, 1.1\} \text{ kHz}$, satisfying $\Delta_{31} = 2\Delta_{21}$ [31]. We consider two vibrations with identical temperatures $k_B T_a = k_B T_b = 1.5 \text{ kHz}$. The truncation number of each vibrational Fock space is $N = 15$. The one-dimensional slices on the top and right of the two–dimensional contour plot are taken at $\nu_b/\Delta_{31} = 0.746$ and $\nu_a/\Delta_{31} = 0.746$, respectively. (b) Schematic diagram identifying the different single- and multi-mode VAET features of the 2D VAET plot for the trimeric chromophore system shown in (a).
Figure 3. Schematics of the various VAET processes contributing to the 2D VAET spectrum of figure 2. Panels (a)–(c) show single-mode VAET and panels (d)–(e) show multimode VAET. Depicted are schematics of one-, two-, and four-phonon transfer processes, together with the corresponding Feynman diagrams connecting the initial state $|e_1\rangle$ and final state $|e_3\rangle$. The interaction amplitudes $W_{q_{1}x_{1}jk}$ and $W_{q_{1}x_{1},q_{2}x_{2}jk}$, with $x_{i} \in \{a,b\}$, and $q_{i} \in \{+,−\}$ appearing below some of the Feynman diagrams are defined in the supplementary material [31].

processes as single mode two-phonon absorption (TPhonA) in figure 3(b). The corresponding transfer probabilities in the weak site-site coupling limit ($J<\Delta$) are given by $\alpha^4(W_{a}^{−a}−)^{2}W_{a}^{−a}−\sim \alpha^4t_{4}κ_{4}A_{12}A_{23}A_{32}A_{21}$ and $\alpha^4(W_{b}^{−b}−)^{2}W_{b}^{−b}−\sim \alpha^4t_{4}κ_{4}B_{21}$ with $\alpha \sim 1$ for weak coupling as before, and $A_{ij}$ and $B_{ij}$ given in equations (A1)–(A4). Further perturbative analysis with respect to $J/\Delta$ reveals that the transition $|e_1\rangle \rightarrow |e_2\rangle \rightarrow |e_3\rangle$ is a second-order process when the absorbed phonons are both borrowed from the bridging vibration $\nu_a$ (since $A_{12} \propto \frac{J}{\Delta}$ and $A_{23} \propto \frac{J}{\Delta}$, see appendix A and reference [31]), but becomes a third-order process when the two phonons are provided by the terminal mode $\nu_b$ (since $B_{23} \propto \frac{(J/\Delta)^3}{\Lambda}$ and $B_{23} \propto \frac{J}{\Delta}$). Therefore, by a similar argument to the one-phonon VAET above, i.e. multiplying the above transfer probability by a prefactor $2n_{a}^{2}$ or $2n_{b}^{2}$ [31] to account for thermal averaging over the vibrational modes, it is then evident that just as in the one-phonon VAET process, the vibration ($\nu_a$) coupled to the bridge site has a stronger impact on the two-phonon VAET processes than the vibration $\nu_b$ connected to the terminal, i.e. acceptor site. This stronger impact of the bridge site vibration results from the form of its interaction with the excitonic states in the single excitation manifold as described by equation (5). This shows that the bridging $\nu_a$ mode couples to the neighboring excitonic states $|1\rangle$ and $|2\rangle$ in a spatially anticorrelated manner, while the $\nu_b$ vibrational mode couples to the $|1\rangle$ and $|2\rangle$ states in a positively correlated manner. (Note that both modes have spatially anticorrelated coupling with regard to states $|3\rangle$ and $|3\rangle$). In a simple semiclassical dynamical picture, anticorrelated couplings bring the localized excitonic states into resonance and thus promote energy transfer, while correlated couplings preserve the non-resonant relationship and suppress energy transfer. Thus the bridging $\nu_a$ mode enhances the energy
transfer from [1] to [2] and thereby promotes the overall transfer from donor to acceptor. The stronger role of coupling to a spatially anticorrelated vibrational mode rather than a spatially correlated mode is also seen with spatially anti-correlated classical noise, see e.g. [37].

Another observable feature of the single-mode VAET in figure 2(a) is the four-phonon process at $\nu_a/\Delta_{31} = 0.25$ or $\nu_b/\Delta_{31} = 0.25$, which is described by the Feynman diagrams in figure 3(c). Comparison between the corresponding vertical and horizontal lines in figure 2(a) supports the conclusion above that the vibration $\nu_a$ which is coupled to the bridge site has a stronger impact on the energy transfer than the vibration coupled to the terminal site. Since this four-phonon VAET is a higher order process than that considered in our perturbation theory, we do not provide an analytical expression for the transfer probability here.

We also find that the two-phonon VAET at $\nu_{a(b)}/\Delta_{31} = 0.5$ is dominant over the one-phonon VAET at $\nu_{a(b)}/\Delta_{31} = 1$. This is particularly marked for the single-mode VAET enabled by the vibration $\nu_a$ that is coupled to the bridge site. This is evident from the vertical lines in figure 2(a) and the one-dimensional slice located above this. While the dominance of TPhonA VAET is clearly visible for the bridging site vibration, it is also manifested to a lesser degree for the terminal site vibration (see one-dimensional slice to the right of figure 2(a) where the integrated strength of TPhonA VAET is clearly stronger [31], despite a slightly lower maximal value). This dominance of the two-phonon VAET over one-phonon VAET is particularly marked in the weak coupling regime (recall $\kappa_a = \kappa_b = 0.01$ kHz for figure 2), but will also be evident in the strong coupling regime results presented in section 5 below. The reason for this dominance is the relatively high temperature considered here, i.e. $k_b T_{a(b)} = 1.5$ kHz, which ensures availability of the required number of phonons for both one- and two-phonon VAET, while the probability of energy transfer increases with average phonon number. Thus, for the one-phonon VAET, the average phonon numbers are $n_{a(b)} \sim 1$ when $\nu_{a(b)}/\Delta_{31} = 1$, while for the two-phonon VAET, the average phonon numbers are $n_{a(b)} \sim 2.4$ when $\nu_{a(b)}/\Delta_{31} = 0.5$. In the latter situation there is a higher than required average phonon number for $\nu_a(b)$, implying that the two-phonon processes are more likely ($1 < 2.4/2 = 120\%$). This analysis also holds when the temperature becomes so low that the necessary number of phonons cannot be taken from the thermal state, e.g. for $k_b T_{a(b)} = 0.5$ kHz, where the two-phonon VAET is still dominant relative to one-phonon VAET. Here the average phonon number is $n_{a(b)} \sim 0.143$ when $\nu_{a(b)}/\Delta_{31} = 1$, and $n_{a(b)} \sim 0.548$ when $\nu_{a(b)}/\Delta_{31} = 0.5$. Since $14.3\% < 0.548/2 = 27.4\%$, the two-phonon VAET is still dominant at this lower temperature (see also section 4.3 below).

Finally, we note that the single-mode two- and four-phonon VAET features seen in figure 2 are in good agreement with the additional partially-resolved peaks observed in the recent experimental study of single-mode VAET in a dimer system emulated with trapped ions [20].

4.2. Multimode VAET

The collective behaviors of multiple vibrations enable unique signatures of VAET arising in our trimeric system, relative to those due to individual ones of single vibrations presented above. Such signatures are represented by the diagonal and anti-diagonal lines in figures 2(a) and (b). They include cooperativity and interference of the two vibrations. Of particular interest for the former is the manifestation of the phononic analog of Göppert-Mayer’s two-photon absorption [23], constituting the anti-diagonal lines, and the inverse of this that combines vibrational and excitonic transitions, which we refer to as heteroexcitation, and which constitute the diagonal lines.

4.2.1. Cooperative two-phonon absorption VAET

The anti-diagonal lines in figure 2(a) signify cooperative processes in which phonons from both modes are involved in a VAET process. For example, the line $\nu_a/\Delta_{31} + \nu_b/\Delta_{31} = 1$ signifies a double-mode two-phonon cooperative VAET process. We designate this as a cooperative TPhonA process (c-TPhonA) in figure 2(b). This cooperative process with a simultaneous absorption of phonons from two vibrations in assisting the energy transfer constitutes a phononic analogue of two-phonon absorption [23].

At the symmetric lattice point $\{\nu_a/\Delta_{31}, \nu_b/\Delta_{31}\} = \{0.5, 0.5\}$ satisfying the resonance condition $\nu_a = \nu_b = \Delta_{21} = \Delta_{32}$, the transition from $|e_i\rangle$ to $|e_j\rangle$ proceeds via the bridge state $|e_2\rangle$ and is assisted by two strongly cooperative processes consisting of absorption of a single phonon from one mode, followed by a second phonon from the other mode, with perturbative transfer probability $\alpha^4(W_{32,21}^{a-b})^4W_{32,21}^{a-b}$ or $\alpha^4(W_{32,21}^{a-b})^4W_{32,21}^{a-b}$ [31], as illustrated in figure 3(d). The two transfer processes having absorption of two phonons from distinct vibrational modes in different orders can interfere with each other, giving rise to a double-mode two-phonon interference VAET. The Feynman pathways for this interference are shown in the right hand (red) subpanel of figure 3(d) and the associated perturbative expression for the probability is $\alpha^4(W_{32,21}^{a-b})^4W_{32,21}^{a-b} + \alpha^4(W_{32,21}^{b-a})^4W_{32,21}^{b-a} [31]$. Figure 4 shows the time dependence of $P_s(t)$ at $(0.5, 0.5)$ (solid green line) together with corresponding time traces for nearby points along the $(0.5, \nu_b/\Delta_{31})$ (dashed
blue and yellow lines). This shows that the symmetric point (green line) is a point of destructive interference along the $\nu_b$ axis, since it has a smaller maximal probability than the time traces of the nearby points. Similarly comparing the time traces of $P_3(t)$ for points along the $(\nu_a/\Delta_{31}, 0.5)$ line shows that the point $(0.5, 0.5)$ is a point of constructive interference along the $\nu_a$ axis, since here the green curve has a higher maximal value than those of nearby points (red and cyan dot-dashed curves).

At all points away from the symmetric lattice point, i.e. along the rest of the anti-diagonal line $\nu_a/\Delta_{31} + \nu_b/\Delta_{31} = 1$ with $\nu_a \neq \nu_b$, the transition from $|e_1\rangle$ to $|e_2\rangle$ involves a virtual intermediate state, i.e. $|e_2'\rangle$ rather than $|e_2\rangle$ as illustrated in the lower left subpanel of figure 3(d). These points therefore show relatively small transfer probability in figure 2. We point out that the upper portion of the anti-diagonal with $\nu_b > \nu_a$ is noticeably less intense than the lower part where $\nu_b < \nu_a$. This is once again a consequence of the stronger impact of the vibration $\nu_a$ that is coupled to the bridge site in assisting the energy transfer, relative to that of the vibration coupled to the terminal site. In situations for which the impact of the vibration $\nu_b$ becomes dominant in the energy transfer, for example the Hamiltonian with site-correlated vibrational modes analyzed in section 7, this effect is reversed.

Similarly, the second anti-diagonal line visible in figure 2(a), i.e. $\nu_a/\Delta_{31} + \nu_b/\Delta_{31} = 0.5$ at the bottom left, signifies a double-mode, four-phonon cooperative VAET involving two processes of two-phonon absorption each. Here the lattice point, i.e. $\{\nu_a/\Delta_{31}, \nu_b/\Delta_{31}\} = \{0.25, 0.25\}$, can host an interference between two transfer pathways involving different ordering of the two-phonon absorptions, while the rest of this anti-diagonal line, i.e. $\nu_a \neq \nu_b$, shows a relatively low transfer probability due to the off-resonant nature of the intermediate virtual state. This constitutes a higher-order phononic analogue of two-photon absorption, which is illustrated in figure 3(e).

4.2.2. Heteroexcitation VAET

In addition to these cooperative VAET processes for which both vibrations contribute phonons to assist excitonic energy transfer, we also find evidence of VAET processes in which a phonon from one vibrational mode can simultaneously excite not only the electronic system but also the other vibrational mode. This is a new kind of cooperative mechanism of VAET, which we shall refer to as ‘heteroexcitation’. It is evidenced by the diagonal lines in figure 2(a), which are also shown with their assignments as solid diagonal lines in figure 2(b). For example, the line $\nu_a/\Delta_{31} - \nu_b/\Delta_{31} = 1$ indicates that one phonon of vibrational mode $\nu_a$ generates an electronic transition from site 1 to 3, together with absorption of a single phonon in mode $\nu_b$. The line $\nu_a/\Delta_{31} - \nu_b/\Delta_{31} = 0.5$ represents processes in which two phonons of vibrational mode $\nu_a$ generate the same electronic transition, but now together with absorption of two phonons in mode $\nu_b$. An analogous interpretation applies to the line $\nu_b/\Delta_{31} - \nu_a/\Delta_{31} = 0.5$.

We note that the alternative heteroexcitation associated with the diagonal line $\nu_b/\Delta_{31} - \nu_a/\Delta_{31} = 1$, shown as the dotted diagonal line at the top left of figure 2(b), in which one phonon from vibrational mode $\nu_b$ generates an excitonic transition together with absorption of a phonon of vibrational mode $\nu_a$ is not
Figure 5. 2D VAET spectra showing Max[$P_3(t)$] in a time period $t \in [0, 400]$ ms for different vibrational temperatures \{$k_B T_a, k_B T_b$\} in the weak coupling regime. (a) \{$k_B T_a, k_B T_b$\} = \{0.5, 0.5\} kHz, (b) \{$k_B T_a, k_B T_b$\} = \{1.5, 0.5\} kHz, and (c) \{$k_B T_a, k_B T_b$\} = \{0.5, 1.5\} kHz. All calculations employed phonon truncation at $N = 15$ and site–vibration coupling strength $\kappa_a = \kappa_b = 0.01$ kHz. (d) Time trace of the transfer probability $P_3(t)$ at the resonance points $(\nu_a/\Delta_{31}, \nu_b/\Delta_{31}) = (0.5, 0.5)$ and $(\nu_a, \nu_b) = (0.52, 0.52)$ kHz, for temperatures $k_B T_a = k_B T_b = 0.5$ kHz, 1.5 kHz, 2 kHz, 4 kHz, with $N = 40$ phonon truncation and site–vibration couplings $\kappa_a = \kappa_b = 0.05$ kHz. All other parameters are the same as in figure 2.

observable in figure 2(a). This is because of the weaker impact of the vibration coupled to the terminal site. This vibration now has to provide one phonon to be absorbed by both the timer and the other vibration, which is a significantly weaker process at this temperature. However this transition would appear on further increasing the temperature of mode $b$ ($k_B T_b$), so we also show the relevant Feynman diagrams for this process in figure 3(e).

We note that while the reverse of two photon absorption, namely one photon exciting two atoms, has been discussed previously, it was assumed there that atoms of identical frequency are excited by a single photon [26], consistent with the larger wavelength of optical photons relative to atoms. The heteroexcitations seen here constitute a generalized phononic analog of that optical phenomenon, where now not only the energies, but also the nature of the two degrees of freedom being excited can be different. Another interesting interpretation of this process is that of redistribution of energy from one phonon reservoir to another, mediated by the electronic degrees of freedom.

4.3. Vibrational temperature effects

One interesting capability of artificial energy transport as studied with emulations using e.g. trapped ions, that is not possible in real molecular systems, is the ability to individually vary the effective temperature of different vibrational modes. Here we assess the effects of these temperatures on VAET features. Figure 5 presents 2D VAET spectra at three different temperatures from that in figure 2, including also the presence of a temperature bias between the two vibrations in panels (b) and (c).

In the absence of a temperature bias, i.e. when the vibrational temperatures are equal (panel (a)), comparison with the higher vibrational temperature spectrum of figure 2 ($k_B T_a = k_B T_b = 1.5$ kHz) shows that collective VAET features such as the cooperative behavior evidenced by the anti-diagonal and diagonal
lines in the 2D spectrum become weaker as the vibrational temperature decreases, indicating a suppression of VAET processes. However the two-phonon VAET is still dominant over the one-phonon VAET, as discussed in section 4.1.

When a temperature bias between the two vibrations is present, as in panels (b) and (c), we find that increasing either $k_B T_a$ [figure 5(b)] or $k_B T_b$ [figure 5(c)] will enhance the transfer processes assisted by either of the vibrations coupled to the bridge or to the acceptor. This suggests that the weaker impact of the vibration coupled to the acceptor seen above could be enhanced by selectively raising the temperature of this mode in an emulation experiment.

Panels (b) and (c) of figure 5 show that the presence of a temperature bias across the two vibrations can also enhance heteroexcitations at $|\nu_a - \nu_b| = \Delta_{31}$, $\Delta_{31}/2$, relative to that seen for equal temperatures in figure 5(a). Such enhancement of heteroexcitations would increase with further increase of the temperature bias.

The time dependence of energy transfer probability in VAET processes is also strongly dependent on the vibrational temperatures. Figure 5(d) shows the time evolution of the transfer probability at the resonance points $(\nu_a/\Delta_{31}, \nu_b/\Delta_{31}) = (0.5, 0.5)$ and $(\nu_a, \nu_b) = (0.52, 0.52)$ kHz in figures 2 and 5(a). We see that increasing the temperature generically enhances the energy transfer, with the maximum probability reaching values up to $\sim 0.5$ when $k_B T_a = k_B T_b = 4$ kHz.

4.4. Dissipative effects

In contrast to the assistance provided by undamped vibrations for excitation energy transfer discussed above, the decay of an electronic excitation at each site, resulting from e.g. spontaneous emission or
coupling to damped vibrational environments, is expected to suppress energy transfer processes. Here we study the effect of such relaxation processes, using a non-Hermitian approach that in the single excitation subspace is equivalent to use of the Lindblad master equation with a relaxation operator [42] (see detailed analysis in the supplementary material [31]).

Including a non-Hermitian Hamiltonian term, the system under such dissipation is described by $\hat{H}_{\text{eff}} = \hat{H}_0 - \frac{i}{\hbar} \sum_{j=1}^{3} \gamma_j \langle \phi_j | \phi_j \rangle$ where $\hat{H}_0 = \hat{H}_s + \hat{H}_v + \hat{H}_\text{int}$ given by equation (1). The effective Hamiltonian in the single electronic excitation subspace is then obtained as $\tilde{\hat{H}}_{\text{eff}} = \Xi \hat{H}_{\text{eff}} \Xi = \tilde{\hat{H}}_0 - \frac{i}{\hbar} (\gamma_1 |1\rangle \langle 1| + \gamma_2 |2\rangle \langle 2| + \gamma_3 |3\rangle \langle 3|)$, where $\tilde{\hat{H}}_0$ is given by equation (5) [31]. The average effect of dissipation on the excitation energy transfer is then obtained by repeating the 2D VAET spectral calculations with $\tilde{\hat{H}}_0$ replaced by $\tilde{\hat{H}}_{\text{eff}}$.

Figure 6 shows the 2D VAET spectrum with dissipation given by parameters $\gamma_1 = \gamma_2 = \gamma_3 = \gamma = 0.001$ kHz. We see suppression of all energy transfer processes, particularly those along the anti-diagonal and diagonal lines, relative to the dissipation-free results in figure 2(a). As expected, the single-mode two-phonon VAET is the most pronounced VAET process in figure 6.

Figure 7(a) shows that for a specific VAET transfer process, e.g. the single mode TPhonA VAET at the resonant position $\nu_0/\Delta_{31} = 0.5$, the time-dependent probability of finding an excitation at the acceptor, $P_3(t)$, is increasingly suppressed for all $t$ as $\gamma$ increases. To analyze which sites contribute to this suppression, figure 7(b) shows calculations with different dissipative parameters $\gamma_j$ at each site. Only small variations are seen, within the general trend that a strong dissipation at the donor site provides the greatest suppression (red dotted line), followed by having the strongest dissipation at the acceptor site (blue solid line). Interestingly, when the strongest dissipation is at the bridge site, the energy transport is most robust to the dissipation (yellow and green dashed lines).

5. VAET signatures in the presence of strong site–vibration coupling

As the site–vibration coupling strength increases, different VAET features emerge and the balance between single- and multi-phonon VAET processes changes. We explore these changes by considering larger coupling strengths $\kappa_a = \kappa_b = 0.03$ kHz and $0.1$ kHz, summarized in figures 8(a) and (b), respectively. The top and right side slices in each of these plots are taken at $\nu_0/\Delta_{31} = 0.746$ (right slice) and $\nu_b/\Delta_{31} = 0.746$ (top slice).

In addition to the basic VAET features from figure 2(a) (where $\kappa_a = \kappa_b = 0.01$ kHz), we now observe additional multiphonon VAET processes in figure 8(a) that involve three, five, and six phonons, indicated by vertical lines at $\nu_0/\Delta_{31} = 1/3, 1/5, \text{and } 1/6$, respectively. For the larger site–vibration coupling strength $\kappa_a = \kappa_b = 0.1$ kHz shown figure 8(b), these vertical lines become more distinct and also start to shift noticeably away from the excitonic resonant transition frequencies. We also see that in the strong coupling regime, not only do the one-phonon (e.g. $\nu_0/\Delta_{31} = 1$) and two-phonon (e.g. $\nu_0/\Delta_{31} = 0.5$) VAET processes become more comparable in intensity, but also the impact of the vibration coupled to the acceptor, $\nu_b$, becomes comparable to that of the bridging vibration $\nu_a$. Thus, we now see local maxima at $\nu_0/\Delta_{31}, \nu_b/\Delta_{31} = 1$ and $0.25$, in both the right and top slices of figures 8(a) and (b). The greater structure...
Figure 8. 2D VAET spectra for the trimeric chromophore system coupled to two non-interacting vibrations in the strong site–vibration coupling regime. Panels (a) and (b) show the maximum transfer probability $\text{Max}[P_3(t)]$ in a time period $t \in [0, 400]$ ms for two values of the site–vibration coupling $\kappa_a = \kappa_b = \kappa$: (a) $\kappa = 0.03$ kHz and (b) $\kappa = 0.1$ kHz. The slices on the top and right side of each contour plot are taken at $\nu_b/\Delta_{31} = 0.746$ and $\nu_a/\Delta_{31} = 0.746$, respectively. (c) Time trace of the energy transfer probability $P_3(t)$ for several combinations of $\kappa_a, \kappa_b$ at the resonance points $(\nu_a/\Delta_{31}, \nu_b/\Delta_{31}) = (0.5, 0.5)$ and $(\nu_a, \nu_b) = (0.52, 0.52)$ kHz. The vibrational temperatures are $k_B T_a = k_B T_b = 1.5$ kHz. All other parameters are the same as in figure 2.
in these intensity patterns contrasts with the simpler structure obtained for weak site–vibration coupling in figure 2(a).

To further demonstrate the effects of strong site–vibration coupling on the VAET, we plot in figure 8(c) the time evolution of the \( P_3(t) \) at the resonance point \( (\nu_a/\Delta_{31}, \nu_b/\Delta_{31}) = (0.5, 0.5) \) for a two-phonon VAET process at various values of the coupling strength \( \kappa = \kappa_a = \kappa_b \). When the electronic sites are decoupled from the vibrations, i.e. \( \kappa_a = \kappa_b = 0 \), the blue reference curve in figure 8(c) shows Rabi oscillations characterized by the transition frequency \( \nu_a = \Omega = \sqrt{\Delta^2 + 2J^2} = 0.52 \text{ kHz} \), with corresponding oscillatory period \( 2\pi/\nu_a \sim 12 \text{ ms} \) (approx. eight cycles in each period of 100 ms). When the coupling is nonzero, we observe modulated Rabi-like oscillations that show slow oscillations superimposed on the fast oscillations with the frequency \( \Omega \). See, for example, the solid orange curve in figure 8(c), for which \( \kappa_a = \kappa_b = 0.01 \text{ kHz} \). As \( \kappa \) increases to 0.05 kHz (green curve) and beyond to 0.1 kHz (red curve), the initial rise of \( P_3(t) \) is faster and the first maximum higher. However, further increase of the site–vibration coupling strength beyond 0.1 kHz reverses this trend. In the next section we shall see that this is a result of the formation of vibronic states with strong mixing of excitonic and vibrational degrees of freedom, giving rise to very different transition frequencies.

6. Vibronic spectral analysis of VAET and role of cross-coupling terms in the effective Hamiltonian

6.1. Vibronic states

In order to better understand the origin of the VAET features, we have calculated the energy spectrum for the trimer excitonic system coupled to the two vibrational modes including three vibrational levels \[ \Delta \] as a function of the scaled frequencies \( (\nu_a/\Delta_{31}, \nu_b/\Delta_{31}) \), for specific values of the coupling strengths. This reveals the energies of the vibronic states formed as a consequence of the two exciton–vibration couplings. Figure 9 shows the corresponding two dimensional vibronic spectrum for the case of coupling strengths \( \kappa_a = \kappa_b = 0.03 \text{ kHz} \). The figure clearly shows the presence of avoided crossings that derive from the exciton–vibration coupling. For example, along the horizontal line \( \nu_a/\Delta_{31} = 0.5 \), whenever \( \nu_a/\Delta_{31} \) approaches a resonant transition frequency of the trimer excitonic system (i.e. zero detuning at \( \nu_a/\Delta_{31} = 0.25, 0.5, 1 \) as shown in figure 2), this gives rise to an avoided crossing due to the site–vibration coupling. Each avoided crossing in the spectrum shown in figure 9 indicates a vibronic state, i.e. a mixing of the electronic and vibrational degrees of freedom [2].

Some of the avoided crossings in the vibronic energy spectrum correspond to VAET features discussed above. A perturbative analysis of the vibronic energies predicts the presence of avoided crossings at the degenerate states. Thus the specific avoided crossings magnified in figures 9(b) and (c) indicate the hybridized vibronic states \( \{110\} \pm \{300\} \) and \( \{111\} \pm \{301\} \) represent the excitonic state \( |e_i\rangle \), and vibrational occupation states \( |j\rangle \) and \( |k\rangle \), respectively) that give rise to the one-phonon VAET feature along the vertical line \( \nu_a/\Delta_{31} = 1 \) in figure 2(a). Similarly, the states \( \{121\} \pm \{301\} \) avoid crossing in figure 9(d) are associated with the single-mode two-phonon VAET indicated by the vertical line, i.e. \( \nu_a/\Delta_{31} = 0.5 \), in figure 2. We also see vibronic states associated with the cooperative VAET features. In figure 9(e), the avoided crossing of states \( \{120\} \pm \{301\} \) corresponds to an intersection of the horizontal line \( \nu_a/\Delta_{31} = 0.5 \) and the off-diagonal line \( 2\nu_a - \nu_b = \Delta_{31} \) in figure 2 that indicates the double-mode cooperative VAET.

We note that the avoided crossings in the vibronic spectrum become more pronounced as the coupling strength \( \kappa_a \) or \( \kappa_b \) increases, consistent with the perturbative analysis. This means that not only does the gap between the two adjacent levels increase, but also the shift from the excitonic resonant transition frequencies (e.g. \( \nu_a/\Delta_{31} = 1, 0.5, 0.25 \)) will be larger. This trend is also visible in the cross-sectional slices in figures 8(a) and (b). Consequently, for given frequencies \( \nu_a, \nu_b \), increasing either \( \kappa_a \) or \( \kappa_b \) to values so large that they are comparable with the excitonic energy differences will be expected to suppress energy transfer processes below the values seen for smaller coupling. Indeed, this is consistent with the decrease in \( P_3(t) \) seen for large \( \kappa_a = \kappa_b \) values in figure 8(c).

6.2. Effect of cross couplings in single excitation subspace

The VAET features presented above are based on the consideration of the effective Hamiltonian equation (5) derived as the single electronic excitation restriction of the model in equation (1) for the trimeric chromophore system. This trimeric model, generalized from an experimentally investigated dimer for an artificial excitonic system realized in a trapped ion system [20], contains interaction of the vibrations with both excited and the ground states, i.e. \( \kappa_a \sigma_z^{(2)}(a + a) + \kappa_b \sigma_z^{(3)}(b + b) \). We saw that the resulting effective model in the single electronic excitation manifold has cross coupling terms, i.e. an interaction of a vibration with the excited states of unconnected sites.
Figure 9. Vibronic energy spectrum of the effective excitonic levels $|\epsilon_i\rangle$ coupled to two vibrational modes $|j\rangle$ and $|k\rangle$ with $N=3$ levels each, as a function of $\nu_a/\Delta_{31}$. Here only eighteen of the twenty seven lowest energy levels are shown. Panels (b)–(e) show enlarged views of each avoided crossing in panel (a). The parameters are $\{\tilde{\omega}_1, \tilde{\omega}_2, \tilde{\omega}_3, J_{12}, J_{23}\} = \{-0.5, 0, 0.5, 0.1, 0.1\}$ kHz and $\nu_b = \Delta_{21} = \Delta_{32} = 0.52$ kHz and $\kappa_a = \kappa_b = 0.03$ kHz.
Here we analyze the effects of the cross coupling terms on the excitation energy transfer. To isolate the effects resulting from these terms, we rewrite the effective Hamiltonian in equation (5) as

\[
\tilde{H}_{\text{e}}(\zeta) = \tilde{\omega}_1 |1\rangle\langle 1| + \tilde{\omega}_2 |2\rangle\langle 2| + \tilde{\omega}_3 |3\rangle\langle 3| + \eta_1 |1\rangle\langle 2| + |2\rangle\langle 1| + \eta_2 |2\rangle\langle 3| + |3\rangle\langle 2| \\
+ \kappa_0 (a^\dagger + a)(-\zeta |1\rangle\langle 2| - |2\rangle\langle 3| - |3\rangle\langle 1|) + \kappa_0 (b^\dagger + b)(-\zeta |1\rangle\langle 2| - |2\rangle\langle 3| - |3\rangle\langle 1|) \\
+ \nu_0 a^\dagger a + \nu_0 b^\dagger b,
\]

with variable parameter \(\zeta\) which interpolates between equation (5) for \(\zeta = 1\) and the usual single excitation manifold effective Hamiltonian for molecular excitons without cross coupling terms for \(\zeta = 0\). The latter case corresponds to the full Hamiltonian, equation (1), with the site–vibration coupling in equation (4) replaced by \(\kappa_0 \sigma^{(2)}_a \sigma^{(2)} (a^\dagger + a) + \kappa_0 \sigma^{(3)}_b \sigma^{(3)} (b^\dagger + b)\).

Figure 10 shows the two-dimensional VAET spectra for two symmetric trimeric systems with identical energy gaps (i.e. \(\Delta_{31} = \Delta_{32}\)) that allow interference VAET to appear. Comparison of either the two left panels (a) and (c) with \(\Delta_{31} = \Delta_{32} = 0.332\) kHz, or the two right panels with \(\Delta_{31} = \Delta_{32} = 0.52\) kHz, shows that the cross coupling terms in \(\tilde{H}_\text{e}(\zeta = 1)\) significantly enhance the energy transfer. For example, the one-phonon VAET at \(\nu_0 = \Delta_{33} = 1.04\) kHz, which shows high intensity for \(\tilde{H}_\text{e}(\zeta = 1)\) (panel (b)), is considerably less intense \(\tilde{H}_\text{e}(\zeta = 0)\) (panel (d)).

Comparing now the left and right panels of either the upper (\(\zeta = 1\)) or lower (\(\zeta = 0\)) row shows the effect of modifying the energy barrier for both Hamiltonians. Thus the higher probabilities for the two-phonon VAET processes seen in panel (a) are due to the lower excitonic energy barrier \(\tilde{\omega}_3 - \tilde{\omega}_2 = \tilde{\omega}_2 - \tilde{\omega}_1 = 0.3\) kHz which is more similar to the excitonic coupling \(J = 0.1\) kHz, than that of panel (b) for which \(\tilde{\omega}_3 - \tilde{\omega}_2 = \tilde{\omega}_2 - \tilde{\omega}_1 = 0.5\) kHz.

The appearance of an interference VAET requires a specific condition, i.e. \(\Delta_{31} = \Delta_{32}\). To isolate the interference VAET features we therefore present in figure 11 2D VAET spectra for two asymmetric systems that do not host any interferences. The upper row of figure 11 shows spectra with \(\{\tilde{\omega}_1, \tilde{\omega}_2, \tilde{\omega}_3\}\) equal to

\[
\{\tilde{\omega}_1, \tilde{\omega}_2, \tilde{\omega}_3\} = \{-0.3, 0.3\} \text{kHz} \quad \text{and} \quad \{\tilde{\omega}_1, \tilde{\omega}_2, \tilde{\omega}_3\} = \{-0.5, 0, 0.5\} \text{kHz}
\]
Figure 11. 2D VAET spectra of an asymmetric trimeric chromophore system described the effective Hamiltonian $\bar{H}(\zeta)$, equation (5) with $\zeta = 1$ (upper row) and $\zeta = 0$ (lower row). The parameter values $\{\tilde{\omega}_1, \tilde{\omega}_2, \tilde{\omega}_3\}$ specified above the panels give excitonic energy differences $\{\Delta_{21}, \Delta_{32}\} = \{0.508, 0.343\}$ kHz (panels (a), (c)), $\{0.343, 0.508\}$ kHz (panels (b), (f)), with $\Delta_{31} = \Delta_{21} + \Delta_{32}$ in all cases. The other parameters are $J_{12} = J_{23} = 0.1$ kHz, $\kappa_A = \kappa_B = 0.01$ kHz, $k_B T_A = k_B T_B = 0.749$ kHz, and $N = 10$.

$\{-0.5, 0, 0.3\}$ kHz (a) and $\{-0.3, 0, 0.5\}$ kHz (b), implying different energy gaps of $\{\Delta_{21}, \Delta_{32}\} = \{0.508, 0.343\}$ kHz. We see that the double-mode two-phonon cooperative VAET, located at the lattice point $\{\nu_a, \nu_b\} = \{\Delta_{21}, \Delta_{32}\}$ in panel (a) and at $\{\nu_a, \nu_b\} = \{\Delta_{32}, \Delta_{21}\}$ in panel (b) is now the only dominant process. The corresponding time traces are shown in figure 12 where it is evident that they have a maximal value intermediate between those of symmetrically distributed neighboring points, implying an absence of interference at the symmetric points $\nu_a = \nu_b = \Delta_{21} = \Delta_{32}$. This is in contrast to the 2D VAET spectra for systems with identical energy gaps $\Delta_{21} = \Delta_{32}$ in figure 10, where the interferences at the crossing point of vertical ($\nu_a = 0.332$ kHz) and horizontal ($\nu_b = 0.332$ kHz) lines in panel (a) and at the crossing point of $\nu_a = 0.52$ kHz and $\nu_b = 0.52$ kHz in panel (b) are clearly visible. The corresponding time traces (not shown), show destructive interference along the vertical lines $|\nu_a = 0.332$ kHz (figure 10(a)) and $\nu_a = 0.52$ kHz (figure 10(b)), and constructive interference along the horizontal lines $|\nu_b = 0.332$ kHz (figure 10(a)) and $\nu_b = 0.52$ kHz (figure 10(b)). We also present the corresponding results for the effective Hamiltonian $H_{\zeta}(\zeta = 0)$ in the lower row of figure 11, to emphasize the key role of the cross coupling terms in amplifying these cooperative VAET processes. The interference features are no longer visible here, confirming the critical role of the cross-correlated vibrations in enabling these quantum features.

7. VAET with explicitly correlated vibrational modes

The energy transfer in the trimeric chromophore system discussed in sections 2–6 relies on the assistance of two independent vibrational modes that are coupled to the bridge and acceptor sites, respectively [see equation (4)]. Experimental realization of this ideal Hamiltonian with the local and independent control of the site–vibration interaction for a trapped-ion quantum simulator requires that the ionic states be coupled to transverse vibrational modes. This is more challenging than coupling to the longitudinal vibrations, requiring stabilization with regard to the trapping frequency. Coupling to longitudinal modes allows instead access to normal modes that are linear combinations of local vibrations, exemplified for a three-ion system.
dynamics with and without dissipation in the weak coupling regime are presented in figures 13(a) and (b), non-Hermitian decay of chromophore excitations with parameter respectively. This difference is due to two specific differences in the Hamiltonian of both correlated and anti-correlated site–vibration couplings. It is thus of interest to analyze the possibility of V AET processes in such a Hamiltonian possessing Hamiltonian of equation (4), we now have one vibrational mode, of vibration along the longitudinal axis of a linear chain of three ions. In contrast to the transverse coupling \( H \), it has been claimed to drive non-adiabatic electronic energy transfer in photosynthetic light-harvesting systems [10]. It is notable that the values of \( \text{Max}[P_{3}(t)] \) for the effective model \( \tilde{H}^{\prime} = \tilde{H}_{\text{eff}} - \gamma |\langle 2 |1 + 2/2| + |3/3\rangle| \) in figure 13(a) and (b), respectively.

It is notable that the values of \( \text{Max}[P_{3}(t)] \) in figure 13(a) are systematically larger than the corresponding values in figure 2(a). This difference is due to two specific differences in the Hamiltonian of equation (12) relative to that of equations (1)–(4). Firstly, in equation (12) the donor and acceptor are directly coupled through a Coulomb term \( J_{d3} \). This promotes direct transfer from donor to acceptor, without involvement from the bridge site. Secondly, the vibrational mode \( \nu_{c} \) serves to vibrationally assist this direct transfer process. This additional transfer mechanism and its vibrational enhancement lead to the larger \( \text{Max}[P_{3}(t)] \). Figure 13(a) shows that this system with explicitly correlated couplings to the longitudinal vibrational modes generates a very different relative impact of the symmetric stretch \( \nu_{c} \) and the
Figure 13. The VAET features of the trimeric chromophore system weakly coupled to correlated and anti-correlated vibrational models described by the effective Hamiltonian equation (12) for the cases of (a) without ($\gamma = 0$) and (b) with ($\gamma = 0.001$ kHz) dissipation. The color bar in (a) is same as in figure 2(a) for comparison, but note the change in scale of panel (b) relative to panel (a). The parameters are $\{\tilde{\omega}_1',\tilde{\omega}_2',\tilde{\omega}_3'\} = \{-1,0,1\}$, $\{J_{12}',J_{23}',J_{13}'\} = \{0.1,0.1,0.08\}$, $\{\kappa_c',\kappa_d'\} = \{0.005,0.005\}$, $\{k_B T_c,k_B T_d\} = \{1.5,1.5\}$ kHz, which are equivalent to those in figure 2(a).
asymmetric stretch vibration $\nu_d$ on the VAET spectra from that seen for the local transverse couplings in sections 2–6. This is evident both in the ratios of single mode two-phonon to one-phonon VAET processes (horizontal and vertical lines), and in the variable intensities of the two-mode two-phonon VAET processes (antidiagonal lines). As we explain in detail below, this different impact reflects the fact that with the longitudinal modes, the asymmetric stretch $\nu_d$ couples more strongly to the bridge site than to the donor and acceptor sites, while the symmetric stretch $\nu_c$ couples only to the latter. This is true both in the full Hamiltonian $\hat{H}_{\text{inc}}$ and in the corresponding effective Hamiltonian, equation (12).

The single mode one-phonon VAET line for the symmetric stretch (vertical line $\nu_c/\Delta_{31} = 1$) is more intense than that for the asymmetric stretch (horizontal line $\nu_d/\Delta_{31} = 1$). We note that since $f_{13} \neq 0$, this one-phonon process between states $|e_1\rangle$ and $|e_2\rangle$, which become approximately $|1\rangle$ and $|3\rangle$ in the weak site–site coupling regime, does not necessarily require a coupling to the bridge site. Furthermore, mode $\nu_c$ promotes this transfer directly and does so efficiently, because it dynamically reduces the energy gap between donor and acceptor due to the anticorrelated displacements of site energies resulting from coupling to this mode, as noted above. In contrast, mode $\nu_d$ causes correlated displacements of the energies of $|1\rangle$ and $|3\rangle$ [see equation (12)], and thus is less effective at promoting this transfer with a single phonon VAET process. This is in direct analogy to the effects of anti-correlated versus correlated classical fluctuations on energy transfer studied in [33, 34, 37].

The two-phonon lines $\nu_d/\Delta_{31} = 0.5$ and $\nu_c/\Delta_{31} = 0.5$ show an even greater disparity, to the extent that the two-phonon VAET for the symmetric stretch ($\nu_c/\Delta_{31} = 0.5$) is not dominant over the corresponding one-phonon process. The strongest feature in the VAET spectrum is now the single mode two-phonon absorption in $\nu_d$, i.e. the horizontal line $\nu_d/\Delta_{31} = 0.5$. This parallels the analogous dominance of the single mode two-phonon absorption for the mode coupled to the bridge site in the VAET spectrum of figure 2(a) (vertical line at $\nu_d/\Delta_{31} = 0.5$). The anomalous observation of the one-phonon symmetric stretch VAET for $\nu_c$ being more intense than the two-phonon process results from the fact that this mode is completely decoupled from the excited state of the bridge site in both equations (11) and (12). This is quite different from not only the interaction of mode $\nu_d$ in equation (12), but also that of modes $\nu_c$ and $\nu_b$ in equation (5), all of which include some coupling to the excited state of the bridge site in the effective Hamiltonian for the single excitation subspace.

More marked is the behavior in the anti-diagonal lines representing multi-mode VAET (corresponding to TPhonA in figure 2(b)). For example, the anti-diagonal line $\nu_c/\Delta_{31} + \nu_d/\Delta_{31} = 1$ shows significant intensity in the sector $\nu_d > \nu_c$ but negligible intensity in the sector $\nu_d < \nu_c$. When dissipation is taken into account, figure 13(b) shows that all transfer processes are suppressed, similar to what is seen for the uncorrelated trimeric system above (see figure 6).

We have additionally considered a vanishing value of the direct donor–acceptor coupling $f_{13}$ to characterize the impact of this coupling on the enhancements derived from the correlated vibrational modes [31]. As expected, this leads to smaller values of $\text{Max}[P(t)]$ due to the removal of the direct excitonic coupling between donor and acceptor. In addition, we find that the one-phonon transition from $|e_1\rangle$ to $|e_3\rangle$, which is approximated by $|1\rangle$ and $|3\rangle$, respectively, in the weak site-site coupling regime, can no longer be assisted by the symmetric stretch. Thus, in this case there is no vertical line at $\nu_c/\Delta_{31} = 1$ representing a one-phonon VAET process (see figure S6 in the supplemental material). This is because while the symmetric stretch mode $\nu_c$ undergoes anticorrelated coupling with the donor and acceptor sites (i.e. with their exciton states $|1\rangle$ and $|3\rangle$), in the absence of direct excitonic coupling it cannot enhance energy transfer from site 1 to site 3.

8. Discussion and conclusions

We have systematically studied the phenomenon of vibrationally assisted energy transfer, VAET, in a donor–bridge–acceptor trimeric chromophore system coupled to two vibrations over a range of coupling strengths. In this work we focused on two types of systems. The first derives from a Hamiltonian with uncorrelated local coupling, as would be obtained by coupling to transverse modes in a trapped ion quantum emulator. The second derives from explicitly correlated non-local coupling, as would be obtained by coupling to normal modes of longitudinal motion in a trapped ion quantum emulator. The parameters considered in this work are within the regime of current trapped-ion experiments [20] and in all cases we considered a parameter set ensuring energetically uphill transitions from both donor to bridge chromophores and bridge to acceptor chromophores.

In the case of local site–vibration couplings, we found a rich array of VAET phenomena going beyond the one-phonon VAET observed previously with a trapped ion quantum emulator [20]. In particular, we also find clearly resolved signatures of two- and even four-phonon absorption processes in the 2D VAET spectrum at weak site–vibration coupling strengths, while increasing the coupling strength introduces up to
six-phonon VAET processes. The two-phonon VAET processes constitute a phononic analogue of the well-known two-photon absorption [23] and we refer to them as TPhonA. They are found to be dominant for all coupling strengths, although the relative contributions of both one- and greater than two-phonon VAET processes do increase with coupling strength, gaining intensity from off-resonant contributions in the strong coupling regime. At all values of coupling strength, we find that for every VAET process the vibration coupled to the bridge has a significantly stronger impact than the terminal vibration, consistent with its central spatial location for energy transport across the chain of sites.

We also found that the two vibrations can give rise to multi-mode VAET processes in which they behave collectively, specifically via cooperation and interference that enhance the efficiency of energy transfer relative to that obtained from VAET with a single vibrational mode. This includes cooperative TPhonA in which the two phonons derive from different modes, possibly with different frequencies. We also observe an interesting phenomenon that is formally related to the reverse of this, namely processes in which a phonon from one vibrational mode simultaneously excites both the excitonic states of the trimeric chromophore system and the other vibrational mode. We term this process ‘heteroexcitation’. A vibronic spectral analysis of the VAET features allowed detailed assignment and rationalization of the spectra, revealing the constructive effects of cross coupling terms in our derived effective model. Detailed analysis of transfer processes showing quantum interference was arrived at by considering a generalized asymmetric trimeric analog of the symmetric model for which the bulk of the numerical calculations were made.

The collective VAET features were found to be reduced but not completely suppressed by dissipative effects. We showed that they can however be enhanced by raising the temperature of the vibrational modes, as well as by increasing the strength of the site–vibration coupling.

In the case of explicitly correlated non-local site–vibration couplings, as would be obtained by coupling ions to longitudinal modes, we found generically similar VAET features but with quite different relative strengths. The most important parameter determining the integrated strength of excitonic energy transfer was seen to be the vibrational coupling to the bridge site of the chromophore system.

Our projection of the full Hamiltonian onto a single excitation subspace generates an effective Hamiltonian with induced cross-correlations in the effective site–vibration coupling that can be mapped onto excitonic energy transport for molecular chromophores coupled to correlated vibrational modes. The richness of the VAET spectra found here raises the intriguing question as to whether some of these VAET processes may be operating in natural systems. In particular, the results show the important role played by resonant vibrations in enhancing uphill energy transport. Such modes provide sharp features in the 2D VAET spectra, indicating a significant enhancement of the generic quantum ratcheting of energy transport that is derived from coherent coupling to a quantum vibrational bath [30]. As illustrated in table 1, the parameters considered in our study are scaled versions of parameters found in natural photosynthetic systems. This motivates further analysis of whether examples of the more complex VAET phenomena such as two-phonon absorption and heteroexcitations are present in any natural systems.

For trapped-ion simulations of molecular excitation energy transfer between interacting pigment molecules modeled as two-level systems that are coupled to vibrational modes, the quantum simulator would consist of a chain of ions, e.g. Ca\(^{+}\), confined in a radio-frequency Paul trap with well defined sites determined by the trap geometry and the Coulomb interaction between the ions [20]. Each ion in this ‘ion crystal’ represents the site of single pigment molecule, with two internal electronic states of the ions encoding the two relevant molecular energy levels at that site. The lower energy level represents the ground state and the higher energy level the molecular (Frenkel) exciton state. It is convenient to use the internal ionic states that are commonly employed as qubit states for quantum computation with the particular trapped ion species. For example, with Ca\(^{+}\) the two magnetic substates \(|S\rangle (m_I = 1/2)\) and \(|D\rangle (m_I = 1/2)\) are used, which can be addressed by an optical transition [20]. The quantum states representing a single excitation localized on one molecular site correspond then to the combined three-ion states \(|DSS\rangle, |SDS\rangle, \) and \(|SSD\rangle\). The exciton–exciton interaction between individual sites can be engineered by the use of a (global) laser beam incident on all sites with tones detuned from the qubit transition by the axial vibrational frequencies of the ion chain. Selecting a specific normal vibrational mode allows that mode of the ion crystal to act as a bus that can transfer excitation between distinct sites via the two-qubit Mølmer–Sørensen quantum interaction [44]. This inter-site exciton–exciton interaction is complemented by site–vibration couplings that are achieved with the use of tightly focused laser beams that are localized on individual ions.

We emphasize that the cooperative behavior of multiple vibrations seen in this work act not only to enhance the excitation energy transfer but also demonstrate a rich set of VAET phenomena. Following the experimental observation of single-mode one-phonon VAET for a dimeric system in a trapped-ion quantum emulator [20], generalization of such experiments to three and more ions [22], as well as to other emulation platforms [21] appears feasible. We look forward to experimental verification of the predictions.
of VAET signatures for two-phonon absorption and for heteroexcitations in emulations of a trimeric chromophore system.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Appendix A. Key results of perturbative analysis of energy transfer

Here we summarize some key results from the analytical perturbative calculations provided in the supplementary material [31] that are used in the main text. In the interaction picture, the coefficients \( A_{jk}, B_{jk} \) that determine the perturbative factors discussed in section 4 are given explicitly as functions of \( J, \Delta \) and \( \Omega \) as

\[
A_{12} = A_{21} = \frac{2\Delta J}{\Omega^2 \sqrt{2|J|^2 + \Delta(\Delta + \Omega)}},
\]

\[
A_{23} = A_{32} = \frac{2\Delta J}{\Omega^2 \sqrt{2|J|^2 + \Delta(\Delta - \Omega)}},
\]

\[
B_{12} = B_{21} = \frac{2J^3}{\Omega^2 \sqrt{2|J|^2 + \Delta(\Delta + \Omega)}},
\]

\[
B_{23} = B_{32} = \frac{2J^3}{\Omega^2 \sqrt{2|J|^2 + \Delta(\Delta - \Omega)}},
\]

\[
A_{13} = A_{31} = -\frac{2J^2}{\Omega^2},
\]

\[
B_{13} = B_{31} = \frac{J^2}{\Omega^2},
\]

with \( \Delta = \tilde{\omega}_2 - \tilde{\omega}_1 = \tilde{\omega}_3 - \tilde{\omega}_2 \) and \( \Omega = \sqrt{\Delta^2 + 2J^2} \). The energy transfer probability at the acceptor can be written as

\[
P_3(t) = \text{tr} \left[ U(t) \sigma_3 U(t) \right],
\]

where \( U(t) = e^{-iH_0 t} U(t) e^{iH_0 t} \) and the evolution operator in the interaction picture is \( U(t) = T e^{-i \int_0^t \mathcal{H}_I(t') dt'} \), with \( T \) the time-ordering operator. To calculate the probability \( P_3(t) \), we write the donor and acceptor states in the site basis in terms of eigenstates, giving

\[
|1\rangle = \alpha|e_1\rangle - \beta|e_2\rangle + \gamma|e_3\rangle \quad \text{and} \quad |3\rangle = \gamma|e_1\rangle + \beta|e_2\rangle + \alpha|e_3\rangle,
\]

where \( \alpha = \sqrt{\frac{J + \Delta(\Delta + \Omega)}{\sqrt{\Omega^2 + 2J^2}}} \), \( \beta = \frac{1}{\sqrt{2}} \), and \( \gamma = \sqrt{\frac{J + \Delta(\Delta - \Omega)}{\sqrt{\Omega^2 + 2J^2}}} \). Note that in the weak site–site coupling limit, i.e. \( J \ll \Delta \), we have \( \alpha \to 1 \) and \( \beta, \gamma \to 0 \) and the excitonic eigenstates \( |e_3\rangle \) and \( |e_1\rangle \) can then be approximated by \( |3\rangle \) and \( |1\rangle \), respectively [31].

Appendix B. Convergence

As demonstrated in the main text, a large transfer probability can be realized by increasing either the vibrational temperatures \( k_B T_a \) and \( k_B T_b \), or the site–vibration coupling strengths \( \kappa_a, \kappa_b \). However higher values of temperature or site–vibration coupling might cause convergence issues if the truncation number \( N \) of each vibrational Fock space is not large enough. To address this issue and confirm convergence of the numerical results, we show in figure 14 the transfer probability for various values of \( N \), at vibrational temperatures \( k_B T_a = k_B T_b = 1.5 \text{ kHz} \) for several values of the site–vibration coupling. When the coupling
strength is weak, e.g. $\kappa_a = \kappa_b = 0.01$ kHz in figure 14(a), and when it is increased to 0.05 kHz and 0.1 kHz as in figures 14(b) and (c), respectively, the results are already convergent for $N = 15$. This provides evidence for the accuracy of our results in figure 2(a). Increasing the coupling strength to an ultra-strong regime [45], e.g. to $\kappa_a = \kappa_b = 0.5$ kHz, which is comparable to the excitonic transition frequency, requires a value as large as $N = 30$ to achieve a good convergence, as shown in figure 14(d). Similarly, convergence of the spectra in the very low vibrational frequency regime (i.e. smaller $\nu_a (b) / \Delta_{31}$) might be expected to require a larger value of $N$. However, the general form of the spectra in this region is already converged at $N = 15$, as shown explicitly in the supplemental material [31].

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