


Phonon Signatures in Photon Correlations

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We show that the second-order, two-time correlation functions for phonons and photons emitted from a vibronic molecule in a thermal bath result in bunching and antibunching (a purely quantum effect), respectively. Signatures relating to phonon exchange with the environment are revealed in photon-photon correlations. We demonstrate that cross-correlation functions have a strong dependence on the order of detection giving insight into how phonon dynamics influences the emission of light. This work offers new opportunities to investigate quantum effects in condensed-phase molecular systems.

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Correlation measurements of photon emission provide powerful tools for demonstrating quantum effects. Among the most striking examples is the experimental discovery of antibunching in the photon emission of fluorescing atoms [1,2], which provided the first direct demonstration of the quantum properties of light [3]. Antibunching [4] is the phenomenon whereby the emission of a second photon immediately after a first is suppressed. The joint probability of detecting two photons at time t and $t + \tau$ is quantified by the second-order correlation function [5]. While in classical emission, this function may have a maximum for $\tau = 0$, second-order correlations falling off as $\tau \rightarrow 0$ can appear only as a purely quantum phenomenon. The second-order correlation function thus forms a powerful statistical tool that has been used to study fundamental properties of photon emission and photon-mediated interactions, for example bunching and antibunching in transmission through waveguides [6] and in emission from plasmonic nanojunctions [7], pattern formation in photoinduced nucleation [8], photon-blockade effects [9] in optical cavities [10–14] (including modified response at strong coupling [15]), atomic arrays [16,17], as well as superatom behavior in ensembles of quantum emitters [17,18]. Higher-order correlations can further reveal two-photon blockade [19].

In all of these examples, the correlations are exhibited by emitted light. However, the usefulness of quantum correlation functions extends beyond the study of photons. Similar techniques have also been applied to describe phonon blockade in optomechanical [20,21] and spin-mechanical [22,23] systems. Intriguingly, second-order cross-correlation

functions between nonidentical particles and quasiparticles can reveal, for example, photon-magnon blockade in a ferrimagnetic material coupled to a microcavity [24], and photon-phonon bunching and antibunching in a qubit-phonon-plasmon system under strong coupling [25].

In recent years, there has been significant interest in the nature of electronic and vibrational coherence in condensed-phase resonance energy transfer in molecular systems [26,27]. However, its exact nature, whether classical or quantum, remains controversial [28,29]. This is because experiments typically used to investigate this measure optical responses resulting from an induced macroscopic polarization, which is a classical property [30]. Quantum-optical techniques, such as correlation measurements [31,32], offer an avenue to investigate genuine quantum effects in molecular systems directly.

Here, we develop an open quantum system model for a vibronic molecule driven by a continuous monochromatic laser field (Fig. 1). We include both vibrational and electronic degrees of freedom as well as coupling to a thermal environment. We calculate photon-photon, phonon-phonon, and photon-phonon correlations during cyclic pumping while the molecule undergoes vibrational relaxation (VR). The key result is that signatures relating to phonon exchange with the environment, which are revealed in phonon-phonon correlations, can be accessible through the measurement of photon emission. By examining photon-phonon cross-correlation functions [24,25,32–34], we explain how phonon dynamics influences the emission of light. Measurements of such features could help elucidate the impact of vibrational excitations on the quantum nature of light-matter interaction processes in systems ranging from subwavelength molecular arrays [35] to large organic molecules [36].

We consider a model system consisting of a simple molecule with two electronic levels, each with a set of N vibrational states, coupled to an infinite ensemble of overdamped quantum harmonic oscillator modes [37–39].

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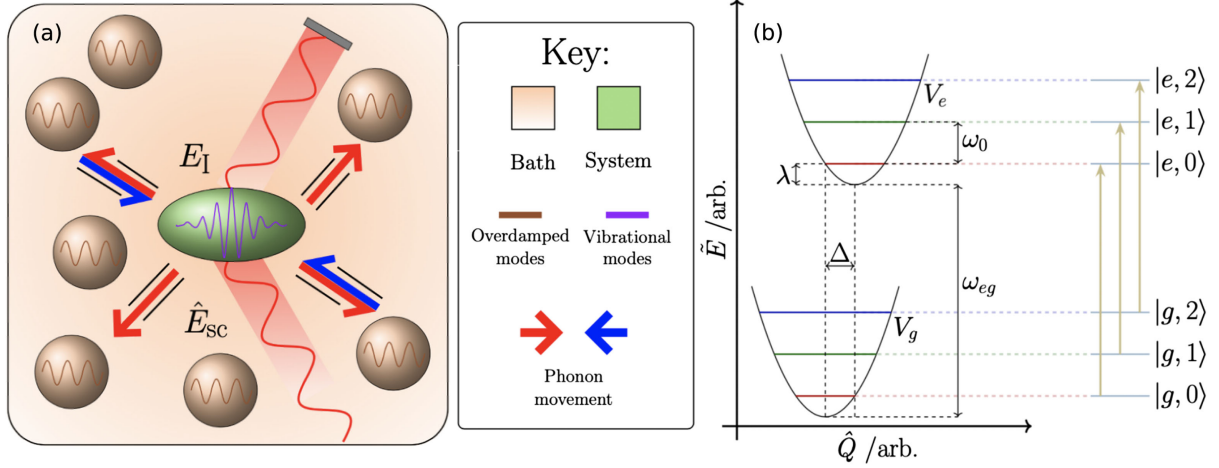


FIG. 1. (a) Schematic of the molecule coupled to bath modes and driven by laser field E_I , resulting in the scattered field \hat{E}_{sc} . Phonon movement between system and environment indicated by arrows. (b) Diabatic energy levels, with excited state displacement Δ , system reorganization energy λ , fundamental transition frequency ω_{eg} , and system mode frequency ω_0 . Corresponding adiabatic levels on the far right.

Similar models have previously been used to investigate the role of a vibrational environment on the open quantum system dynamics of molecules [40,41].

The total Hamiltonian is the formal sum

$$\hat{H}_{\text{tot}} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB} + \hat{H}_{SF}, \quad (1)$$

which describes the system, the bath, and the system-bath interaction, as well as the coupling between the system and the photon field. The molecule is driven by a continuous, monochromatic laser field $\mathbf{E}_I = E_0 \mathbf{e} [\exp(i\omega_{eg}t/\hbar) + \exp(-i\omega_{eg}t/\hbar)]$, with polarization \mathbf{e} and frequency ω_{eg} resonant with the fundamental transition between the ground ($|g\rangle$) and excited ($|e\rangle$) electronic levels, such that $\hat{H}_{SF} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{E}_I(r, t)$. Here, $\hat{\boldsymbol{\mu}} = \mu_{eg} \mathbf{d} (|e\rangle\langle g| + |g\rangle\langle e|)$ is the transition dipole moment of magnitude μ_{eg} and direction \mathbf{d} , such that $\hat{H}_{SF} = E_0 \mu_{eg} \mathbf{e} \cdot \mathbf{d} [\exp(i\omega_{eg}t/\hbar) + \exp(-i\omega_{eg}t/\hbar)] [|e\rangle\langle g| + |g\rangle\langle e|]$ [42]. Driving by the laser results in stimulated photon emission yielding a scattered electric field with positive-frequency component $\hat{E}_{sc}^+ \sim \exp(i\omega_{eg}t/\hbar) |e\rangle\langle g|$ [43].

The vibrational degrees of freedom are described by

$$\hat{H}_S = |g\rangle \hat{h}_g \langle g| + |e\rangle \hat{h}_e \langle e|. \quad (2)$$

The nuclear Hamiltonians for the ground and excited electronic states are, respectively, defined by

$$\hat{h}_g = \hbar\omega_0 \left(\hat{b}^\dagger \hat{b} + \frac{1}{2} \right), \quad (3)$$

$$\hat{h}_e = \hbar(\omega_{eg} + \lambda) + \hbar\omega_0 \left(\hat{b}^\dagger \hat{b} - \sqrt{\frac{\lambda}{\omega_0}} (\hat{b} + \hat{b}^\dagger) + \frac{1}{2} \right), \quad (4)$$

where ω_0 is the system mode frequency, \hat{b}^\dagger and \hat{b} are system phonon creation and annihilation operators, corresponding to the vibrational states of the molecule, and λ is the system reorganization energy [44]. This model is constructed in a diabatic (D) basis that separates the vibrational levels from the electronic states, leading to explicit off-diagonal couplings. As a result, the electronic excited state, Eq. (4), appears displaced by $\Delta = \sqrt{2\lambda\omega_0^{-1}}$ relative to the electronic ground state [see also Fig. 1(b)]. This displacement accounts for the change in the equilibrium geometry of the electronic excited state. Note that an increase in the system reorganization energy, λ , corresponds to an increased displacement, Δ . The excited potential also experiences an energy shift $\hbar\omega_{eg}$ corresponding to the fundamental transition.

Instead of working in the diabatic basis, used above for conceptual clarity in the construction of the Hamiltonian, one can obtain adiabatic (A) eigenstates, $|g, 0\rangle, |g, 1\rangle, \dots, |e, 0\rangle, |e, 1\rangle, \dots$ (see Fig. 1), by diagonalizing \hat{H}_{tot} through a unitary transformation $\hat{H}_{\text{tot}}^A = (\hat{U}^{AD})^\dagger \hat{H}_{\text{tot}}^D \hat{U}^{AD}$ [41,45]. The presence of the system reorganization energy in Eq. (4) means that the energy eigenstates (the energy of the adiabatic states) are identical to the energies of the vibrational levels in the diabatic picture, as illustrated in Fig. 1(b). The adiabatic states correspond directly to the laboratory observables.

Vibrational relaxation occurs as a result of escape of system phonons to the environment, modeled as an infinite ensemble of harmonic oscillator modes. The system-bath coupling is then described by

$$\hat{H}_B + \hat{H}_{SB} = \sum_{\alpha} \frac{\hat{p}_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} m_{\alpha} \omega_{\alpha}^2 \left(\hat{x}_{\alpha} - \frac{g_{\alpha} \hat{Q}}{2m_{\alpha} \omega_{\alpha}^2} \right)^2, \quad (5)$$

where $\hat{Q} = (\hat{b} + \hat{b}^\dagger)/\sqrt{2}$, and m_α , \hat{p}_α , and \hat{x}_α are the mass, momentum, and the coordinate of the environmental harmonic modes, which correspond to bath phonons. The coupling strength g_α of the α th harmonic oscillator is determined by the spectral density, $J(\omega) = \sum_\alpha g_\alpha^2 (2m_\alpha)^{-1} \times \omega_\alpha \delta(\omega - \omega_\alpha)$. This model for the surrounding environment is very general and allows in principle even the modeling of non-Markovian system-bath coupling [40]. Here, however, we work in the Markovian limit and simplify the environment to an overdamped Brownian oscillator profile, $J(\omega) = 2\eta\omega\Lambda(\omega^2 + \Lambda^2)^{-1}$, with bath reorganization energy η and dissipation rate Λ . The overdamped spectral density introduces stochastic, Gaussian fluctuations in the nuclear dynamics, representative of low frequency intermolecular modes from the interaction of the molecule with the solvent. The coupling of the system and bath nuclear coordinates leads to vibrational dephasing [47,48] and dissipation. Several different approaches exist for solving the generally computationally demanding equations of motion resulting from Eq. (1) and similar open quantum systems [7,13,31,49–51]. Here, we employ the hierarchical equations of motion method [52,53] in the overdamped limit from Ref. [40] to evolve the vibronic molecule, equivalent to the Hamiltonian vibration model for a vibronic monomer in Ref. [41].

The hierarchical equations of motion simulations of the quantum dynamics allow us to numerically compute the correlation functions for the emission of photons and phonons from the molecule. In particular, the correlated emission of photons and phonons is quantified by the normalized second-order correlation function

$$g_{c_1 c_2}^{(2)}(t, \tau) = \frac{\langle \hat{c}_1(t) \hat{c}_2(t + \tau) \hat{c}_2^\dagger(t + \tau) \hat{c}_1^\dagger(t) \rangle}{\langle \hat{c}_1(t) \hat{c}_1^\dagger(t) \rangle \langle \hat{c}_2(t) \hat{c}_2^\dagger(t) \rangle}. \quad (6)$$

When the operators are chosen such that $\hat{c}_{1,2} = \hat{a} = \mu_{eg}|g\rangle\langle e|$, the photon annihilation operator, we obtain the photon-photon correlation function $g_{aa}^{(2)}$, which reflects the joint probability of a photon being emitted at time $t + \tau$ given that a photon was emitted at time t . By appropriately choosing $\hat{c}_{1,2}$ from the photon and phonon operators \hat{a} and \hat{b} , respectively, we can correspondingly construct the phonon-phonon correlation function $g_{bb}^{(2)}$ and, notably, the photon-phonon and phonon-photon cross-correlation functions $g_{ab}^{(2)}$ and $g_{ba}^{(2)}$ in a manner similar to Refs. [24,25,32–34].

We now employ the correlation functions (6) to probe quantum effects [54] in the molecular system in its thermal environment. In particular, we determine the presence of antibunching [4], defined as $g_{c_1 c_2}^{(2)}(t, \tau = 0) < g_{c_1 c_2}^{(2)}(t, \tau > 0)$. This implies that the probability of a second emission event immediately following a first is suppressed. Note that this definition encompasses not only photon-photon

or phonon-phonon correlation, but is also generalized [24,25] to include cross-correlations where the two emission events consist of one photon and one phonon. Correspondingly, bunching is defined to occur when the probability of simultaneous emission is enhanced, $g_{c_1 c_2}^{(2)}(t, \tau = 0) > g_{c_1 c_2}^{(2)}(t, \tau > 0)$.

In the following, we assume that all emitted photons and phonons are detected, regardless of scattering directions, e.g., by imagining the system enclosed by a detector and use the quantum regression theorem [5,42,55–57] to compute second-order correlations as

$$g_{c_1 c_2}^{(2)}(t, \tau) = \frac{\text{Tr}[\hat{c}_1^\dagger \hat{c}_1 \exp(\mathcal{L}\tau) (\hat{c}_2 \hat{\rho} \hat{c}_2^\dagger)]}{\text{Tr}(\hat{c}_1 \hat{\rho} \hat{c}_1^\dagger) \text{Tr}(\hat{c}_2 \hat{\rho} \hat{c}_2^\dagger)}, \quad (7)$$

where $\hat{\rho} = \hat{\rho}(t)$ is the density matrix at time t and \mathcal{L} is the Liouvillian operator for the time evolution of the system. The molecule is initially equilibrated with its thermal environment, in the absence of the driving field, so that the density matrix of the system is correlated with the bath. This ensures that the vibrational states of the molecule are in the correct Boltzmann distribution. The overdamped hierarchy is then used to evolve the dynamics in the presence of the driving field over several optical cycles to find $\hat{\rho}(t)$. To compute $g_{c_1 c_2}^{(2)}(t, \tau)$, one then takes $\hat{c}_2 \hat{\rho}(t) \hat{c}_2^\dagger$ as the initial state for a subsequent evolution in τ taking care to preserve continuity of the driving field.

Figures 2(a)–(c) show the two-time photon correlation function, $g_{aa}^{(2)}(t, \tau)$, as a function of the photon-photon separation time τ for the molecular system defined in Eq. (1). For this and following simulation results, we assume (unless otherwise specified) $\eta = 5 \text{ cm}^{-1}$, $\Lambda = 200 \text{ cm}^{-1}$, $\omega_0 = 500 \text{ cm}^{-1}$, $\Delta = 1.2$ such that $\lambda \approx 260 \text{ cm}^{-1}$, $\omega_{eg} = 10^4 \text{ cm}^{-1}$, $E_0 = 10^7 \text{ NC}^{-1}$, and $T = 298 \text{ K}$. These parameters ensure that coupling to the bath is weak, and we are operating in the Markovian limit. We truncate the number of vibrational levels at $N = 10$, which is sufficiently large for the results to be insensitive to the truncation. These parameters are comparable to real molecules with electronic and vibrational transition frequencies $\sim 10^4 \text{ cm}^{-1}$ and $\sim 10^2 \text{ cm}^{-1}$, respectively [58,59]. The weakly coupled Markovian bath parameters are typical of commonplace nonpolar solvents [40,41].

As population is initialized to a Boltzmann distribution, excitation results in a wave packet that moves within the harmonic potential [60–62]. When the system reorganization energy $\lambda = 0$, the effect of the monochromatic laser field is to drive population between the ground vibronic states and the equivalent excited states ($|g, 0\rangle \rightarrow |e, 0\rangle$, $|g, 1\rangle \rightarrow |e, 1\rangle, \dots$). The resulting Rabi oscillations are reflected in $g_{aa}^{(2)}$ and show in photon antibunching. However when $\lambda > 0$, VR occurs and the excited state wave packet population becomes different to that of the ground state. This results in the emergence of a minor

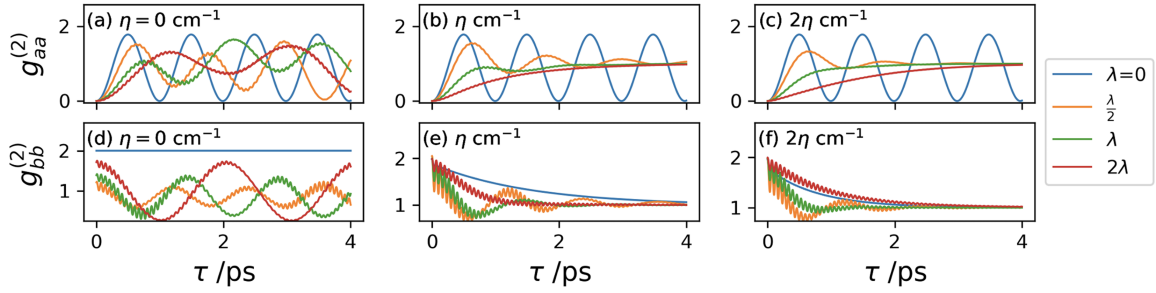


FIG. 2. (a)–(c) $g_{aa}^{(2)}(\tau)$ photon-photon correlation function; (d)–(f) $g_{bb}^{(2)}(\tau)$ phonon-phonon correlation function, scanning over bath (η) and system (λ) reorganization energies.

oscillation in $g_{aa}^{(2)}$, at the vibrational mode frequency, which implies that the experimentally measurable second-order photon correlation function contains an observable phonon signature despite the fact that phonons are not directly detected. This signature appears because of the change in Franck-Condon overlap (i.e., the overlap integral of the bound eigenstates of the electronic excited state with the ground state) [63]. The Franck-Condon overlap of the fundamental transitions reduces with increasing λ , increasing the Rabi oscillation period and more population enters the vibronic $|e, 0\rangle$ state via VR.

Increased bath reorganization energy η damps the Rabi oscillations as phonons dissipate into the bath, leading to the formation of a steady state [Figs. 2(b) and (c)]. We then evaluate $g_{aa}^{(2)}(t, \tau)$ as a function of τ at a time t after reaching the steady state, in keeping with common convention. When no steady state forms [$\eta = 0$, Fig. 2(a)], but Rabi-like oscillations persist indefinitely [64], the choice of t , and therefore the normalization of $g_{aa}^{(2)}$ as a function of τ [cf. Eq. (6)] is not obvious [43,45,65]. We choose t such that the denominator in Eq. (6) corresponds to its value in the steady state when $\eta > 0$.

Figures 2(d)–(f) show the corresponding phonon-phonon correlation, $g_{bb}^{(2)}(\tau)$. When $\lambda = \eta = 0$ the population moves resonantly between the ground and excited states and with no VR [66], resulting in a constant phonon-phonon $g_{bb}^{(2)}(\tau)$. Despite the lack of phonon dissipation ($\eta = 0$), a pronounced oscillation at the mode frequency appears for $\lambda > 0$ as the excited state displacement results in a nonstationary population distribution out of thermal equilibrium. For the same reason, $g_{bb}^{(2)}(\tau)$ also tracks the Rabi oscillation when $\lambda > 0$ and phonon bunching is apparent. Additionally introducing coupling to the environment bath, $\eta > 0$, we find a rapid decay of $g_{bb}^{(2)}$ with τ due to the strong dissipation.

Both the $g_{aa}^{(2)}$ and $g_{bb}^{(2)}$, by definition, have no dependence on the order of detection events since τ separates the detection of identical particles. In both cases there is a single source of vibrational character. For the $g_{aa}^{(2)}$ this is indirect, from the strong dependence of photons on the vibrational populations, while for $g_{bb}^{(2)}$ this is from direct

measurement of the phonon number. In both cases, vibrational character is observed as oscillations at the vibrational mode frequency ω_0 .

We can understand the appearance of phonon signatures in the photon correlations from the cross-correlation functions $g_{ab}^{(2)}(\tau)$ and $g_{ba}^{(2)}(\tau)$ (Fig. 3), where the order of detection does matter. Specifically, the second detection event determines the dominant character of the cross-correlation function as a function of τ . In $g_{ab}^{(2)}$, the phonon detection is second, and we observe the primary behavior of the phonon correlation [cf. Figs. 2(d)–(f)] with photon correlation-function characteristics superimposed. The first detection event can be thought of as an instantaneous measurement of photon number and contains no vibrational information. The second detection event—the phonon—occurs a time τ later, during which vibrational transitions may occur. However, because the fast phonon signatures are very small with respect to the electronic contributions their impact on the excited-state adiabatic population is minimal, i.e., there is no significant minor oscillation [45]. Consequently, neither detection event incurs vibrational character. Figures 3(a)–(c) also show phonon bunching, i.e., a photon detection is likely to be immediately followed by another phonon, reflecting the nonequilibrium population distribution following photon emission.

By contrast, the phonon-photon correlation function $g_{ba}^{(2)}(\tau)$ [Figs. 3(d)–(f)] corresponds to the observation of a phonon followed by a photon. Since the photon detection is second, characteristics of $g_{aa}^{(2)}$ [Figs. 2(a)–(c)] dominate, with phonon characteristics superimposed. The first detection event—the phonon—is an instantaneous measurement of phonon number and thus has intrinsic vibrational character at the molecule mode frequency. However, the second detection event—the photon—also introduces additional vibrational character due to vibrational transitions occurring between the detections. Consequently, there are two sources of vibrational character in $g_{ba}^{(2)}$: (1) intrinsically from the first detection event, and (2) from phonon effects during the optical cycles leading to the photon emission.

For $\lambda = 0$, $g_{ba}^{(2)}(\tau)$ remains at a small, nonzero constant value regardless of the bath coupling. However, increasing

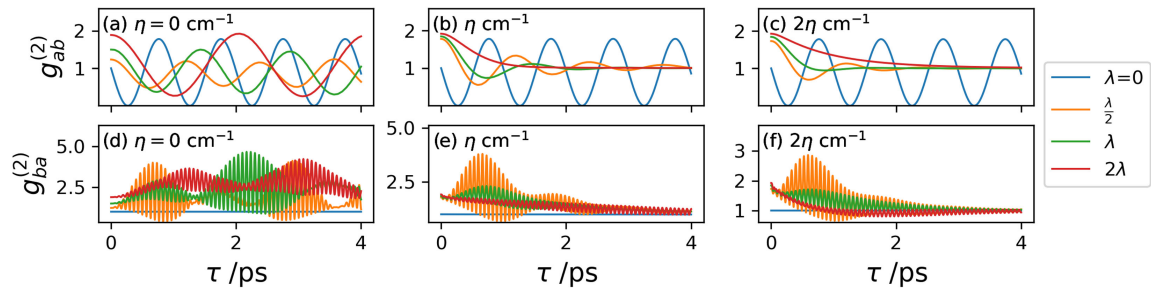


FIG. 3. (a)–(c) $g_{ab}^{(2)}(\tau)$ cross-correlation function; (d)–(f) $g_{ba}^{(2)}(\tau)$ cross-correlation function, scanning over bath (η) and system (λ) reorganization energies.

the system reorganization energy introduces strong oscillations and the correlation function may drop below the $\lambda = 0$ value. This is explained by a large proportion of the wave packet population undergoing vibrational transitions. This effect persists for small τ even with strong bath dissipation, but it is destroyed for later τ by the influence of the environment. Note that similar to $g_{aa}^{(2)}(\tau)$, $g_{ba}^{(2)}(\tau)$ exhibits antibunchinglike behavior, i.e., a photon is less likely to be emitted directly after a phonon. This is because photon emission at ω_{eg} from higher vibrational levels is increasingly suppressed for larger λ due to decreasing Franck-Condon overlap. This means that phonon emission tends to inhibit subsequent photon emission when $\tau \approx 0$.

Dynamical impact of lattice phonons on quantum-dot emitters embedded in a solid-state system was recently theoretically and experimentally shown to result in a characteristic signature in the photon spectrum [67]. System phonons are not defined in the quantum-dot model, but are integral to molecules and the proximate source of the signatures predicted here. Our results suggest that measurements of two-photon correlations could explicitly elucidate differences in the impact of system phonons and the phonon environment.

In conclusion, we have demonstrated theoretically photon antibunching in the fluorescence of a vibronic molecule under continuous laser drive and a thermal environment and that the photon-photon correlations exhibit signatures of the phonon interaction with the bath, suggesting that these are experimentally directly measurable. These appear as oscillations at the system-mode frequency on top of slower modulations associated with the electronic Rabi-like oscillations. Theoretically also considering phonon detection and photon-phonon cross-correlation functions, we have shown how vibrational contributions are understood as arising either directly, through phonon detection, or indirectly, through photon detection subsequent to phonon emission. As such, the order of particle detection can dramatically impact the behavior of the correlation functions, which could in principle be exploited to investigate the phonon impact on photon emission. More immediately, these correlation functions present an opportunity to investigate phonon dynamics indirectly using existing

quantum-optical techniques to understand the impact on quantum versus classical processes in molecular systems.

Data used in this publication available at [68].

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- [1] H. J. Kimble, M. Dagenais, and L. Mandel, Photon Antibunching in Resonance Fluorescence, *Phys. Rev. Lett.* **39**, 691 (1977).
- [2] H. J. Kimble, M. Dagenais, and L. Mandel, Multiatom and transit-time effects on photon-correlation measurements in resonance fluorescence, *Phys. Rev. A* **18**, 201 (1978).
- [3] D. F. Walls, Evidence for the quantum nature of light, *Nature (London)* **280**, 451 (1979).
- [4] H. Paul, Photon antibunching, *Rev. Mod. Phys.* **54**, 1061 (1982).
- [5] H. J. Carmichael and D. F. Walls, A quantum-mechanical master equation treatment of the dynamical Stark effect, *J. Phys. B At. Mol. Phys.* **9**, 1199 (1976).
- [6] Huaixiu Zheng, Daniel J. Gauthier, and Harold U. Baranger, Strongly correlated photons generated by coupling a three- or four-level system to a waveguide, *Phys. Rev. A* **85**, 043832 (2012).
- [7] R. Avriller, Q. Schaeverbeke, T. Frederiksen, and F. Pistolesi, Photon-emission statistics induced by electron tunneling in plasmonic nanojunctions, *Phys. Rev. B* **104**, L241403 (2021).
- [8] Kunio Ishida and Keiichiro Nasu, Theoretical study of transient x-ray speckles in photoinduced nucleation, *J. Phys. Soc. Jpn.* **81**, 063708 (2012).

- [9] A. Imamoğlu, H. Schmidt, G. Woods, and M. Deutsch, Strongly Interacting Photons in a Nonlinear Cavity, *Phys. Rev. Lett.* **79**, 1467 (1997).
- [10] K. M. Birnbaum, A. Boca, R. Miller, A. D. Boozer, T. E. Northup, and H. J. Kimble, Photon blockade in an optical cavity with one trapped atom, *Nature (London)* **436**, 87 (2005).
- [11] C. Lang, D. Bozyigit, C. Eichler, L. Steffen, J. M. Fink, A. A. Abdumalikov, M. Baur, S. Filipp, M. P. da Silva, A. Blais, and A. Wallraff, Observation of Resonant Photon Blockade at Microwave Frequencies Using Correlation Function Measurements, *Phys. Rev. Lett.* **106**, 243601 (2011).
- [12] Wen-Wu Deng, Gao-Xiang Li, and Hong Qin, Photon blockade via quantum interference in a strong coupling qubit-cavity system, *Opt. Express* **25**, 6767 (2017).
- [13] Bing Gu and Shaul Mukamel, Photon correlation signals in coupled-cavity polaritons created by entangled light, *ACS Photonics* **9**, 938 (2022).
- [14] Ya-Ting Guo, Fen Zou, Jin-Feng Huang, and Jie-Qiao Liao, Retrieval of photon blockade effect in the dispersive Jaynes-Cummings model, *Phys. Rev. A* **105**, 013705 (2022).
- [15] A. Ridolfo, M. Leib, S. Savasta, and M. J. Hartmann, Photon Blockade in the Ultrastrong Coupling Regime, *Phys. Rev. Lett.* **109**, 193602 (2012).
- [16] A. Cidrim, T. S. do Espirito Santo, J. Schachenmayer, R. Kaiser, and R. Bachelard, Photon Blockade with Ground-State Neutral Atoms, *Phys. Rev. Lett.* **125**, 073601 (2020).
- [17] L. A. Williamson, M. O. Borgh, and J. Ruostekoski, Supercavity Picture of Collective Nonclassical Light Emission and Dipole Blockade in Atom Arrays, *Phys. Rev. Lett.* **125**, 073602 (2020).
- [18] Mingyuan Chen, Jiangshan Tang, Lei Tang, Haodong Wu, and Keyu Xia, Photon blockade and single-photon generation with multiple quantum emitters, *Phys. Rev. Res.* **4**, 033083 (2022).
- [19] Ling-Juan Feng and Shang-Qing Gong, Two-photon blockade generated and enhanced by mechanical squeezing, *Phys. Rev. A* **103**, 043509 (2021).
- [20] M. Hassani Nadiki and M. K. Tavassoly, Phonon blockade in a system consisting of two optomechanical cavities with quadratic cavity-membrane coupling and phonon hopping, *Eur. Phys. J. D* **76**, 58 (2022).
- [21] Zi-Yuan Li, Guang-Ri Jin, Tai-Shuang Yin, and Aixi Chen, Two-phonon blockade in quadratically coupled optomechanical systems, *Photonics Spectra* **9**, 70 (2022).
- [22] Yan Wang, Jin Lei Wu, Jin Xuan Han, Yan Xia, Yong Yuan Jiang, and Jie Song, Enhanced Phonon Blockade in a Weakly Coupled Hybrid System via Mechanical Parametric Amplification, *Phys. Rev. Appl.* **17**, 024009 (2022).
- [23] Tai-Shuang Yin, Guang-Ri Jin, and Aixi Chen, Enhanced phonon antibunching in a circuit quantum acoustodynamical system containing two surface acoustic wave resonators, *Micromachines* **13**, 591 (2022).
- [24] Mahboobeh Moslehi, Hamid Reza Baghshahi, Mohammad Javad Faghihi, and Sayyed Yahya Mirafzali, Photon and magnon blockade induced by optomagnonic microcavity, *Eur. Phys. J. Plus* **137**, 777 (2022).
- [25] Ting-ting Ma, Dmitri B. Horoshko, Chang-shui Yu, and Sergei Ya. Kilin, Photon and phonon statistics in a qubit-plasmon-phonon ultrastrong-coupling system, *Phys. Rev. A* **105**, 053718 (2022).
- [26] Gregory D. Scholes, Graham R. Fleming, Lin X. Chen, Alán Aspuru-Guzik, Andreas Buchleitner, David F. Coker, Gregory S. Engel, Rienk Van Grondelle, Akihito Ishizaki, David M. Jonas, Jeff S. Lundeen, James K. McCusker, Shaul Mukamel, Jennifer P. Ogilvie, Alexandra Olaya-Castro, Mark A. Ratner, Frank C. Spano, K. Birgitta Whaley, and Xiaoyang Zhu, Using coherence to enhance function in chemical and biophysical systems, *Nature (London)* **543**, 647 (2017).
- [27] Garth A. Jones and David S. Bradshaw, Resonance energy transfer: From fundamental theory to recent applications, *Front. Phys.* **7**, 100 (2019).
- [28] William H. Miller, Perspective: Quantum or classical coherence?, *J. Chem. Phys.* **136**, 210901 (2012).
- [29] Tomáš Mančal, A decade with quantum coherence: How our past became classical and the future turned quantum, *Chem. Phys.* **532**, 110663 (2020).
- [30] Shaul Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).
- [31] Arzu Kurt, Two-time correlation functions beyond quantum regression theorem: Effect of external noise, *Quantum Inf. Process.* **20**, 238 (2021).
- [32] Masashi Ban, Two-time correlations functions and quantumness of an open two-level system, *Eur. Phys. J. D* **73**, 12 (2019).
- [33] Shilan Abo, Grzegorz Chimczak, Anna Kowalewska-Kudłaszyk, Jan Peřina, Ravindra Chhajlany, and Adam Miranowicz, Hybrid photon-phonon blockade, *Sci. Rep.* **12**, 17655 (2022).
- [34] Joanna K. Kalaga, Wiesław Leoński, Radosław Szcześniak, and Jan Peřina, Mixedness, coherence and entanglement in a family of three-qubit states, *Entropy* **24**, 324 (2022).
- [35] R. Holzinger, S. A. Oh, M. Reitz, H. Ritsch, and C. Genes, Cooperative subwavelength molecular quantum emitter arrays, *Phys. Rev. Res.* **4**, 033116 (2022).
- [36] Jiratheep Pruchyathamkorn, William J. Kendrick, Andrew T. Frawley, Andrea Mattioni, Felipe Caycedo-Soler, Susana F. Huelga, Martin B. Plenio, and Harry L. Anderson, A complex comprising a cyanine dye rotaxane and a porphyrin nanoring as a model light-harvesting system, *Angew. Chem., Int. Ed. Engl.* **59**, 16455 (2020).
- [37] Heinz-Peter Breuer, Elsi-Mari Laine, Jyrki Piilo, and Bassano Vacchini, Colloquium: Non-Markovian dynamics in open quantum systems, *Rev. Mod. Phys.* **88**, 021002 (2016).
- [38] Heinz-Peter Peter Breuer and Francesco Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, New York, 2002).
- [39] Ulrich Weiss, *Quantum Dissipative Systems* (Oxford University Press, New York, 1993).
- [40] Dale Green, Ben S. Humphries, Arend G. Dijkstra, and Garth A. Jones, Quantifying non-markovianity in underdamped versus overdamped environments and its effect on spectral lineshape, *J. Chem. Phys.* **151**, 174112 (2019).

- [41] Ben S. Humphries, Dale Green, and Garth A. Jones, The influence of a hamiltonian vibration vs a bath vibration on the 2d electronic spectra of a homodimer, *J. Chem. Phys.* **156**, 084103 (2022).
- [42] B. R. Mollow, Power spectrum of light scattered by two-level systems, *Phys. Rev.* **188**, 1969 (1969).
- [43] Roy J. Glauber, The quantum theory of optical coherence, *Phys. Rev.* **130**, 2529 (1963).
- [44] Dassia Egorova, Maxim F. Gelin, and Wolfgang Domcke, Analysis of cross peaks in two-dimensional electronic photon-echo spectroscopy for simple models with vibrations and dissipation, *J. Chem. Phys.* **126**, 074314 (2007).
- [45] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.131.143601> for non-normalized correlation functions and discussion of bases, which includes Ref. [46].
- [46] M. R. Andrews, M.-O. Mewes, N. J. van Druten, D. S. Durfee, D. M. Kurn, and W. Ketterle, Direct, nondestructive observation of a bose condensate, *Science* **273**, 84 (1996).
- [47] Peter Hamm and Martin Zanni, *Concepts and Methods of 2D Infrared Spectroscopy* (Cambridge University Press, Cambridge, England, 2011).
- [48] Akihito Ishizaki and Yoshitaka Tanimura, Nonperturbative non-Markovian quantum master equation: Validity and limitation to calculate nonlinear response functions, *Chem. Phys.* **347**, 185 (2008).
- [49] Rafael Carballeira, David Dolgitzer, Peng Zhao, Debing Zeng, and Yusui Chen, Stochastic Schrödinger equation derivation of non-Markovian two-time correlation functions, *Sci. Rep.* **11**, 11828 (2021).
- [50] Ali A. Alkathiri, Shami A. M. Alsallami, N. H. Abdel-Wahab, S. Abdel-Khalek, and E. M. Khalil, On the interaction between Λ -type five-level atom and one-mode squeezed coherent field, *Results Phys.* **39**, 105739 (2022).
- [51] Mingrui Yang, Matija Čufar, Elke Pahl, and Joachim Brand, Polaron-depletion transition in the yrast excitations of a one-dimensional bose gas with a mobile impurity, *Condens. Matter Phys.* **7**, 15 (2022).
- [52] Yoshitaka Tanimura and Ryogo Kubo, Time evolution of a quantum system in contact with a nearly Gaussian-Markovian noise bath, *J. Phys. Soc. Jpn.* **58**, 101 (1989).
- [53] Yoshitaka Tanimura, Numerically, “exact” approach to open quantum dynamics: The hierarchical equations of motion (heom), *J. Chem. Phys.* **153**, 020901 (2020).
- [54] U. Fano, Quantum theory of interference effects in the mixing of light from phase-independent sources, *Am. J. Phys.* **29**, 539 (1961).
- [55] Melvin Lax, Formal theory of quantum fluctuations from a driven state, *Phys. Rev.* **129**, 2342 (1963).
- [56] Melvin Lax, Quantum noise. X. Density-matrix treatment of field and population-difference fluctuations, *Phys. Rev.* **157**, 213 (1967).
- [57] Howard J. Carmichael, *Statistical Methods in Quantum Optics I* (Springer, Berlin, Heidelberg, 1999), pp. 19–24.
- [58] F. V. Camargo, H. L. Anderson, S. R. Meech, and I. A. Heisler, Full characterization of vibrational coherence in a porphyrin chromophore by two-dimensional electronic spectroscopy, *J. Phys. Chem. A* **119**, 95 (2015).
- [59] J. Lu, Y. Lee, and J. M. Anna, Extracting the frequency-dependent dynamic stokes shift from two-dimensional electronic spectra with prominent vibrational coherences, *J. Phys. Chem. B* **124**, 8857 (2020).
- [60] Laurence A. Nafie, Adiabatic molecular properties beyond the Born–Oppenheimer approximation. Complete adiabatic wave functions and vibrationally induced electronic current density, *J. Chem. Phys.* **79**, 4950 (1983).
- [61] Pavel Malý, Oscar J. G. Somsen, Vladimir I. Novoderezhkin, Tomáš Mančal, and Rienk Van Grondelle, The role of resonant vibrations in electronic energy transfer, *Chem. Phys. Chem.* **17**, 1356 (2016).
- [62] Sabine Kopec, Philipp Ottiger, Samuel Leutwyler, and Horst Köppel, Vibrational quenching of excitonic splittings in h-bonded molecular dimers: Adiabatic description and effective mode approximation, *J. Chem. Phys.* **137**, 184312 (2012).
- [63] Edward Condon, A theory of intensity distribution in band systems, *Phys. Rev.* **28**, 1182 (1926).
- [64] I. I. Rabi, Space quantization in a gyrating magnetic field, *Phys. Rev.* **51**, 652 (1937).
- [65] Leonard Mandel and Emil Wolf, *Optical Coherence and Quantum Optics* (Cambridge University Press, Cambridge, England, 1995).
- [66] Marlan O. Scully and M. Suhail Zubairy, *Quantum Optics* (Cambridge University Press, Cambridge, England, 1997).
- [67] Alistair J. Brash, Jake Iles-Smith, Catherine L. Phillips, Dara P. S. McCutcheon, John O’Hara, Edmund Clarke, Benjamin Royall, Luke R. Wilson, Jesper Mørk, Maurice S. Skolnick, A. Mark Fox, and Ahsan Nazir, Light Scattering from Solid-State Quantum Emitters: Beyond the Atomic Picture, *Phys. Rev. Lett.* **123**, 167403 (2019).
- [68] Ben S. Humphries, Dale Green, Magnus O. Borgh, and Garth A. Jones, Phonon signatures in photon correlations (2023), [10.5281/zenodo.8325538](https://arxiv.org/abs/10.5281/zenodo.8325538).