

Frequency-domain stimulated and spontaneous light emission signals at molecular junctions

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Using a diagrammatic superoperator formalism we calculate optical signals at molecular junctions where a single molecule is coupled to two metal leads which are held at different chemical potentials. The molecule starts in a nonequilibrium steady state whereby it continuously exchanges electrons with the leads with a constant electron flux. Expressions for frequency domain optical signals measured in response to continuous laser fields are derived by expanding the molecular correlation functions in terms of its many-body states. The nonunitary evolution of molecular states is described by the quantum master equation. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4892108]

I. INTRODUCTION

Nonlinear spectroscopy has been a useful probe for studying the structure of molecules and dynamics in complex environments. This can provide valuable information at the nano scale by detecting various types of optical signals, for example, spontaneous and stimulated. Fluorescence has been used to detect and study single molecule dynamics^{1–3} which is governed by quantum effects and strongly influenced by the configuration of environment.

In this paper, we present a diagrammatic formulation of spontaneous⁴ and stimulated^{5,6} signals from a single molecule which is coupled to two current-carrying metal contacts. The interaction with the leads is treated nonperturbatively within the quantum master equation approach. This allows us to account for the nonunitary evolution of the molecule states in a nontrivial way. Electron transport in molecular junctions has been a very active area of research^{7–11} due to its fundamental importance in understanding nonequilibrium dynamics and many-body interaction effects on electron transfer and applications to molecular electronics. However the corresponding optical response is less understood. Tip enhanced spontaneous Raman scattering from a single molecule in a scanning tunneling microscopy has been demonstrated experimentally.¹²⁻¹⁵ On the theoretical front, current-induced fluorescence at molecular junctions has been studied using the nonequilibrium Green's function (NEGF)¹⁶ and many-body formulations.¹⁷ Spontaneous Raman scattering from a molecular junction has also been recently calculated using NEGF.^{18,19} Here we use a superoperator formalism which readily distinguishes between the Raman and fluorescence contributions to spontaneous light emission (SLE).

The optical signals from a molecular junction are fundamentally different from those in isolated molecule. In a current-carrying state^{18,19} the molecule is stochastically exchanging electrons with the leads. It therefore explores its various accessible charged (both cation and anion) states. Both neutral and charged states can emit light. This enables the spectroscopic study of the dynamics of molecular charged states and their correlations. Moreover, initially (just before the interaction with the radiation field) the molecule is in a nonequilibrium state and contains (nonequilibrium) populations of the neutral as well as the excited (charged) states and their coherences. These depend on the external bias in a nontrivial way. The time evolution is nonunitary and involves scattering between different charged states of the molecule. These pose a challenge to compute optical response of molecules at junctions.

Our approach here is based on Liouville space superoperator formulation.²⁰⁻²² We present diagrams for various processes that contribute to these signals. The diagrams are intuitive and the algebraic expressions for signals can be read directly from these diagrams, following the rules given in Sec. III of Ref. 20.

The superoperator formalism has several advantages over the Hilbert space formulation. The time evolution of the state vector (wavefunction) is the prime quantity of interest in the Hilbert space, while in the Liouville space formulation we follow the time evolution of the density matrix. This seemingly not-so-important difference between two approaches leads to significant simplification in the Liouville space description which provides a better intuitive physical picture. The time evolution of the density matrix requires evolving both the ket and the bra simultaneously, i.e., both the populations and coherences evolve together. This simultaneous evolution of the bra and the ket is readily described in real time in terms of the superoperator formulation. Both the equilibrium as well as nonequilibrium formulations can be treated on the same footing. In Hilbert space, the nonequilibrium systems are treated by defining the time evolution on Keldysh contour²³ in terms of an artificial time (the contour time), instead of the real (physical) time. Both the bra and the ket evolve forward on the contour sequentially. In real time, the bra evolves forward while the ket evolves backward. This renders it difficult to interpret various approximations made during the formulation, until the quantities are mapped onto real time, which is done at the end of the formulation.²⁴ Furthermore, in Liouville space, causal and non-causal (response and correlation)

functions appear naturally and have straightforward interpretations in terms of different combinations of Liouville space pathways. This allows us to develop the nonequilibrium formulation directly in terms of the response and correlation functions, starting from the microscopic picture. This is facilitated by the use of symmetric and antisymmetric (or "+" and "-") superoperators that also offers a convenient bookkeeping for time-ordering of various interactions.²¹ In Hilbert space, on the other hand, one first needs to compute the timeordered and anti-time ordered functions, and the causal functions are then obtained in terms of linear combinations of these functions only after the real-time mapping has been performed. The detail superoperator algebra, for both the fermion and the bosons, has been reviewed in Ref. 21. Here we adopt this formulation to compute optical signals from current carrying molecular junctions.

The signal in a junction depends on the nonequilibrium density matrix of the molecule and its time evolution which can be computed either using the NEGF²⁵ or quantum master equation (QME).²⁶ In NEGF, the density matrix of the molecule is renormalized with respect to the interactions with the leads and the signal must be computed self-consistently, making it difficult to distinguish between contributions coming from the negatively and positively charged molecular states. This information is however readily accessible by expansion in many-body space.²⁷ The present scheme combines the many-body expansion with the QME. The QME includes the molecule-lead interactions non-perturbatively and properly accounts for the dependence on the applied bias. It is more intuitive than the NEGF method since it does not require self-consistent calculation. In this approach, the computational burden is shifted to obtaining the many body states.

The paper is organized as follows. In Sec. II, we introduce the model Hamiltonian and discuss the diagrammatic method to compute the spontaneous signal. We present a scheme to combine the QME with the many-body expansion to compute the signal. In Sec. III we present results for the stimulated signal. We discuss corresponding diagrams and present the algebraic expressions for the signal. As a special case we look at pump-probe signal. Finally, we conclude in Sec. IV.

II. MODEL HAMILTONIAN

We consider a single molecule connected with two metallic leads held at different chemical potentials. After the molecule has reached a nonequilibrium steady state (NESS) with constant flux, it is optically excited by laser beams and subsequent frequency resolved stimulated and spontaneous signals are detected.

The entire system Hamiltonian is given as

$$H(t) = H_0 + H_{MF}(t) + H_{tun},$$
 (1)

where $H_0 = H_M + H_F + H_A + H_B$ represents the Hamiltonian for isolated molecule H_M , which describes electronic and vibrational degrees of freedom and need not be specified further at this stage, the relevant laser field modes H_F ,

$$H_F = \sum_s \hbar \omega_s a_s^{\dagger} a_s, \qquad (2)$$

where ω_s is the frequency corresponding to the radiation field mode, and the leads *A* and *B*:

$$H_{A,B} = \sum_{\nu \in A,B} \epsilon_{\nu} c_{\nu}^{\dagger} c_{\nu}, \qquad (3)$$

where ϵ_{ν} represents the ν th electron energy state of the leads. $c^{\dagger}(c)$ and $a^{\dagger}(a)$ denote single particle fermionic and bosonic creation (annihilation) operators, respectively. The last two terms in (1) represent molecule-field and molecule-lead coupling, respectively,

$$H_{MF}(t) = \sum_{s} \left(\hat{\mathcal{E}}_{s}(t) \hat{V}^{\dagger} + \hat{\mathcal{E}}_{s}^{\dagger}(t) \hat{V} \right), \tag{4}$$

$$H_{tun} = \sum_{\nu i} \left(T_{i\nu} c_{\nu}^{\dagger} c_{i} + T_{i\nu}^{*} c_{i}^{\dagger} c_{\nu} \right), \tag{5}$$

where $\hat{\mathcal{E}}_s(t) = E_s(r, t)\hat{a}_s(t)\exp(i\phi_s)$ represents annihilation operator of a photon mode of frequency ω_s with phase ϕ_s . $E_s(r, t)$ is the laser pulse envelope. \hat{V} is the dipole lowering operator which brings the molecule down from an excited state to a lower energy state. T_{iv} is the tunneling matrix element between the orbitals of the metallic lead and the molecule.

A. The Spontaneous light emission signal

In order to obtain a finite SLE signal, the state of the detected field mode must change from its vacuum state to some occupied state. Since field states are coupled to molecular states, energy conservation dictates that this can be done by de-exciting the molecule from higher to lower energy states. This requires action on the molecular density matrix by one molecule-field interaction from the left (ket) and one from the right (bra). Both interactions must bring the molecule from a higher to a lower energy state. These interactions are represented by arrows at time t and τ in the diagrams in Fig. 1. The molecular electronic excited states can be populated either by the laser excitation or transferring an electron between the leads and the molecule. Note that in the absence of laser field, the current induced signal is generated solely due to interaction with the leads. Current induced fluorescence was studied in Ref. 17 by treating the nonequilibrium evolution



FIG. 1. Loop diagrams representing the spontaneous emission signal (Eq. (7)) from a molecular junction. ω_1 is the incoming and ω_2 is the emitted photon frequency. Time increases from bottom up. Interaction at time *t* is chronologically the last while time ordering for all other interactions (τ, τ_1, τ_2) can be interchanged. The propagation along the contour is determined by the Hamiltonian, $H_M + H_A + H_B + H_{tun}$.

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perturbatively in the lead-molecule coupling. Here we consider signals induced by both the leads and the laser interactions. The interactions with the incoming fields are denoted by arrows at times τ_1 and τ_2 . Since the molecule is coupled to the leads it continuously makes transitions between various charged states and therefore the interactions at τ_1 and τ_2 may correspond to absorption or emission of a photon in the incoming mode. By considering all possible combinations of interactions at τ_1 and τ_2 , we obtain four diagrams shown in the figure. Note that the interaction at time t is the last interaction as it corresponds to the detection time. This interaction is with the ket of the density matrix. This is an arbitrary choice made in order to remove any ambiguity from the diagram rules. The signal is given by the real part of diagrams. Thus all diagrams complex conjugate to the ones shown in Fig. 1 will have the last interaction from the right (bra). Other interaction times τ , τ_1 , and τ_2 are not time-ordered. These interactions for various time orderings represent different Liouville space pathways to prepare the molecule in its excited state. For an isolated molecule with fixed charge and initially in the ground state, the signal is given by a single loop diagram (Fig. 1(d)).²⁰

Expressions for the SLE signal can be read directly from the diagrams in Fig. 1. This will be done using Liouville space superoperator notation^{21,28} which is briefly summarized below. A Hilbert space operator X which acts on a state vector $|S\rangle$ corresponds to two superoperators, the "left," X_L , and the "right," X_R , which act on Liouville vector state $|S, S'\rangle\rangle \equiv |S\rangle\langle S'|$. The two representations are related as

$$\begin{split} X_{L}|S, S'\rangle &\equiv X|S\rangle\langle S'| \\ X_{R}|S, S'\rangle &\equiv |S\rangle\langle S'|X. \end{split}$$
(6)

Thus the left and the right operators independently evolve the ket and the bra of the density matrix, respectively. We further introduce the symmetric and anti-symmetric combinations of superoperators $X_+ = X_L + X_R$ and $X_- = X_L$ $-X_R$, respectively. Thus a +(-) operation in Liouville space corresponds to an anticommutation (commutation) operation in Hilbert space, $X_+|S, S'\rangle \equiv \{X, |S\rangle\langle S'|\}$ and $X_-|S, S'\rangle\rangle \equiv [X, |S\rangle\langle S'|]$.

To lowest order in the incoming field modes the SLE signal can be expressed in terms of four correlation functions which correspond to the four diagrams in Fig. 1. The other factors are obtained using the diagram rules defined in Ref. 20,

$$\begin{split} S_{\rm sp}(\omega_{2};\omega_{1}) &= \frac{2}{\hbar^{4}} \Re \bigg\{ \int_{t_{0}}^{t} d\tau e^{i\omega_{2}(t-\tau)} \int_{t_{0}}^{t} d\tau_{1} \int_{t_{0}}^{t} d\tau_{2} \\ & \left[\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{L}^{\dagger}(\tau_{1}) V_{L}(\tau_{2}) \rangle \langle \hat{T} \mathcal{E}_{1L}(\tau_{1}) \mathcal{E}_{1L}^{\dagger}(\tau_{2}) \rangle \right. \\ & \left. + \langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{R}^{\dagger}(\tau_{1}) V_{R}(\tau_{2}) \rangle \langle \hat{T} \mathcal{E}_{1R}(\tau_{1}) \mathcal{E}_{1R}^{\dagger}(\tau_{2}) \rangle \right. \\ & \left. - \langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{R}^{\dagger}(\tau_{1}) V_{L}(\tau_{2}) \rangle \langle \hat{T} \mathcal{E}_{1L}(\tau_{1}) \mathcal{E}_{1L}^{\dagger}(\tau_{2}) \rangle \right. \\ & \left. - \langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{L}^{\dagger}(\tau_{1}) V_{R}(\tau_{2}) \rangle \langle \hat{T} \mathcal{E}_{1L}(\tau_{1}) \mathcal{E}_{1R}^{\dagger}(\tau_{2}) \rangle \right] \bigg\}, \end{split}$$

where ω_2 is the detected signal frequency and ω_1 is the incoming field frequency. Note that the evolution between two dipole operators in Eq. (7) is dressed by the molecule-leads interaction. Diagrams (1(a))–(1(c)) are possible since the molecule is being continuously excited between different charge states due to the interaction with the leads. The signal in Eq. (7) can be obtained from microscopic considerations as shown in Appendix A.

The loop diagrams in Fig. 1 represent the total SLE signal which contains both fluorescence and Raman contributions.²⁹ These diagrams are analogous to the Hilbert space formulation in terms of Keldysh contour. The diagrams in Fig. 1 are identical to the Keldysh loop if, instead of the physical time, one defines an artificial time on the loop. In that case, one first evolves the bra forward in time and then the ket in the backward time. The spontaneous Raman signal from a molecular junction has been recently calculated in Ref. 18 using the Keldysh formalism. That calculation is based on different diagrams. Here we obtain the full set of diagrams for SLE starting from the rate of change in the number of photons in the detected mode. Diagram (b) in Fig. 8 of Ref. 18 does not contribute to the optical signal, while diagrams (a) and (c) are incomplete contributions to our diagram (1 d). Moreover, the authors have only considered diagrams where the two incoming field modes are on two different branches of Keldysh contour. However we show that additional diagrams, where field modes are on the same branch (diagrams (a) and (b)), are equally important and should be taken into account. Note that in such processes (diagrams (a) and (b)), the two interactions with the incoming radiation fields do not create any population change. For example, the first interaction in Fig. 1(a) corresponds to de-excitation of the ket. This interaction alone does not create any population change but induces a coherence between the excited and the de-excited state. To change the population, we need another de-excitation from the bra side also, which is the case in diagrams (c) and (d). The strength of such contributions then depends on the probability of excited states being occupied and the ground (or de-excited state) being empty. The leads can populate (by transferring an electron) excited states and de-populate (by removing an electron) lower states, both the excited and the de-excited states have finite probabilities (these are non-equilibrium probabilities) and the signal depends on both probabilities.

B. Algebraic expressions for SLE signal based on ladder diagrams

Depending on the relative time-ordering of bra and ket interactions, each diagram in Fig. 1 may be further decomposed into six fully time-ordered ladder diagrams. In Appendix A, we present the ladder diagrams and outlined a scheme to compute the diagrams. The net SLE signal is

$$S_{\rm sp} = 2\Re(S^{(a)} + S^{(b)} - S^{(c)} - S^{(d)}),\tag{8}$$

where $S^{(a)}$ denotes the contribution from the first diagram in Fig. 1 and so on. The final result is

$$S^{(a)}(\omega_{2};\omega_{1}) = \frac{1}{\hbar^{4}} |E_{1}|^{2} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{2}) \left\{ V_{fg}^{*} \mathcal{G}_{eg;hp}(0) \left(V_{hq} V_{ar}^{*} \mathcal{G}_{qp;rb}(\omega_{1}) + V_{ra} V_{qf}^{*} \mathcal{G}_{qp;rb}(-\omega_{1}) \right) + V_{ge}^{*} \mathcal{G}_{gf;hp}(\omega_{2} - \omega_{1}) \left(V_{pq}^{*} V_{ra} \mathcal{G}_{hq;rb}(-\omega_{1}) + V_{rb}^{*} V_{hq} \mathcal{G}_{qp;ar}(\omega_{2}) \right) + V_{eg} \mathcal{G}_{gf;hp}(\omega_{1} + \omega_{2}) \left(V_{pq}^{*} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{1}) + V_{rb}^{*} V_{qh}^{*} \mathcal{G}_{qp;ar}(\omega_{2}) \right) \right\},$$
(9)

where $\rho_{ab} = \langle a | \hat{\rho} | b \rangle$ is the matrix element of the nonequilibrium density matrix between the many-body states $|a\rangle$ and $|b\rangle$, $V_{ab} = \langle a | \hat{V} | b \rangle$ is the transition dipole matrix element, and $\mathcal{G}_{ab;cd}(\omega) = i \langle \langle ab | (\omega I - i\mathcal{L})^{-1} | cd \rangle \rangle$ is the Liouville time-evolution, where \mathcal{L} is the Liouville operator. $|E_1|^2$ is the incoming field intensity.

The SLE expression in (9) is different from that for an isolated molecule. The dependence on the molecule-lead interaction and the external applied bias, which drives the molecule out of equilibrium, are implicit through the steady-state matrix element ρ_{ab} , the evolution $\mathcal{G}_{ab;cd}(\omega)$, and the sum over many-body states that includes neutral as well as the charged molecular states.

The contribution from the other three diagrams can be obtained similarly. We get,

$$S^{(b)}(\omega_{2};\omega_{1}) = \frac{1}{\hbar^{4}} |E_{1}|^{2} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{2}) \left\{ V_{fg}^{*} \mathcal{G}_{eg;hp}(0) \left(V_{pq}^{*} V_{br} \mathcal{G}_{hq;ar}(-\omega_{1}) + V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(\omega_{1}) \right) + V_{fg}^{*} \mathcal{G}_{eg;hp}(\omega_{2} - \omega_{1}) \left(V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(\omega_{2}) + V_{qp}^{*} V_{br} \mathcal{G}_{hq;ar}(-\omega_{1}) \right) + V_{gf} V_{pq}^{*} V_{rb}^{*} \mathcal{G}_{eg;hp}(\omega_{1} + \omega_{2}) \left(\mathcal{G}_{hq;ar}(\omega_{1}) + \mathcal{G}_{hq;ar}(\omega_{2}) \right) \right\},$$
(10)

$$S^{(c)}(\omega_{2};\omega_{1}) = \frac{1}{\hbar^{4}} |E_{1}|^{2} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{2})
\left\{ V_{fg}^{*} \mathcal{G}_{eg;hp}(0) \left(V_{pq}^{*} V_{ra} \mathcal{G}_{hq;rb}(-\omega_{1}) + V_{hq} V_{rb}^{*} \mathcal{G}_{qp;ar}(\omega_{1}) \right) \right]
+ V_{fg}^{*} \mathcal{G}_{eg;hp}(\omega_{2} - \omega_{1}) \left(V_{pq}^{*} V_{ra} \mathcal{G}_{hq;rb}(-\omega_{1}) + V_{hq} V_{rb}^{*} \mathcal{G}_{qp;ar}(\omega_{2}) \right)
+ V_{eg} V_{pq}^{*} V_{rb}^{*} \mathcal{G}_{gf;hp}(\omega_{1} + \omega_{2}) \left(\mathcal{G}_{hq;ar}(\omega_{1}) + \mathcal{G}_{hq;ar}(\omega_{2}) \right) \right\},$$
(11)

$$S^{(d)}(\omega_{2};\omega_{1}) = \frac{1}{\hbar^{4}} |E_{1}|^{2} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{2})
\left\{ V_{fg}^{*} \mathcal{G}_{eg;hp}(0) \left(V_{qh}^{*} V_{br} \mathcal{G}_{qp;ar}(-\omega_{1}) + V_{ar}^{*} V_{qp} \mathcal{G}_{hq;rb}(\omega_{1}) \right)
+ V_{ge} \mathcal{G}_{gf;hp}(\omega_{2} - \omega_{1}) \left(V_{pq}^{*} V_{br} \mathcal{G}_{hq;ar}(-\omega_{1}) + V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(\omega_{2}) \right)
+ V_{gf} \mathcal{G}_{eg;hp}(\omega_{1} + \omega_{2}) \left(V_{qp}^{*} V_{rb}^{*} \mathcal{G}_{qp;ar}(\omega_{2}) + V_{pq}^{*} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{1}) \right) \right\}.$$
(12)

In the following we describe how the steady state density matrix element ρ_{ab} and the evolution operator $\mathcal{G}(\omega)$ may be computed.

cording to the following equation in Liouville space:

$$\frac{\partial}{\partial t}|\rho\rangle\rangle = \mathcal{L}|\rho\rangle\rangle,$$
 (13)

where the Liouville operator is

$$\mathcal{L} = H_{M-} + \sum_{i} \left[2\alpha_{i}c_{iR}^{\dagger}c_{iL} + 2\beta_{i}c_{iL}^{\dagger}c_{iR} - \beta_{i}c_{iR}^{\dagger}c_{iR} - \beta$$

with $\alpha_i = \Gamma_l(1 - f_l(\epsilon_i)) + \Gamma_r(1 - f_r(\epsilon_i))$ and $\beta_i = \Gamma_l f_l(\epsilon_i) + \Gamma_r f_r(\epsilon_i)$ with $f_l(f_r)$ representing the Fermi functions for the left

C. Calculation of nonequilibrium density matrix and reduced evolution

We assume that the lead-molecule coupling is weak and the time-evolution may be described in terms of quantum master equation. The molecular density-matrix evolves ac-

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(right) lead. The Liouville operator connects the density matrix block for *n* number of electrons to the blocks with $n \pm 1$ number of electrons, it thus connects the many-body states of neutral molecule to excited states of the singly charged molecule. Equation (13) gives

$$\frac{\partial}{\partial t}\rho_{ab}(t) = -i\omega_{ab}\rho_{ab} + \sum_{MN}\sum_{i} \left\{ \left(2\alpha_{i}\langle a|c_{i}|M\rangle\langle N|c_{i}^{\dagger}|b\rangle + 2\beta_{i}\langle a|c_{i}^{\dagger}|M\rangle\langle N|c_{i}|b\rangle \right)\rho_{MN} - \left(\alpha_{i}\langle M|c_{i}^{\dagger}|N\rangle\langle N|c_{i}|b\rangle + \beta_{i}\langle M|c_{i}|N\rangle\langle N|c_{i}^{\dagger}|b\rangle \right)\rho_{aM} - \left(\alpha_{i}\langle a|c_{i}^{\dagger}|N\rangle\langle N|c_{i}|M\rangle + \beta_{i}\langle a|c_{i}|N\rangle\langle N|c_{i}^{\dagger}|M\rangle \right)\rho_{Mb} \right\}.$$
(15)

This equation can be written in terms of a vector equation, Eq. (13), in the basis of molecular many-body states. The steady-state is obtained from the solution of the above set of linear equations for $\dot{\rho} = 0$.

Matrix element of the evolution operator is given by,

$$\mathcal{G}_{ab;cd}(\omega) = i \sum_{\nu} \frac{\langle \langle ab | R_{\nu} \rangle \rangle \langle \langle L_{\nu} | cd \rangle \rangle}{\omega - i\zeta_{\nu}}, \tag{16}$$

where we have used the resolution of identity operator in terms of the left and right eigenvectors of the nonunitary operator \mathcal{L} . The index ν runs over all right eigenvalues ζ_{ν} of \mathcal{L} ,

$$\mathcal{L}|R_{\nu}\rangle\rangle = \zeta_{\nu}|R_{\nu}\rangle\rangle$$

$$\langle\langle L_{\nu}|\mathcal{L} = \zeta_{\nu}^{*}\langle\langle L_{\nu}|.$$
(17)

Equations (9)–(12) together with Eqs. (15) and (16) are main equations to compute SLE signal from junctions.

We can further simplify the SLE expressions if we assume that interaction with the leads only contributes to the life-time of the many-body states and does not destroy/create new states, that is, it does not create electronic excitations (this can be the case if the energy gaps between different electronic many-body states are much larger than the applied bias). In that case \mathcal{G} is diagonal, $\mathcal{G}_{ab;cd} = \mathcal{G}_{ab}\delta_{ac}\delta_{bd}$, where $\mathcal{G}_{ab} = \langle \langle ab | \mathcal{G} | ab \rangle \rangle$, and the signal is given by $S^{(d)}$ alone which further simplifies to the following expression:

$$S^{(d)}(\omega_{2};\omega_{1}) = \frac{1}{\hbar^{4}} |E_{1}|^{2} \sum_{abcde} \frac{\rho_{ab} V_{dc}}{\omega_{2} - \omega_{cd} + i\Gamma} \left[\frac{V_{be} V_{de}^{*} V_{ac}^{*}}{\omega_{ce} - i\Gamma} \right]$$
$$\times \left(\frac{1}{\omega_{1} - \omega_{cb} + i\Gamma} - \frac{1}{\omega_{1} - \omega_{ae} - i\Gamma} \right)$$
$$+ \frac{V_{ac}^{*}}{\omega_{2} - \omega_{1} - \omega_{ad} + i\Gamma}$$
$$\times \left(\frac{V_{de}^{*} V_{be}}{\omega_{1} + \omega_{ae} - i\Gamma} - \frac{V_{ed}^{*} V_{eb}}{\omega_{2} + \omega_{ae} + i\Gamma} \right)$$

$$-\frac{V_{eb}^{*}}{\omega_{1}+\omega_{2}-\omega_{ce}+i\Gamma}\left(\frac{V_{ae}^{*}V_{ed}}{\omega_{2}-\omega_{ae}+i\Gamma}+\frac{V_{ac}^{*}V_{ed}}{\omega_{1}-\omega_{cb}+i\Gamma}\right)\right],$$
(18)

where $\omega_{ab} = \omega_a - \omega_b$ is the energy difference between the many-body states, Γ represents the lifetime of excitation due to coupling with the leads. Here we have treated leads within the wide-band approximation and Γ contains contributions from both the left (*A*) and the right (*B*) leads, $\Gamma = \Gamma_A$ + Γ_B which is the same as the retarded (advanced) selfenergy that appears in the NEGF formulation. Here this selfenergy contribution appears due to the retarded evolution between successive interactions in presence of the interaction with the leads. Note that the signal implicitly depends on the applied bias through dependence on the nonequilibrium (steady-state) density matrix. The first term inside the square brackets in Eq. (18) represents fluorescence contribution while others contain Raman-like resonances of the type $\omega_1 \pm \omega_2 = \omega_{ab}$.

III. STIMULATED SIGNALS

We now turn to frequency-domain heterodyne-detected stimulated signal^{5,6,27} where, in addition to the leads, the molecule is coupled to four optical modes with complex field amplitudes that are defined as $\mathcal{E}(t) = \sum_{j=1}^{4} \mathcal{E}_{j}(e^{i\phi_{j}-i\omega_{j}t})$ + c.c. We assume as before that the fields are in coherent state. These four fields can be easily distinguished by the externally controlled phases ϕ_i and/or by their frequencies ω_i . Note that the signal in general depends on all possible combinations of the phases $\pm \phi_1 \pm \phi_2 \pm \phi_3 \pm \phi_4$ but the desired phase component can be separated out using phase cycling scheme which is also possible for single molecules, thanks to the current laser technology, and is demonstrated in recent experiment.³⁰ To derive the stimulated signal we consider ω_4 as the frequency of the detected signal and $\omega_1, \omega_2, \omega_3$ as the incoming field frequency and select a particular phase component corresponding to the combination $\phi = \phi_1 - \phi_2 + \phi_3$ $-\phi_4$. Since the molecule is in nonequilibrium steady state we must consider all possible interactions, i.e., either emission or absorption from the left (ket) and from the right (bra). To third order in the incoming field this leads to $2^3 = 8$ possible loop diagrams depicted in Fig. 2. Algebraic expression for each diagram can be written down in terms of the "left" and "right" superoperators, as was done in Sec. II. However these expressions can be combined together and expressed in a compact form in terms of the "+" and "-" superoperators.

$$S_{\text{stim}}(-\omega_{4};\omega_{3},-\omega_{2},\omega_{1}) = \frac{2}{\hbar^{4}} \Re \int_{t_{0}}^{t} d\tau_{3} \int_{t_{0}}^{t} d\tau_{2} \int_{t_{0}}^{t} d\tau_{1} \times e^{i\phi} \mathcal{E}_{4}^{*}(t) \mathcal{E}_{3}(\tau_{3}) \mathcal{E}_{2}^{*}(\tau_{2}) \mathcal{E}_{1}(\tau_{1}) \times \langle T V_{L}(t) V_{-}^{\dagger}(\tau_{3}) V_{-}(\tau_{2}) V_{-}^{\dagger}(\tau_{1}) \rangle,$$
(19)

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where $V_{-} = V_L - V_R$ and $V_{-}^{\dagger} = V_L^{\dagger} - V_R^{\dagger}$. Note that interactions at τ_1 , τ_2 , and τ_3 are not time-ordered. Moreover, because of the time translational invariance the energy conservation dictates that $\omega_1 - \omega_2 + \omega_3 - \omega_4 = 0$. The stimulated signal can be formally written as

$$S_{\text{stim}} = 2 \sum_{x} \Re(S_{\text{stim}}^{(x)}), \quad x = a, b, c, d, e, f, g, h,$$
 (20)

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where $S_{\text{stim}}^{(a)}$ is the contribution from the diagram in Fig. 2(a) and so on.

Following the procedure discussed in Sec. II, we can calculate this loop diagrams and express the signal in terms of sum over states. Here we give the expression for diagram (a) in Fig. 2. In Appendix B we present time-ordered ladder diagrams and corresponding expressions for diagrams (b)-(h) in Fig. 2,

$$S_{\text{stim}}^{(a)}(-\omega_{4};\omega_{3},-\omega_{2},\omega_{1}) = \frac{1}{\hbar^{4}} e^{i\phi} \mathcal{E}_{4}^{*} \mathcal{E}_{3} \mathcal{E}_{2}^{*} \mathcal{E}_{1} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{1}-\omega_{2}+\omega_{3}) \left\{ V_{ge}^{*} \mathcal{G}_{gf;hp}(\omega_{1}-\omega_{2}) \left(V_{hq} V_{ar}^{*} \mathcal{G}_{qp;rb}(\omega_{1}) + V_{qh}^{*} V_{ra} \mathcal{G}_{qp;rb}(-\omega_{2}) \right) + V_{eg} V_{qh}^{*} V_{ar}^{*} \mathcal{G}_{gf;hp}(\omega_{1}+\omega_{3}) \left(\mathcal{G}_{qp;rb}(\omega_{1}) + \mathcal{G}_{qp;rb}(\omega_{3}) \right) + V_{ge}^{*} \mathcal{G}_{gf;hp}(\omega_{3}-\omega_{2}) \left(V_{qh}^{*} V_{ra} \mathcal{G}_{qp;rb}(-\omega_{2}) + V_{hq} V_{ar}^{*} \mathcal{G}_{qp;rb}(\omega_{3}) \right) \right\}.$$
(21)

For an isolated molecule (in the absence of the leads) with fixed charge and initially in the ground state, the signal is given by the diagrams (a), (c), and (g).

A. Application to the pump-probe signal

We now present one particular type of stimulated emission signal known as the pump probe signal. It is one of the simplest kind of nonlinear optical techniques which involves two fields: the pump field with frequency ω_1 , phase ϕ_1 and the probe field with frequency ω_2 and phase ϕ_2 .

Similar to the SLE signal, we denote the interactions at time t and τ due to the detected mode (probe) and τ_1 and τ_2 due to incoming field modes (pump). The interaction at τ , τ_1 ,

and τ_2 represents both absorption and emission of a photon as in current carrying state the molecule has finite probability to stay at ground as well as in excited states. We note that the first four diagrams in Fig. 3 coincide with the SLE signal. The only difference being that these contributions to the signal are now also proportional to the probe radiation intensity $|E_2|^2$. The net signal is therefore written as

$$S_{\rm PP} = 2|E_2|^2 \Re(S^{(e)} - S^{(f)} + S^{(g)} - S^{(h)}) - 2|E_2|^2 S_{\rm sp}.$$
(22)

For the loop diagram (e) we have the following expression for the signal:

$$S^{(e)}(\omega_{2};\omega_{1}) = \frac{2}{\hbar^{4}} |E_{1}|^{2} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{2}) \{ V_{ge}^{*} \mathcal{G}_{gf;hp}(0) (V_{qh}^{*} V_{ra} \mathcal{G}_{qp;rb}(-\omega_{1}) + V_{ar}^{*} V_{hq} \mathcal{G}_{qp;rb}(\omega_{1})) + V_{eg} V_{qh}^{*} V_{ar}^{*} \mathcal{G}_{gf;hp}(\omega_{1} + \omega_{2}) (\mathcal{G}_{qp;rb}(\omega_{1}) + \mathcal{G}_{qp;rb}(\omega_{2})) + V_{ge}^{*} \mathcal{G}_{gf;hp}(\omega_{2} - \omega_{1}) (V_{hq} V_{ar}^{*} \mathcal{G}_{qp;rb}(\omega_{2}) + V_{qh}^{*} V_{ra} \mathcal{G}_{qp;rb}(-\omega_{1})) \}.$$

$$(23)$$

Similarly for the other three diagrams (f)-(h) we have the following expressions:

$$S^{(f)}(\omega_{2};\omega_{1}) = \frac{2}{\hbar^{4}} |E_{1}|^{2} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{2}) \{ V_{ge}^{*} \mathcal{G}_{gf;hp}(0) (V_{hq} V_{rb}^{*} \mathcal{G}_{qp;ar}(\omega_{1}) + V_{pq}^{*} V_{ar} \mathcal{G}_{hq;rb}(-\omega_{1})) + V_{eg} \mathcal{G}_{gf;hp}(\omega_{1} + \omega_{2}) (V_{qh}^{*} V_{rb}^{*} \mathcal{G}_{qp;ar}(\omega_{1}) + V_{pq}^{*} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{2})) + V_{fg}^{*} \mathcal{G}_{eg;hp}(\omega_{2} - \omega_{1}) (V_{qh}^{*} V_{ra} \mathcal{G}_{qp;rb}(-\omega_{1}) + V_{hq} V_{ar}^{*} \mathcal{G}_{qp;rb}(\omega_{2})) \},$$

$$S^{(g)}(\omega_{2};\omega_{1}) = \frac{2}{\hbar^{4}} |E_{1}|^{2} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{2}) \{ V_{ge}^{*} \mathcal{G}_{gf;hp}(0) (V_{qp} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{1}) + V_{qh}^{*} V_{br} \mathcal{G}_{qp;rc}(-\omega_{1})) + V_{gf} V_{qh}^{*} V_{ar}^{*} \mathcal{G}_{eg;hp}(\omega_{1} + \omega_{2}) (\mathcal{G}_{qp;rb}(\omega_{1}) + \mathcal{G}_{qp;rb}(\omega_{2})) + V_{ge}^{*} \mathcal{G}_{gf;hp}(\omega_{2} - \omega_{1}) (V_{qp} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{2}) + V_{qh}^{*} V_{br} \mathcal{G}_{qp;rc}(-\omega_{1})) \},$$

$$(25)$$

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$$S^{(h)}(\omega_{2};\omega_{1}) = \frac{2}{\hbar^{4}} |E_{1}|^{2} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{2}) \{ V_{ge}^{*} \mathcal{G}_{gf;hp}(0) (V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(\omega_{1}) + V_{pq}^{*} V_{br} \mathcal{G}_{hq;ar}(-\omega_{2})) + V_{fg}^{*} \mathcal{G}_{eg;hp}(\omega_{2} - \omega_{1}) (V_{qh}^{*} V_{br} \mathcal{G}_{qp;ar}(-\omega_{1}) + V_{qp} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{2})) + V_{gf}^{*} \mathcal{G}_{eg;hp}(\omega_{1} + \omega_{2}) (V_{qh}^{*} V_{rb}^{*} \mathcal{G}_{qp;ar}(\omega_{1}) + V_{pq}^{*} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{2})) \}.$$
(26)

Note that the pump-probe signal here is independent of the phase of the laser fields. Also note that the extra factor of 2 in Eq. (22) appears because for incoherent signal we have two possible phase combinations $\phi_1 - \phi_1 + \phi_2 - \phi_2$ and $-\phi_1 + \phi_1 + \phi_2 - \phi_2$.

IV. CONCLUSIONS

We have presented a diagrammatic approach in Liouville space to compute spontaneous and stimulated optical signals from a current carrying molecular junction. Signals are computed within the leading order perturbation in the molecule-electromagnetic field interaction. Diagrams are derived from the first principle and can be interpreted intuitively. The expressions for the signal are read directly from the diagrams and are expressed in terms of sum over molecule many-body states. These many-body states involve both neutral and charged (cation and anion) states of the molecule. The nonequilibrium evolution of the system can be accounted for by combining the diagrammatic approach with the Lindblad density matrix formulation. This allowed us to distinguish fluorescence and Raman-like signals in the spontaneous signal from junctions. This distinction is not obvious



FIG. 2. Loop diagrams for stimulated signal calculated to the third order of H_{MF-} . Interaction at time *t* is chronologically the last while time ordering for all other interactions (τ_1 , τ_2 , τ_3) can be interchanged. The propagation along the contour is determined by the Hamiltonian $H_M + H_A + H_B + H_{turn}$.



FIG. 3. Loop diagrams contribute to the pump-probe signal. Note that diagrams (a)-(d) are same as SLE in Fig. 1.

in NEGF approach. We have included the lead interaction non-perturbatively which introduces finite probability for the molecular charged state to change during the evolution between two field interactions. This makes it difficult to unambiguously distinguish signals from cation, anion, or neutral states of the molecule. Other measurements may be required for this identification.

Here we have focused only on the frequency resolved signals. The formulation can however be extended readily to study other types of optical signals, for example, timeresolved, which will be discussed elsewhere.

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APPENDIX A: DERIVATION OF EQS. (7)-(12)

In the main text we presented intuitive arguments to draw loop diagrams for the SLE signal that is used to obtain Eq. (7). Here we first present a short derivation of Eq. (7) without using loop diagrams and then show how these diagrams can be computed.

We start from a general expression of SLE. A detail microscopic derivation can be found in Refs. 20 and 27. In general, SLE signal in mode ω_2 can be written as

$$\begin{split} S(\omega_2) &= \frac{2}{\hbar^2} \Re \int_{t_0}^t d\tau e^{i\omega_2(t-\tau)} \langle \hat{T} V_L(t) V_R^{\dagger}(\tau) \rangle \\ &= \frac{2}{\hbar^2} \Re \int_{t_0}^t d\tau e^{i\omega_2(t-\tau)} \langle \hat{T} V_L(t) V_R^{\dagger}(\tau) e^{-\frac{i}{\hbar} \int_{t_0}^t d\tau_1 H_{MF^-}(\tau_1)} \rangle. \end{split}$$
(A1)

Here the trace is with respect to the interacting density matrix for the molecule+leads+incoming radiation field. Since the evolution is with respect to the interacting system, the charged state of the molecule is changed by the interactions between the leads and the optical transitions are induced by field interactions.

Equation (A1) is a general expression for SLE signal which has been used extensively in the literature.²⁸ The signal can be computed perturbatively in the incoming molecule-field coupling by expanding the time-ordered exponential in H_{MF-} . The leading order contribution comes from the second order in H_{MF} . This perturbative expansion can be mapped order-by-order onto a series of loop diagrams. At leading order, we can make the following substitution:

$$\begin{split} \left\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) \mathrm{e}^{-\frac{t}{\hbar} \int_{t_{0}}^{t} d\tau_{1} H_{MF^{-}}(\tau_{1})} \right\rangle \\ &= -\frac{1}{2\hbar^{2}} \int_{t_{0}}^{t} d\tau_{1} \\ &\times \int_{t_{0}}^{t} d\tau_{2} \langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) H_{MF^{-}}(\tau_{1}) H_{MF^{-}}(\tau_{2}) \rangle, \quad (A2) \end{split}$$

where the trace on the right-hand side is now with respect to the product density matrix of the molecule+lead and free radiation (incoming) field. The time evolution is with respect to the free field Hamiltonian and the molecule+lead Hamiltonian. These two Hamiltonians commute, which allows us to separate the two traces. Substituting $H_{MF-} =$ $(H_{MF})_L - (H_{MF})_R = \mathcal{E}_{2L}(t)V_L^{\dagger}(t) + \mathcal{E}_{2L}^{\dagger}(t)V_L(t) - V_R^{\dagger}(t)\mathcal{E}_{2R}(t)$ $- V_R(t)\mathcal{E}_{2R}^{\dagger}(t)$, the correlation function in Eq. (A2) decomposes into the following eight terms:

$$\begin{split} \left\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) H_{MF-}(\tau_{1}) H_{MF-}(\tau_{2}) \right\rangle \\ &= \left\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{L}^{\dagger}(\tau_{1}) V_{R}(\tau_{2}) \right\rangle \left\langle \hat{T} \mathcal{E}_{2L}(\tau_{1}) \mathcal{E}_{2R}^{\dagger}(\tau_{2}) \right\rangle \\ &+ \left\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{R}^{\dagger}(\tau_{1}) V_{L}(\tau_{2}) \right\rangle \left\langle \hat{T} \mathcal{E}_{2R}(\tau_{1}) \mathcal{E}_{2L}^{\dagger}(\tau_{2}) \right\rangle \\ &- \left\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{L}^{\dagger}(\tau_{1}) V_{R}(\tau_{2}) \right\rangle \left\langle \hat{T} \mathcal{E}_{2R}(\tau_{1}) \mathcal{E}_{2R}^{\dagger}(\tau_{2}) \right\rangle \\ &- \left\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{R}^{\dagger}(\tau_{1}) V_{R}(\tau_{2}) \right\rangle \left\langle \hat{T} \mathcal{E}_{2R}^{\dagger}(\tau_{1}) \mathcal{E}_{2R}^{\dagger}(\tau_{2}) \right\rangle \\ &+ \left\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{L}(\tau_{1}) V_{R}^{\dagger}(\tau_{2}) \right\rangle \left\langle \hat{T} \mathcal{E}_{2L}^{\dagger}(\tau_{1}) \mathcal{E}_{2R}(\tau_{2}) \right\rangle \\ &+ \left\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{R}(\tau_{1}) V_{L}^{\dagger}(\tau_{2}) \right\rangle \left\langle \hat{T} \mathcal{E}_{2L}^{\dagger}(\tau_{1}) \mathcal{E}_{2L}(\tau_{2}) \right\rangle \\ &- \left\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{R}(\tau_{1}) V_{R}^{\dagger}(\tau_{2}) \right\rangle \left\langle \hat{T} \mathcal{E}_{2R}^{\dagger}(\tau_{1}) \mathcal{E}_{2R}(\tau_{2}) \right\rangle \\ &- \left\langle \hat{T} V_{L}(t) V_{R}^{\dagger}(\tau) V_{R}(\tau_{1}) V_{R}^{\dagger}(\tau_{2}) \right\rangle \left\langle \hat{T} \mathcal{E}_{2R}^{\dagger}(\tau_{1}) \mathcal{E}_{2R}(\tau_{2}) \right\rangle, \tag{A3}$$

where the time evolution in the correlation functions for V's is described only in terms of the molecule+lead Hamiltonian. Note that the last four terms are identical to the first four if we interchange τ_1 and τ_2 (dummy) indices. Substituting it in Eq. (A2) and then in Eq. (A1) leads to Eq. (7).

1. Calculation of molecule correlation function appears in Eq. (7)

We next compute the molecule correlation functions that appear in Eq. (7). For this we need to consider various time orderings of interactions at times τ , τ_1 , and τ_2 depicted in Fig. 1. Thus each diagram in Fig. 1 splits into six fully time-ordered diagrams. Each representing a specific Liouville space pathways that contributes to the SLE signal. These diagrams are shown in Figs. 4 and 5.

Let us consider the first diagram (a1) in Fig. 4 for the specific time ordering $t > \tau > \tau_1 > \tau_2$. After the leads are traced out, we can formally write the corresponding correlation function as,

where $|\rho\rangle\rangle$ is the nonequilibrium steady state density matrix and the time-evolution operator $\mathcal{G}(t) = e^{\mathcal{L}t}$, where \mathcal{L} is the Liouvillian operator defined in the molecular space. Then we can write the expression for the signal from the diagram as

$$S^{(a1)}(\omega_{2};\omega_{1}) = \int_{t_{0}}^{t} d\tau \int_{t_{0}}^{\tau} d\tau_{1} \int_{t_{0}}^{\tau_{1}} d\tau_{2}$$

$$\times e^{i\omega_{2}(t-\tau)} \langle \langle I | V_{L}\mathcal{G}(t-\tau) V_{R}^{\dagger}\mathcal{G}(\tau-\tau_{1})$$

$$\times V_{L}^{\dagger}\mathcal{G}(\tau_{1}-\tau_{2}) V_{L} | \rho \rangle \rangle \langle \mathcal{E}_{1L}(\tau_{1}) \mathcal{E}_{1L}^{\dagger}(\tau_{2}) \rangle. \quad (A5)$$

Now taking the limit $t_0 \rightarrow -\infty$, using the correlation $\langle \mathcal{E}_{1L}(\tau_1)\mathcal{E}_{1L}^{\dagger}(\tau_2)\rangle = e^{-i\omega_1(\tau_1-\tau_2)}$ and making changes of time variables given as $\bar{t} = t - \tau$, $\tau - \tau_1 = t_1$ and $\tau_1 - \tau_2 = t_2$, we obtain

$$S^{(a1)}(\omega_2;\omega_1) = \int_0^\infty d\bar{t} \int_0^\infty dt_1 \int_0^\infty d\tau_2$$
$$\times e^{i\omega_2 \bar{t}} e^{-i\omega_1 t_2} \langle \langle I | V_L \mathcal{G}(\bar{t}) V_R^{\dagger} \mathcal{G}(t_1)$$
$$\times V_L^{\dagger} \mathcal{G}(t_2) V_L | \rho \rangle \rangle, \tag{A6}$$

which we can write as

.

$$S^{(a1)}(\omega_2;\omega_1) = \left\langle \left\langle I | V_L \mathcal{G}(\omega_2) V_R^{\dagger} \mathcal{G}(0) V_L^{\dagger} \mathcal{G}(-\omega_1) V_L | \rho \right\rangle \right\rangle,$$
(A7)

where $\mathcal{G}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \mathcal{G}(\omega) e^{-i\omega t}$. We next use the resolution of unity in Liouville space in terms of many-body states of the molecule,

$$\hat{I} = \sum_{MN} |MN\rangle\rangle\langle\langle MN|, \qquad (A8)$$

where vector $|MN\rangle$ is an operator $|M\rangle\langle N|$ in the Hilbert space. The steady state density matrix is

$$|\rho\rangle\rangle = \sum_{MN} \rho_{MN} |MN\rangle\rangle, \tag{A9}$$

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FIG. 4. Fully time-ordered ladder diagrams for SLE. Each of the four diagrams in Fig. 1 split into six ladder diagrams. Diagrams (a1)-(a6) and (b1)-(b6) corresponding to the diagram (a) and (b) in Fig. 1, respectively.

where $\rho_{MN} = \langle M | \hat{\rho} | N \rangle$ is the matrix element of the density matrix. Inserting Eqs. (A8) and (A9) in (A4), we get

$$S^{(a1)}(\omega_2;\omega_1) = \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} V_{fg}^* V_{qh}^* V_{ra} \mathcal{G}_{cd;ef}(\omega_2)$$
$$\times \mathcal{G}_{eg;hp}(0) \mathcal{G}_{qp;rb}(-\omega_1). \tag{A10}$$

Here $V_{ab} = \langle a | V | b \rangle$ and $\mathcal{G}_{ab;cd}(t) = \langle \langle ab | \mathcal{G}(t) | cd \rangle \rangle$. Similar expressions can be derived for all time-orderings for all the terms in Eq. (A3).

When the leads are absent, only the last term on the rhs of Eq. (7) contributes. The spontaneous signal is then represented by the single diagram of Fig. 1(d). For different time-orderings, this diagram splits into three diagrams shown

in Fig. 6. These diagrams have been discussed in detail in Ref. 20.

APPENDIX B: DERIVATION OF EQ. (19)

The stimulated signal expression for detected mode ω_4 is written as^{5,6,27}

$$S_{\text{stim}}(t) = \frac{2}{\hbar} \Im \left[\mathcal{E}_4^*(t) \left\langle T V_L(t) \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t d\tau H_{MF-}(\tau) \right\} \right\rangle \right].$$
(B1)

The trace here is with respect to the interacting density matrix of the molecule+lead and the time evolution for the operators is with respect to molecule+lead Hamiltonian. The



FIG. 5. Fully time-ordered diagrams for processes contributing to SLE. Diagrams (c1)-(c6) and (d1)-(d6) corresponding to the diagrams (c) and (d) in Fig. 1, respectively.

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FIG. 6. Ladder diagrams representing spontaneous signal from an isolated molecule. The left two diagrams correspond to the fluorescence while the right most diagram is for the Raman scattering. $|g_N\rangle$ is the ground state with N electrons, $|g'_N\rangle$ is the vibrationally excited electronic ground state, and $|e_N\rangle$ is the electronic excited state of N-electrons. The time increases from the bottom up.



fields are in coherent state. We now expand H_{MF-} to the third order in the field-matter interaction and for the phase component $\phi = \phi_1 - \phi_2 + \phi_3 - \phi_4$ we obtain the following expression for the signal:

$$S_{\text{stim}}(t) = \frac{2}{3\hbar^4} \int_{t_0}^t d\tau_3 \int_{t_0}^t d\tau_2 \int_{t_0}^t d\tau_1$$

× $\Re \left(e^{i\phi} \left[\mathcal{E}_4^*(t) \mathcal{E}_3(\tau_3) \mathcal{E}_2^*(\tau_2) \mathcal{E}_1(\tau_1) \right] \right]$
× $\left\langle T V_L(t) V_-^{\dagger}(\tau_3) V_-(\tau_2) V_-^{\dagger}(\tau_1) \right\rangle$
+ $\mathcal{E}_4^*(t) \mathcal{E}_3(\tau_1) \mathcal{E}_2^*(\tau_3) \mathcal{E}_1(\tau_2)$
× $\left\langle T V_L(t) V_-(\tau_3) V_-^{\dagger}(\tau_2) V_-^{\dagger}(\tau_1) \right\rangle$





FIG. 7. Fully time-ordered ladder diagrams for processes contributing to stimulated signal from a molecular junction. Diagrams (a1)-(a6), (b1)-(b6), (c1)-(c6), and (d1)-(d6) correspond to the diagrams (a), (b), (c), and (d) in Fig. 2, respectively.

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$$+ \mathcal{E}_{4}^{*}(t)\mathcal{E}_{3}(\tau_{2})\mathcal{E}_{2}^{*}(\tau_{1})\mathcal{E}_{1}(\tau_{3})$$
$$\times \langle TV_{L}(t)V_{-}^{\dagger}(\tau_{3})V_{-}^{\dagger}(\tau_{2})V_{-}(\tau_{1})\rangle]),$$

where $\mathcal{E}_i(t) = \mathcal{E}_i e^{-i\omega_i t}$, i = 1, 2, 3, 4. Under permutation of the time variables τ_1 , τ_2 , τ_3 one can easily show that second and third terms are the same as the first term which cancels the prefactor 3 in the denominator and obtain Eq. (19).

1. Ladder diagrams corresponding to Fig. 2 and algebraic expressions for stimulated signal

Here we present all the time-ordered diagrams of Figs. 7 and 8 for stimulated emission signal corresponding to the loop diagrams given in Fig. 2.

In the main text we have given the expression for $S_{\text{stim}}^{(a)}$. Here we write down the expression for other diagrams in Fig. 2 with the help of time-ordered ladder diagrams in Figs. 7 and 8,

$$S_{\text{stim}}^{(b)}(-\omega_{4};\omega_{3},-\omega_{2},\omega_{1}) = -\frac{1}{\hbar^{4}}e^{i\phi}\mathcal{E}_{4}^{*}\mathcal{E}_{3}\mathcal{E}_{2}^{*}\mathcal{E}_{1}\sum_{abcde}\sum_{fghpqr}\rho_{ab}V_{dc}\mathcal{G}_{cd;ef}(\omega_{1}-\omega_{2}+\omega_{3})$$

$$\left\{V_{ge}^{*}\mathcal{G}_{gf;hp}(\omega_{1}-\omega_{2})\left(V_{hq}V_{rb}^{*}\mathcal{G}_{qp;ar}(\omega_{1})+V_{pq}^{*}V_{ra}\mathcal{G}_{hq;rb}(-\omega_{2})\right)\right.$$

$$\left.+V_{eg}\mathcal{G}_{gf;hp}(\omega_{1}+\omega_{3})\left(V_{qh}^{*}V_{rb}^{*}\mathcal{G}_{qp;ar}(\omega_{1})+V_{pq}^{*}V_{ar}^{*}\mathcal{G}_{hq;rb}(\omega_{3})\right)\right.$$

$$\left.+V_{fg}^{*}\mathcal{G}_{eg;hp}(\omega_{3}-\omega_{2})\left(V_{qh}^{*}V_{ra}\mathcal{G}_{qp;rb}(-\omega_{2})+V_{hq}V_{ar}^{*}\mathcal{G}_{qp;rb}(\omega_{3})\right)\right\},\tag{B2}$$

4

$$S_{\text{stim}}^{(c)}(-\omega_{4};\omega_{3},-\omega_{2},\omega_{1}) = -\frac{1}{\hbar^{4}}e^{i\phi}\mathcal{E}_{4}^{*}\mathcal{E}_{3}\mathcal{E}_{2}^{*}\mathcal{E}_{1}\sum_{abcde}\sum_{fghpqr}\rho_{ab}V_{dc}\mathcal{G}_{cd;ef}(\omega_{1}-\omega_{2}+\omega_{3})$$

$$\left\{V_{ge}^{*}\mathcal{G}_{gf;hp}(\omega_{1}-\omega_{2})\left(V_{ar}^{*}V_{qp}\mathcal{G}_{hq;rb}(\omega_{1})+V_{qh}^{*}V_{br}\mathcal{G}_{qp;ar}(-\omega_{2})\right)\right.$$

$$\left.+V_{gf}V_{qh}^{*}V_{ar}^{*}\mathcal{G}_{eg;hp}(\omega_{1}+\omega_{3})\left(\mathcal{G}_{qp;rb}(\omega_{1})+\mathcal{G}_{qp;rb}(\omega_{3})\right)\right.$$

$$\left.+V_{ge}^{*}\mathcal{G}_{gf;hp}(\omega_{3}-\omega_{2})\left(V_{qp}V_{ar}^{*}\mathcal{G}_{hq;rb}(\omega_{3})+V_{qh}^{*}V_{br}\mathcal{G}_{qp;ar}(-\omega_{2})\right)\right\},\tag{B3}$$

$$S_{\text{stim}}^{(d)}(-\omega_{4};\omega_{3},-\omega_{2},\omega_{1}) = \frac{1}{\hbar^{4}} e^{i\phi} \mathcal{E}_{4}^{*} \mathcal{E}_{3} \mathcal{E}_{2}^{*} \mathcal{E}_{1} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{1}-\omega_{2}+\omega_{3})$$

$$\left\{ V_{ge}^{*} \mathcal{G}_{gf;hp}(\omega_{1}-\omega_{2}) \left(V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(\omega_{1}) + V_{pq}^{*} V_{br} \mathcal{G}_{hq;ar}(-\omega_{2}) \right) + V_{gf} \mathcal{G}_{eg;hp}(\omega_{1}+\omega_{3}) \left(V_{qh}^{*} V_{rb}^{*} \mathcal{G}_{qp;ar}(\omega_{1}) + V_{pq}^{*} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{3}) \right) + V_{fg}^{*} \mathcal{G}_{eg;hp}(\omega_{3}-\omega_{2}) \left(V_{qh}^{*} V_{br} \mathcal{G}_{qp;ar}(-\omega_{2}) + V_{qp} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{3}) \right) \right\}, \tag{B4}$$

$$S_{\text{stim}}^{(e)}(-\omega_{4};\omega_{3},-\omega_{2},\omega_{1}) = -\frac{1}{\hbar^{4}}e^{i\phi}\mathcal{E}_{4}^{*}\mathcal{E}_{3}\mathcal{E}_{2}^{*}\mathcal{E}_{1}\sum_{abcde}\sum_{fghpqr}\rho_{ab}V_{dc}\mathcal{G}_{cd;ef}(\omega_{1}-\omega_{2}+\omega_{3})$$

$$\left\{V_{fg}^{*}\mathcal{G}_{eg;hp}(\omega_{1}-\omega_{2})\left(V_{hq}V_{ar}^{*}\mathcal{G}_{qp;rb}(\omega_{1})+V_{qh}^{*}V_{ra}\mathcal{G}_{qp;rb}(-\omega_{2})\right)\right.$$

$$\left.+V_{eg}\mathcal{G}_{gf;hp}(\omega_{1}+\omega_{3})\left(V_{pq}^{*}V_{ar}^{*}\mathcal{G}_{hq;rb}(\omega_{1})+V_{qh}^{*}V_{rb}^{*}\mathcal{G}_{qp;ar}(\omega_{3})\right)\right.$$

$$\left.+V_{ge}^{*}\mathcal{G}_{gf;hp}(\omega_{3}-\omega_{2})\left(V_{pq}^{*}V_{ra}\mathcal{G}_{hq;rb}(-\omega_{2})+V_{hq}V_{rb}^{*}\mathcal{G}_{qp;ar}(\omega_{3})\right)\right\},\tag{B5}$$



FIG. 8. Fully time-ordered ladder diagrams for processes contributing to stimulated signal from a molecular junction. Diagrams (e1)-(e6), (f1)-(f6), (g1)-(g6), and (h1)-(h6) corresponding to the diagrams (e), (f), (g), and (h) in Fig. 2, respectively.

$$S_{\text{stim}}^{(f)}(-\omega_{4};\omega_{3},-\omega_{2},\omega_{1}) = \frac{1}{\hbar^{4}} e^{i\phi} \mathcal{E}_{4}^{*} \mathcal{E}_{3} \mathcal{E}_{2}^{*} \mathcal{E}_{1} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{1}-\omega_{2}+\omega_{3}) \\ \left\{ V_{fg}^{*} \mathcal{G}_{eg;hp}(\omega_{1}-\omega_{2}) (V_{hq} V_{rb}^{*} \mathcal{G}_{qp;ar}(\omega_{1}) + V_{pq}^{*} V_{ra} \mathcal{G}_{hq;rb}(-\omega_{2}) \right) \\ + V_{eg} V_{pq}^{*} V_{rb}^{*} \mathcal{G}_{gf;hp}(\omega_{1}+\omega_{3}) (\mathcal{G}_{hq;ar}(\omega_{1})+\mathcal{G}_{hq;ar}(\omega_{3})) \\ + V_{fg}^{*} \mathcal{G}_{eg;hp}(\omega_{3}-\omega_{2}) (V_{pq}^{*} V_{ra} \mathcal{G}_{hq;rb}(-\omega_{2})+V_{hq} V_{rb}^{*} \mathcal{G}_{qp;ar}(\omega_{3})) \right\}, \quad (B6)$$

$$S_{\text{stim}}^{(g)}(-\omega_{4};\omega_{3},-\omega_{2},\omega_{1}) = \frac{1}{\hbar^{4}} e^{i\phi} \mathcal{E}_{4}^{*} \mathcal{E}_{3} \mathcal{E}_{2}^{*} \mathcal{E}_{1} \sum_{abcde} \sum_{fghpqr} \rho_{ab} V_{dc} \mathcal{G}_{cd;ef}(\omega_{1}-\omega_{2}+\omega_{3}) \\ \left\{ V_{fg}^{*} \mathcal{G}_{eg;hp}(\omega_{1}-\omega_{2}) (V_{qp} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{1})+V_{qh}^{*} V_{rb}^{*} \mathcal{G}_{qp;ar}(-\omega_{2})) \right. \\ \left. + V_{gf} \mathcal{G}_{eg;hp}(\omega_{1}-\omega_{2}) (V_{pq} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{1})+V_{qh}^{*} V_{rb}^{*} \mathcal{G}_{qp;ar}(-\omega_{2})) \\ \left. + V_{gf} \mathcal{G}_{eg;hp}(\omega_{3}-\omega_{2}) (V_{pq}^{*} V_{ar}^{*} \mathcal{G}_{hq;rb}(\omega_{1})+V_{qh}^{*} V_{rb}^{*} \mathcal{G}_{hq;ar}(-\omega_{2})) \right. \\ \left. + V_{gf} \mathcal{G}_{eg;hp}(\omega_{3}-\omega_{2}) (V_{pq}^{*} V_{rb}^{*} \mathcal{G}_{hq;ar}(-\omega_{2})+V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(\omega_{3})) \right. \\ \left. + V_{gf}^{*} \mathcal{G}_{eg;hp}(\omega_{1}-\omega_{2}) (V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(-\omega_{2})+V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(-\omega_{2})) \right. \\ \left. + V_{gf} V_{pq}^{*} V_{rb}^{*} \mathcal{G}_{eg;hp}(\omega_{1}-\omega_{2}) (V_{pq} V_{rb}^{*} \mathcal{G}_{hq;ar}(\omega_{1})+V_{pq}^{*} V_{br} \mathcal{G}_{hq;ar}(-\omega_{2})) \right. \\ \left. + V_{gf} V_{pq}^{*} V_{rb}^{*} \mathcal{G}_{eg;hp}(\omega_{1}+\omega_{3}) (\mathcal{G}_{hq;ar}(\omega_{1})+\mathcal{G}_{hq;ar}(\omega_{3})) \right. \\ \left. + V_{gf}^{*} \mathcal{G}_{eg;hp}(\omega_{3}-\omega_{2}) (V_{pq}^{*} V_{rb}^{*} \mathcal{G}_{hq;ar}(-\omega_{2})+V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(\omega_{3})) \right. \\ \left. + V_{fg}^{*} \mathcal{G}_{eg;hp}(\omega_{3}-\omega_{2}) (V_{pq}^{*} V_{rb}^{*} \mathcal{G}_{hq;ar}(-\omega_{2})+V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(\omega_{3})) \right. \\ \left. + V_{gf}^{*} \mathcal{G}_{eg;hp}(\omega_{3}-\omega_{2}) (V_{pq}^{*} V_{rb}^{*} \mathcal{G}_{hg;ar}(-\omega_{2})+V_{qp} V_{rb}^{*} \mathcal{G}_{hq;ar}(\omega_{3})) \right. \\ \left. + V_{gf}^{*} \mathcal{G}_{eg;hp}(\omega_{3}-\omega_{2}) (V_{pq}^{*}$$

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2. Stimulated signal for diagonal $\mathcal{G}(\omega)$

As discussed while calculating SLE signal that if the interaction with the leads does not create any electronic

excitations and contribute only to the life-time of the many body states, then \mathcal{G} is diagonal and the stimulated signal is given by diagrams (a), (c), and (g) in Fig. 2. The expression for the corresponding diagrams is given in the following:

$$S_{\text{stim}}^{(a)} = \frac{1}{\hbar^4} e^{i\phi} \mathcal{E}_4^* \mathcal{E}_3 \mathcal{E}_2^* \mathcal{E}_1 \sum_{abcde} \frac{\rho_{ab} V_{be}}{\omega_1 - \omega_2 + \omega_3 - \omega_{eb} + i\Gamma} \left\{ V_{dc} V_{de}^* V_{ac} \left[\frac{1}{(\omega_1 - \omega_2 - \omega_{db} + i\Gamma)(\omega_1 - \omega_{cb} + i\Gamma)} + \frac{1}{(\omega_3 - \omega_2 - \omega_{db} + i\Gamma)(\omega_3 - \omega_{cb} + i\Gamma)} \right] + \frac{V_{ed} V_{cd}^* V_{ac}^*}{\omega_1 + \omega_3 - \omega_{db} + i\Gamma} \left[\frac{1}{\omega_1 - \omega_{cb} + i\Gamma} + \frac{1}{\omega_3 - \omega_{cb} + i\Gamma} \right] + \frac{V_{de}^* V_{cd}^* V_{ac}}{\omega_2 - \omega_{bc} - i\Gamma} \left[\frac{1}{\omega_1 - \omega_2 - \omega_{db} + i\Gamma} + \frac{1}{\omega_3 - \omega_2 - \omega_{db} + i\Gamma} \right] \right\},$$
(B9)

$$S_{\text{stim}}^{(c)} = -\frac{1}{\hbar^4} e^{i\phi} \mathcal{E}_4^* \mathcal{E}_3 \mathcal{E}_2^* \mathcal{E}_1 \sum_{abcde} \frac{\rho_{ab} V_{dc} V_{bd} V_{ec}^* V_{ae}^*}{\omega_1 - \omega_2 + \omega_3 - \omega_{eb} + i\Gamma} \left\{ \frac{1}{\omega_1 - \omega_2 - \omega_{ed} + i\Gamma} \left(\frac{1}{\omega_1 - \omega_{eb} + i\Gamma} - \frac{1}{\omega_2 - \omega_{da} - i\Gamma} \right) + \frac{1}{\omega_1 + \omega_3 - \omega_{eb} + i\Gamma} \left(\frac{1}{\omega_1 - \omega_{eb} + i\Gamma} + \frac{1}{\omega_3 - \omega_{eb} + i\Gamma} \right) + \frac{1}{\omega_3 - \omega_2 - \omega_{ed} + i\Gamma} \right\} \times \left(\frac{1}{\omega_3 - \omega_{eb} + i\Gamma} - \frac{1}{\omega_2 - \omega_{da} - i\Gamma} \right) \right\},$$
(B10)

$$S_{\text{stim}}^{(g)} = \frac{1}{\hbar^4} e^{i\phi} \mathcal{E}_4^* \mathcal{E}_3 \mathcal{E}_2^* \mathcal{E}_1 \sum_{abcde} \frac{\rho_{ab} V_{dc} V_{ac}^*}{\omega_1 - \omega_2 + \omega_3 - \omega_{eb} + i\Gamma} \left\{ \frac{V_{de}^* V_{be}}{\omega_1 - \omega_2 - \omega_{ca} + i\Gamma} \left(\frac{1}{\omega_1 - \omega_{cb} + i\Gamma} - \frac{1}{\omega_2 - \omega_{ea} - i\Gamma} \right) + \frac{V_{ed} V_{eb}^*}{\omega_3 + \omega_1 - \omega_{ca} + i\Gamma} \left(\frac{1}{\omega_1 - \omega_{cb} + i\Gamma} + \frac{1}{\omega_3 - \omega_{ae} + i\Gamma} \right) + \frac{1}{\omega_3 - \omega_2 - \omega_{ad} + i\Gamma} \left(\frac{V_{ed} V_{eb}^*}{\omega_3 - \omega_{ac} + i\Gamma} - \frac{V_{de}^* V_{be}}{\omega_2 - \omega_{ac} - i\Gamma} \right) \right\}.$$
(B11)

- ¹W. E. Moerner and L. Orrit, Science **283**, 1670 (1999).
- ²W. E. Moerner and L. Kador, Phys. Rev. Lett. 62, 2535 (1989).
- ³D. Brinks, R. Hinder, E. M. H. P. van Dijk, F. D. Stefani, J. B. Nieder, J. Hernando, and N. F. van Hulst, R. Soc. Chem. **43**, 2476 (2014).
- ⁴M. D. Levenson, Phys. Today **30**, 44 (1977).
- ⁵S. Rahav and S. Mukamel, PNAS **107**, 4825 (2010).
- ⁶S. Rahav, O. Roslyak, and S. Mukamel, J. Chem. Phys. **131**, 194510 (2009).
- ⁷S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, 1997).
- ⁸Y. H. Kwok, H. Xie, C. Y. Yam, X. Zheng, and G. H. Chen, J. Chem. Phys. 139, 224111 (2013); X. Zheng, F. Wang, C. Y. Yam, Y. Mo, and G. H. Chen, Phys. Rev. B 75, 195127 (2007).
- ⁹J. Rammer, *Quantum Transport Theory* (Westview Press, USA, 2004).
- ¹⁰S. Ballmann, R. Härtle, P. B. Coto, M. Elbing, M. Mayor, M. R. Bryce, M. Thoss, and H. B. Weber, Phys. Rev. Lett. **109**, 056801 (2012).
- ¹¹U. Harbola, M. Esposito, and S. Mukamel, Phys. Rev. B 74, 235309 (2006).
- ¹²R. Zhang, Y. Zhang, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang, and J. G. Hou, Nature (London) **498**, 82 (2013).
- ¹³X. H. Qiu, G. V. Nazin, and W. Ho, Science **299**, 542 (2003).
- ¹⁴J. H. Tian, B. Liu, X. Li, Z.-L. Yang, B. Ren, S.-T. Wu, N. Tao, and Z.-Q. Tian, J. Am. Chem. Soc. **128**, 14748 (2006).
- ¹⁵D. R. Ward, N. J. Halas, J. W. Ciszek, J. M. Tour, Y. Wu, P. Nordlander, and D. Natelson, Nano Lett. 8, 919 (2008).
- ¹⁶M. Galperin and A. Nitzan, Phys. Rev. Lett. **95**, 206802 (2005).

- ¹⁷U. Harbola, J. B. Maddox, and S. Mukamel, Phys. Rev. B **73**, 075211 (2006).
- ¹⁸M. Galperin, M. A. Ratner, and A. Nitzan, J. Chem. Phys. **130**, 144109 (2009).
- ¹⁹M. Galperin, M. A. Ratner, and A. Nitzan, Nano Lett. 9, 758–762 (2009); M. Galperin and A. Nitzan, J. Phys. Chem. Lett. 2, 2110–2113 (2011); Phys. Chem. Chem. Phys. 14, 9421 (2012); A. J. White, S. Tretiak, and M. Galperin, Nano Lett. 14, 699–703 (2014).
- ²⁰C. A. Marx, U. Harbola, and S. Mukamel, Phys. Rev. A 77, 022110 (2008).
- ²¹U. Harbola and S. Mukamel, Phys. Rep. **465**, 191 (2008).
- ²²S. Mukamel, Phys. Rev. A **71**, 024503 (2005).
- ²³L. V. Keldysh, Sov. Phys. JETP **20**, 1018 (1965).
- ²⁴J.-S. Wang, B. K. Agarwalla, H. Li, and J. Thingna, Front. Phys. 1, (2013).
- ²⁵H. Haug and A. P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors* (Springer-Verlag, Berlin, Heidelberg, 2008).
- ²⁶G. Lindblad, Commun. Math. Phys. 48, 119 (1976).
- ²⁷S. Rahav and S. Mukamel, J. Chem. Phys. **133**, 244106 (2010).
- ²⁸S. Mukamel, Principles of Nonlinear Optical Spectroscopy (Oxford University Press, Oxford, 1995).
- ²⁹E. O. Potma and S. Mukamel, in *Coherent Raman Scattering Microscopy*, edited by J.-X. Cheng and X. S. Xie (Taylor and Francis Group, 2013), Chap. 1.
- ³⁰D. Brinks, F. D. Stefani, F. Kulzer, R. Hildner, T. H. Taminiau, Y. Avlasevich, K. Müllen, and N. F. van Hulst, Nature (London) 465, 905 (2010).