Long-Lived Quasistationary Coherences in a V-type System Driven by Incoherent Light

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We present a theoretical study of noise-induced quantum coherences in a model three-level V-type system interacting with incoherent radiation, an important prototype for a wide range of physical systems ranging from trapped ions to biomolecules and quantum dots. By solving the quantum optical equations of motion, we obtain *analytic* expressions for the noise-induced coherences and show that they exhibit an oscillating behavior in the limit of large excited level spacing Δ ($\Delta/\gamma \gg 1$, where γ is the radiative decay width). Most remarkably, we find that in the opposite limit of small level spacing $\Delta/\gamma \ll 1$, appropriate for large molecules, (a) the coherences can survive for an extremely long time $\tau = (2/\gamma)(\Delta/\gamma)^{-2}$ before eventually decaying to zero, and (b) coherences at short times can be substantial. We further show that the long-lived coherences can survive environmental relaxation and decoherence, suggesting implications to the design of quantum heat engines and to incoherent light excitation of biological systems.

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The dynamics of atomic and molecular systems interacting with noisy electromagnetic fields (such as black body radiation) is a recurring theme of interest in physics, chemistry, and biology. In particular, the possibility of generating long-lived quantum mechanical coherence via the interaction of multilevel atomic and molecular systems with incoherent light has recently attracted much interest [1–4]. Apart from their fundamental importance, such noise-induced coherences have a wide range of proposed applications, ranging from enhancing the efficiency of photovoltaic devices [1] to lasers without inversion [3] and to the design of artificial light-harvesting antenna complexes [2]. The noise-induced coherences are created via quantum (Fano) interference of the transition amplitudes leading to the same final state—processes similar to those giving rise to well-known coherent optical phenomena such as coherent population trapping [5], electromagnetically induced transparency [6], vacuum-induced coherence [7–9], and coherent control [10].

Previous theoretical studies have explored the properties of noise-induced coherences in atomic Λ- and V-type systems [3,11–14] and suggested their role in enhancing the efficiency of photosynthetic energy transfer in light-harvesting antenna complexes [2]. However, this work focused on the analysis of steady-state properties [1–3,12] and paid little attention to the time evolution of the coherences. In an earlier contribution, Hegerfeldt and Plenio [13] considered the dynamics of a three-level atomic ion pumped by incoherent radiation and focused on the nature of the emitted light. They demonstrated that in the limit of large excited-state splitting the intensity correlation function exhibits quantum beat oscillations due to noise-induced coherences, and in the opposite limit the coherences last longer, leading to extended dark periods in the emitted light. However, no closed analytic expressions were derived for the noise-induced coherences, so their time scale and the influence of various system parameters (such as the excited level splitting, and the radiative decay rates) remained unexplored, making it difficult to appreciate and to experimentally observe these coherences in real atomic and molecular systems.

In this Letter, we focus on the dynamical properties of the V-type system, a minimal "building block" for quantum heat engines based on Fano interference [2], crucial to understanding the phenomena of incoherent light excitation in visual phototransduction and solar light harvesting. Our analysis is based on a quantum optical master equation of a non-Lindblad type [3,11] that treats all density matrix elements (state populations and coherences) on an equal footing. This treatment goes beyond the traditional secular approximation, which underlies the standard rate equation formalism for incoherent light excitation of molecular systems [15] but breaks down for nearly degenerate states of the V-type system [13,15], leading to a more complex master equation in which populations and coherences are inextricably coupled. We find analytic solutions to this equation in two opposite limits and show that the populations remain positive at all times, thereby demonstrating the existence of positive-definite solutions of a non-Lindblad-type master equation. Our analytic results show that when the energy splitting Δ between the two upper levels of the V-type system is large compared to the radiative decay widths γ, the off-diagonal elements of the density matrix exhibit coherent oscillations that decay on the time scale $\tau_s = 1/\gamma$ (hereafter we set $\hbar = 1$). We further show that in the limit of small energy splitting between excited-state levels ($\Delta \ll \gamma$), (a) short-time coherences are significant, and (b) the coherence between the

upper energy levels survives on a time scale $\tau_{\text{long}} = (2/\gamma)(\Delta/\gamma)^{-2}$ that by far exceeds any other dynamical time scale in the problem (including that of spontaneous decay), even in the presence of decoherence and relaxation. This remarkable result suggests that coherent dynamics in V-type molecular systems can survive for very long times, with immediate implications for the variety of applications cited above.

To elucidate the time dynamics of the populations and coherences, we solve the Born-Markov quantum optical master equation [16] in the energy basis

$$\dot{\rho}_{ii} = -(r_i + \gamma_i + \Gamma_i)\rho_{ii} + r_i\rho_{cc} - p(\sqrt{r_a r_b} + \sqrt{\gamma_a\gamma_b})\rho^R_{ab},$$
$$\dot{\rho}_{ab} = -\frac{1}{2}(r_a + r_b + \gamma_a + \gamma_b + 2\gamma_d)\rho_{ab} - \mathrm{i}\rho_{ab}\Delta + \frac{p}{2}\sqrt{r_a r_b}(2\rho_{cc} - \rho_{aa} - \rho_{bb}) - \frac{p}{2}\sqrt{\gamma_a\gamma_b}(\rho_{aa} + \rho_{bb}), \quad (1)$$

where $\rho_{ab} = \rho^R_{ab} + \mathrm{i}\rho^I_{ab}$, γ_i is the radiative width of level $|i\rangle$, $i = a, b$ [see Fig. 1(a)], r_i is the incoherent pumping rate, and $p = \boldsymbol{\mu}_{ac}\cdot\boldsymbol{\mu}_{bc}/(\mu_{ac}\mu_{bc})$ quantifies the angle between the $c \to a$ and $c \to b$ transition dipole moments (below we focus on the case $p = 1$, as justified in the Supplemental Material [17]). In Eq. (1), Γ_i are the (phenomenological) relaxation rates, and γ_d is the decoherence rate. For a molecule in the absence of an external environment, $\Gamma_i = \gamma_d = 0$. Following previous theoretical work [3], we adopt $r_a = r_b = r$, $\gamma_a = \gamma_b = \gamma$. This assumption greatly simplifies the analytical solution of Eq. (1) while retaining the essential physics of the problem [23]. We note that in deriving Eq. (1), we do not make the secular approximation, which neglects the elements of the relaxation tensor R_{ijkl} [15] with $\omega_{ij} \neq \omega_{kl}$, where ω_{ij} is the energy gap $\epsilon_i - \epsilon_j$ between eigenstates $|i\rangle$ and $|j\rangle$. This procedure is commonly justified by noting that the oscillatory factors $e^{\mathrm{i}(\omega_{ij}-\omega_{kl})t}$ multiplying R_{ijkl} average to zero if the time scale of interest is much longer than the system evolution time, $1/\omega_{ij}$. The secular approximation breaks down for a V-type system where $\omega_{ab} = \Delta > 0$ can be arbitrarily small. However, the inclusion of nonsecular terms means that Eq. (1) is no longer of the Lindblad type [16], and can therefore have spurious solutions where state populations $\rho_{ii}(t)$ can take unphysical negative values [24]. The use of non-Lindblad-type master equations to describe open quantum systems has been the subject of ongoing debate [4]. Fortunately, as shown here, the existence of positive solutions is guaranteed for a V-type system subject to initial conditions appropriate to weak-field incoherent excitation.

The solution of Eq. (1) can be represented as $\rho_{aa}(t) = -a/a_0 + \sum_i \tilde{c}_i e^{\lambda_i t}$, where λ_i are the roots of the cubic polynomial $\lambda^3 + a_2\lambda^2 + a_1\lambda + a_0 = 0$, and $\tilde{c}_i$ are time-independent coefficients determined from initial conditions appropriate to incoherent excitation from the ground state, $[\rho_{ij}(0) = 0,\ \rho_{cc}(0) = 1]$ (all results below are derived in the Supplemental Material [17]). The *exact* time dynamics of the coherence between the excited-state levels (hereafter referred to as simply "coherence") is $\rho^R_{ab}(t) = -(1/p(r+\gamma))\sum_i \tilde{c}_i(3r + \gamma + \lambda_i)e^{\lambda_i t}$. The behavior of the coherences in a V-type system is thus determined by the values of the roots, λ_i. Two important physical regions can be identified: $\Delta/\gamma \gg 1$ (one real and two complex conjugate λ_i), and $\Delta/\gamma \ll 1$ (real λ_i).

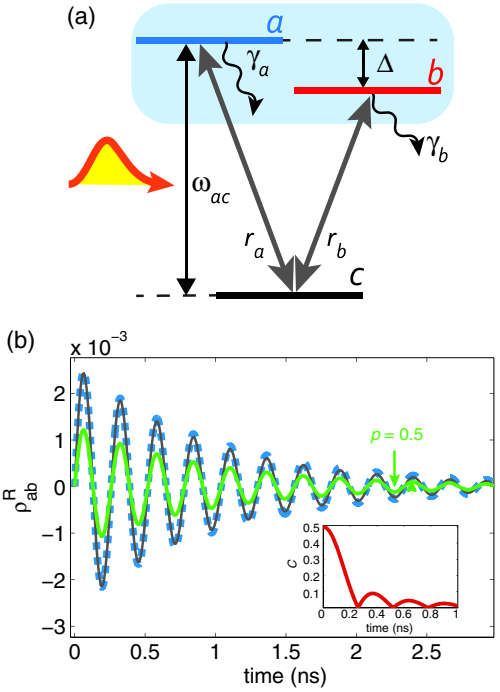

FIG. 1 (color online). (a) The energy level structure of the V-type system. The shaded area represents the effects of environment-induced relaxation and decoherence on the excited states a and b with $\Delta = \epsilon_a - \epsilon_b$. The real part of the two-photon coherence $\rho^R_{ab}(t)$ (b) and the ratio $\mathcal{C} = |\rho_{ab}|/(\rho_{aa} + \rho_{bb})$ (inset). Full lines—exact result (numerical calculations), dashed lines—analytical result obtained in this work in the $\Delta/\gamma \gg 1$ limit ($\gamma/2\pi = 1$ GHz, $\Delta/\gamma = 24$). The incoherent pumping rate $r/\gamma = \bar{n} = 0.063$, where $\bar{n} = 1/[e^{\hbar\omega_{ac}/k_BT} - 1]$ is the thermal occupation number ($k_BT = 0.5$ eV for sunlight), and $\omega_{ac} = 1.41$ eV. Results for $p = 1/2$ are also shown [green (light grey) line].

Consider first the limit of large excited-state splitting, $\Delta/\gamma \gg 1$, applicable to weak-field ($r/\gamma \ll 1$) incoherent excitation [25,26] of small- to medium-sized molecules with typical excited-state lifetimes of 1–10 ns and the density of states of less than 1 state in $\gamma \sim 0.005$–0.05 cm^{-1}. Under these conditions, the roots of the cubic equation are $\lambda_1 = -\gamma$, $\lambda_{2,3} = -\gamma \pm \mathrm{i}\Delta$, and the upper-state population and the real part of the coherence take the form

$$\rho_{aa}(t) = (r/\gamma)[1 - e^{-\gamma t}], \quad (2)$$

$$\rho_{ab}^{R}(t) = (r/\Delta)e^{-\gamma t}\sin(\Delta t) \quad (\Delta/\gamma \gg 1), \tag{3}$$

with the imaginary part of the coherence $\rho_{ab}^{I} = (r/\Delta)e^{-\gamma t}[\cos(\Delta t) - 1]$. Figure 1(b) confirms that the analytic result, Eq. (2), is in excellent agreement with the exact time evolution of $\rho_{ab}^{R}(t)$ obtained by numerical integration of Eq. (1), here for $\Delta/\gamma = 24$. The coherence exhibits damped oscillations with frequency Δ and decays to zero on the time scale $\tau_s = 1/\gamma$; i.e., the decoherence time scale is given here by the radiative lifetime of the excited-state levels, $\tau_s = 1/\gamma$. On short time scales ($t \ll \tau_s$), spontaneous decay can be neglected, and the decoherence time scale, quantified by the ratio $\mathcal{C} = |\rho_{ab}|/(\rho_{aa} + \rho_{bb})$ [26,27], decreases as $1/|\Delta t|$ [27]. This dependence reflects the linear growth of the excited-state population [Eq. (2) yields $\rho_{aa} = rt$ in the limit $t \ll 1/\gamma$], while the coherences are bounded by r/Δ. The inset of Fig. 1(b) illustrates the slow decrease of $\mathcal{C}(t)$, which is consistent with our previous results obtained independently via a different theoretical approach [26–28]. However, Eqs. (2) and (3) are required for longer time scales. As shown in Fig. 1(b), reducing p leads to a decrease of the coherence without affecting the overall time dynamics.

In the opposite limit $\Delta/\gamma \ll 1$, which applies to the incoherent excitation of a V-type system with very closely spaced upper levels (e.g., a polyatomic molecule like anthracene has $\Delta/\gamma \sim 10^{-7}$ [29]), the roots of the cubic equation are given by $\lambda_1 = -2\gamma$, $\lambda_2 = -\gamma$, and $\lambda_3 = -\frac{1}{2}\gamma(\Delta/\gamma)^2$. For the upper-state population and the real part of the coherence we find in the weak pump limit $r/\gamma \ll 1$ ($r/\gamma \sim 10^{-9}$ for sunlight illumination [25])

$$\rho_{aa}(t) = (r/2\gamma)[2 - e^{-2\gamma t} - e^{-(1/2)\gamma(\Delta/\gamma)^2 t}], \tag{4}$$

$$\rho_{ab}^{R}(t) = (r/2\gamma)[e^{-(\gamma/2)(\Delta/\gamma)^2 t} - e^{-2\gamma t}], \tag{5}$$

whereas the imaginary part of the coherence, $\rho_{ab}^{I} = (r\Delta/2\gamma^2)[2e^{-\gamma t} - e^{-2\gamma t} - e^{-(1/2)\gamma(\Delta/\gamma)^2 t}]$, is smaller by the factor $(\Delta/\gamma) \ll 1$. We observe that in the $\Delta/\gamma \to 0$ limit, the time scale for the decay of the first exponent in Eq. (5), $\tau_{\text{long}} = (2/\gamma)(\Delta/\gamma)^{-2}$ approaches infinity. Thus, Eq. (5) establishes the existence of two widely disparate time scales in coherence dynamics: At shorter times ($t \sim 1/\gamma$), the first exponent on the right-hand side is close to unity, so the coherence grows from zero to a quasi-steady-state value $r/2\gamma$. At $t \gg 1/\gamma$, but still short compared to τ_{long}, the coherence remains constant, before eventually decaying to zero at $t > \tau_{\text{long}}$. These coherences, physically similar to those previously described [30,31], result from observing weakly coupled system-radiation field states in the system basis.

To illustrate this behavior, we provide a log plot in Fig. 2 of the time variation of the population $\rho_{aa}(t)$ and of the coherence ρ_{ab}^{R} for $\Delta = 10^{-7}$ eV, in the $\Delta/\gamma \ll 1$ limit. The extremely long survival time of the quasistationary coherence is apparent: for the given parameters, it survives for as long as 10 μs, which is $\sim 10^4$ times longer than the excited states' radiative lifetime. This is a consequence of the continuous pumping and the resultant establishment of a quasisteady state. In the limit of $\Delta \to 0$, the time scale for the existence of the quasistationary coherence approaches infinity, underscoring the crucial role of the excited-state level splitting Δ in determining the noise-induced coherence dynamics. Setting $\Delta = 0$ in Eq. (5) produces a nonzero steady-state value of the coherence $\rho_{ab}^{R}(\infty) = r/2\gamma$, in agreement with prior $\Delta = 0$ results [3]. However, for any $\Delta > 0$ the coherences have a finite lifetime $\tau_{\text{long}} = (2/\gamma)(\Delta/\gamma)^{-2}$. Maximizing the lifetime of the coherences is proposed to be beneficial, e.g., to the design of quantum heat engines based on Fano interference [1,2], and our analysis suggests the benefit of using as small a Δ as possible. As shown in Fig. 2, changing p from 1 to 1/2 causes the coherence to decrease and shortens its lifetime.

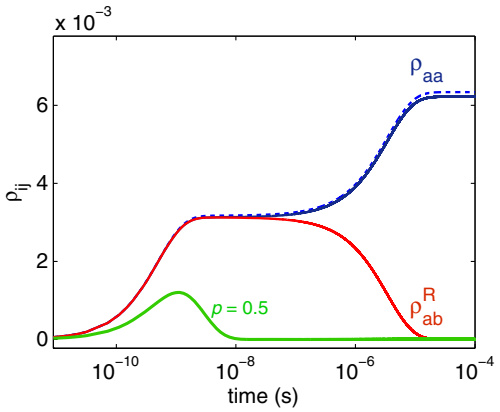

FIG. 2 (color online). Excited-state population and coherence dynamics in the $\Delta/\gamma \ll 1$ limit ($\Delta/\gamma = 0.024$, $\gamma/2\pi = 1$ GHz, $r/\gamma = 0.1\bar{n}$). Exact results (full line), analytic results (dashed line), results for $p = 1/2$ [green (light grey) line].

Both the analytical prediction, Eq. (5), and the numerical results for $p = 1$ establish that the time dependence of excited-state populations closely follows that of the coherences up until $t = \tau_s$, thereby implying significant short-time coherence effects, with $\mathcal{C}(t) = 1/2$. We emphasize that this behavior is drastically different from the $1/|t\Delta|$ decay of the coherence-to-population ratio in the limit $\Delta/\gamma \gg 1$ shown in the inset of Fig. 1(b). This indicates that very closely spaced energy levels maintain coherence on a much longer time scale than levels separated by an energy gap that is large compared to their natural linewidth. Finally, we note that in both small-Δ and large-Δ regimes, the populations $\rho_{ii}(t)$ remain positive at all times in the $r/\gamma \ll 1$ limit.

Effects of relaxation and decoherence.—Thus far we have considered an isolated V-type system. However, the excited states of a system within a condensed-phase environment (e.g., a molecule in a liquid) are subject to

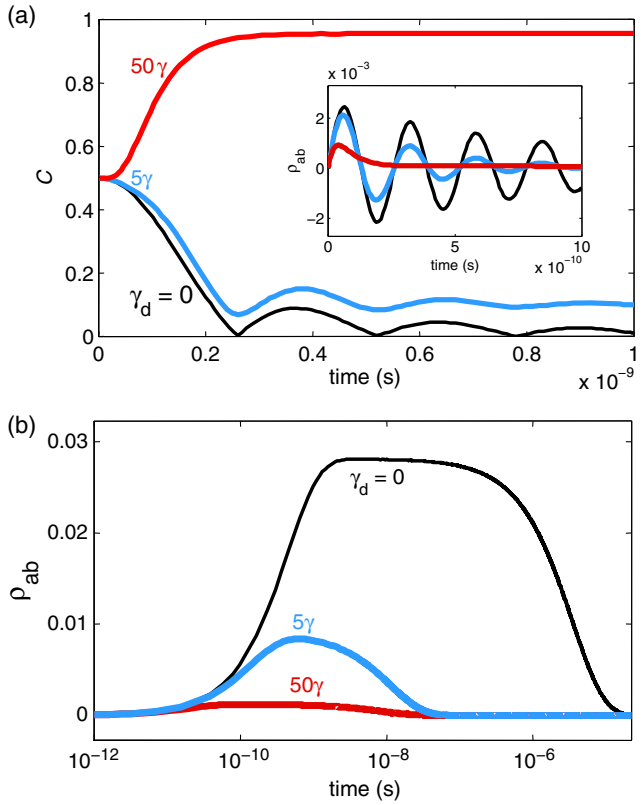

FIG. 3 (color online). Effects of environmental relaxation and decoherence on V-type system dynamics: (a) The $\mathcal{C}$ ratio and the real part of the coherence (inset) as a function of time for $\Delta/\gamma = 24$ and $\gamma_d/\gamma = 0$, 5, 50. The decoherence rates γ_d are shown next to each curve. (b) The real part of the coherence for $\Delta/\gamma = 0.024$ and $\gamma_d/\gamma = 0$, 5, 50. The imaginary part of the coherence is negligible compared to the real part.

relaxation and decoherence. To model these effects, we consider nonzero Γ and γ_d in Eq. (1), and modify the equations to include relaxation to an auxiliary level $|d\rangle$. Figure 3(a) illustrates the effect of environmental relaxation and decoherence in the large-Δ/γ regime using the $\mathcal{C}$ ratio, which quantifies the amount of coherences relative to populations. We observe that for moderate decoherence ($\gamma_d = 5\gamma$) the ratio displays periodic oscillations superimposed on a slowly decaying background. This time dependence is similar to that observed in the absence of relaxation and decoherence; however, the asymptotic value of $\mathcal{C}$ does not decay to zero due to a finite steady-state value of $|\rho_{ab}|$ (not shown).

The origin of this counterintuitive behavior can be understood by noting that relaxation prevents the excited-state population from accumulating by causing decay to the auxiliary level $|d\rangle$. While the coherences are also suppressed by environmental decoherence, this effect is not as significant as relaxation-induced suppression of excited-state populations. As a result, the populations can no longer outgrow the coherences and the value of $\mathcal{C}$ saturates at a steady state. As shown in the inset of Fig. 3(a), the value of the decoherence rate γ_d has a major effect on the dynamics in the $\Delta/\gamma \gg 1$ regime, suppressing the coherent oscillations. Already for $\gamma_d = 5\gamma$, the oscillations are damped on the time scale $\tau_d = 1/\gamma_d$, i.e., much sooner than in the absence of environment ($\tau_s = 1/\gamma$), indicating that in the regime $\gamma_d \gg \gamma$, the decoherence time scale is set by the environment-induced decoherence, rather than spontaneous decay.

Figure 3(b) shows that relaxation and decoherence lead to a suppression of the quasistationary coherences in the $\Delta/\gamma \ll 1$ regime, and cause a decrease in the intermediate "plateau" values reached at $t \gg 1/\gamma$. In addition, the time of reaching the plateau decreases with increasing γ_d, indicating that in the $\gamma_d \gg \gamma$ regime, the dynamics are governed by a time scale $\tau_d = 1/\gamma_d$. Nevertheless, the coherences are still substantial in magnitude, and the $\mathcal{C}$ ratio (not shown) remains close to unity over a large time interval even in the presence of relaxation and decoherence [17].

To begin to explore the applicability of these results to real molecules, we solved the quantum optical master equation for a multilevel analog of the V-type system [17]. The multilevel excited-state coherences were found to qualitatively follow the behavior observed in Figs. 1 to 3, and the coherences to persist relative to the populations. The V-type system thus provides insight into multilevel dynamics, a consequence of the weak intensity of the incoherent light and the absence of direct light-induced coupling between the excited states [17]. Such V-type systems can be explored experimentally by incoherent excitation of single trapped ions [13] or Rydberg atoms [27] and observing the signatures of noise-induced coherences in time-resolved fluorescence signals.

Theoretical work on atomic systems [8,11] and quantum dots [3] has shown that the key condition for the generation of noise-induced coherences—the existence of nonorthogonal transition dipole moments ($p \neq 0$)—requires two closely spaced excited levels with the same values of total angular momentum J' and its space-fixed projection M'. The optimal conditions of $p = 1$ can be realized, e.g., for the closely spaced Rydberg states [27], or excited vibrational states of polyatomic molecules with the same J' and M' (see the Supplemental Material [17]).

In summary, we have presented a theoretical analysis of noise-induced coherences in a V-type molecular system interacting with incoherent radiation, a basic model for a wide array of excitation processes in atomic, molecular, and solid-state systems [32]. This work demonstrates that, contrary to expectation, incoherent light excitation can generate long-lived quasistationary coherences that can survive environment-induced decoherence, and display considerable coherence at short time. As a consequence, these results strongly motivate examination of their role in biological processes, such as cis-trans photoisomerization of retinal [33] (the first step in vision) or photosynthetic energy transfer.

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Note added in proof.—A related V-type system model has just been developed [32].

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[1] M. O. Scully, K. R. Chapin, K. E. Dorfman, M. B. Kim, and A. Svidzinsky, Proc. Natl. Acad. Sci. U.S.A. **108**, 15097 (2011).
[2] K. E. Dorfman, D. V. Voronine, S. Mukamel, and M. O. Scully, Proc. Natl. Acad. Sci. U.S.A. **110**, 2746 (2013).
[3] V. V. Kozlov, Y. Rostovtsev, and M. O. Scully, Phys. Rev. A **74**, 063829 (2006).
[4] C. Creatore, M. A. Parker, S. Emmott, and A. W. Chin, Phys. Rev. Lett. **111**, 253601 (2013).
[5] H. R. Gray, R. M. Whitley, and C. R. Stroud, Jr., Opt. Lett. **3**, 218 (1978); J. Vanier, Appl. Phys. B **81**, 421 (2005).
[6] S. E. Harris, Phys. Today **50**, No. 7, 36 (1997).
[7] G. S. Agarwal, *Quantum Optics* (Cambridge University Press, Cambridge, 2012), Chap. 17.
[8] G. S. Agarwal and A. K. Patnaik, Phys. Rev. A **63**, 043805 (2001).
[9] E. Paspalakis, S.-Q. Gong, and P. L. Knight, Opt. Commun. **152**, 293 (1998).
[10] M. Shapiro and P. Brumer, *Quantum Control of Molecular Processes* (Wiley-VCH, Weinheim, 2012).
[11] M. Fleischhauer, C. H. Keitel, M. O. Scully, and C. Su, Opt. Commun. **87**, 109 (1992).
[12] B.-Q. Ou, L.-M. Liang, and C.-Z. Li, Opt. Commun. **281**, 4940 (2008).
[13] G. C. Hegerfeldt and M. B. Plenio, Phys. Rev. A **47**, 2186 (1993).
[14] T. P. Altenmüller, Z. Phys. D **34**, 157 (1995).
[15] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Atom-Photon Interactions: Basic Processes and Applications* (Wiley-VCH, Weinheim, 2004), Chap. IV.B.4.
[16] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Clarendon Press, Oxford, 2006), Chap. 3.4.
[17] See the Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.113.113601, which includes Refs. [18–22], for the derivation and analytic solution of the equations of motion, calculations on multilevel systems, and a discussion regarding the orientation of transition dipole moments in molecules.
[18] M. O. Scully and M. S. Zubairy, *Quantum Optics* (Cambridge University Press, Cambridge, 1997).
[19] A. K. Patnaik and G. S. Agarwal, Phys. Rev. A **59**, 3015 (1999).
[20] R. Loudon, *The Quantum Theory of Light*, 3rd ed. (Oxford University Press, Oxford, 2000), Chap. 2.
[21] T. V. Tscherbul and P. Brumer (to be published).
[22] G. Herzberg, *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (van Nostrand, New York, 1966), Chap. II.
[23] We verified by the explicit numerical solution of Eq. (1) that the density matrix dynamics obtained for $r_a \neq r_b$ is very similar to that observed for $r_a = r_b$ provided that the pumping rates are within a factor of 2 of one another.
[24] A. Suárez, R. Silbey, and I. Oppenheim, J. Chem. Phys. **97**, 5101 (1992).
[25] K. Hoki and P. Brumer, Procedia Chem. **3**, 122 (2011).
[26] Z. S. Sadeq and P. Brumer, J. Chem. Phys. **140**, 074104 (2014).
[27] T. V. Tscherbul and P. Brumer, Phys. Rev. A **89**, 013423 (2014).
[28] X.-P. Jiang and P. Brumer, J. Chem. Phys. **94**, 5833 (1991); Chem. Phys. Lett. **180**, 222 (1991).
[29] J. Jortner and R. S. Berry, J. Chem. Phys. **48**, 2757 (1968).
[30] L. A. Pachón and P. Brumer, Phys. Rev. A **87**, 022106 (2013).
[31] L. A. Pachón and P. Brumer, J. Math. Phys. (N.Y.) **55**, 012103 (2014).
[32] J. Olsina, A. G. Dijkstra, C. Wang, and J. Cao, arXiv:1408.5385.
[33] T. V. Tscherbul and P. Brumer, J. Phys. Chem. A **118**, 3100 (2014).