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Collapses and revivals of polarization and radiation intensity induced by strong exciton-vibron coupling

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Recently, systems with strong coupling between electronic and vibrational degrees of freedom have attracted a great deal of attention. In this work, we consider the transient dynamics of the system consisting of strongly coupled vibrons and excitons driven by an external monochromatic field. We show that, under coherent pumping, polarization of excitons exhibits complex quantum dynamics which can be divided into three stages. In the first stage, exciton oscillations at its eigenfrequency relax due to the transition of excitation to a set of shifted Fock states of vibrons. We demonstrate that these shifted Fock states play the role of an effective reservoir for the excited exciton state. The time of relaxation to this reservoir depends on exciton-vibron coupling. In the second stage, excitation transits from the reservoir of the vibronic shifted states to electronic degrees of freedom. As a result, revival of oscillations at exciton eigenfrequency appears. Thus, the dynamics of molecular polarization exhibit collapses and revivals. At the final stage, these collapses and revivals dissipate and polarization exhibits the Rayleigh response at the frequency of the external field. Discovered collapses and revivals manifest in the radiation spectrum as a multiple splitting of the spectral line near the exciton transition frequency.

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I. INTRODUCTION

The interaction between electronic and nuclear vibrational degrees of freedom has been investigated for almost a hundred years since the discovery of inelastic Raman scattering in molecules [1] and Brillouin scattering in solids [2]. This interaction is at the origin of many phenomena discovered from that time, including coherent Raman scattering [3–6], Raman and Brillouin lasers [7–9], optomechanics [10–12], polariton chemistry [13,14], and room-temperature vibron-mediated Bose-Einstein condensation [15,16].

The first description of phenomena associated with this interaction was based on the formalism of absorption and emission of quanta of nuclear vibrations, e.g., acoustical or optical phonons. These absorption and emission processes take place during interaction of the incident field with the electronic degrees of freedom [3,17], which parametrically interact with nuclear vibrational degrees of freedom. Developments of theory of open quantum system [18–21] and solid-state theory [22–24] enabled us to gain a more deep understanding of these phenomena. Namely, in the case when the external field interacts with electronic degrees of freedom only (which takes place for Raman-active molecules), the energy of the dipole moment excited by the coherent field results in a shift of nuclei from their equilibrium positions and their subsequent oscillations [25]. Such interaction between electronic and nuclear degrees of freedom can be described by the Fröhlich [22–24] or Holstein-Tavis [13,14,26,27] Hamiltonian. The latter describes the effective shift of the transition frequency of the electronic degree of freedom proportional to the amplitude (generally, depending on time) of nuclear vibrations [25]. This interaction Hamiltonian allowed us to describe spontaneous Raman scattering [25], Raman lasers [28], surface-enhanced Raman scattering (SERS) [29] and formation of third-order nonlinear susceptibility produced by nuclear vibrations [28].

Recently, the systems with strong coupling between electronic degrees of freedom, e.g., exciton, and nuclei vibration degrees of freedom, e.g., optical phonons or vibrons, have been actively investigated [30–32]. The interaction between excitons and vibrons can be described by the Fröhlich constant g of interaction [25,28,33] or, alternatively, Huang-Rhys factor $\alpha = g/\omega_{\mathrm{v}}$ [13,14,26,27]. The large value of the Huang-Rhys factor, $\alpha \simeq 10$, is achieved in organic materials for high-frequency vibrational modes [30–32].

To take into account dissipation processes which inevitably are present in any real molecules, modern theories describe the dynamics of coupled electronic and nuclear degrees of freedom excited by external field in terms of master equation for the density matrix [34]. When reservoir degrees of freedom are eliminated in the Born-Markov approximation, such a master equation has the Lindblad form [35,36]. Besides Hermitian interactions, it takes into account dissipation processes. Generally, to correctly describes the dynamics of open quantum system with the strong coupling between subsystems, it is necessary to find eigenstates of the interacting subsystems [37,38] and then consider relaxation-induced transition between these eigenstates. This approach is called global approach to the master equation for the density matrix [37,38]. It is applied when the distances between eigenstates are larger than the dissipation rates [39] which is fulfilled at least in the case of strong interaction between subsystems of an open quantum system [37]. In the opposite case one can use the local approach which treats relaxation of interacting subsystems independently [40].

Recently, the dynamics of excitons strongly interacting with vibrons have been investigated in the context of phonon lasers [33,41–43], although in the local approach for the Lindblad master equation for the density matrix, or, with applying mean-field theory [28]. In such problems, the attention has been paid to the stationary state of the system. The interest is also of transient dynamics of strongly coupled exciton-vibron systems. Nontrivial temporal dynamics manifest in a wide variety of systems with strong coupling between electronic and vibrational degrees of freedom, e.g., in a lattice with strong coupling between Bloch electrons and vibrational degrees of freedom [44], in the problem of Floquet engineering of molecules strongly coupled with phonons [45], and in the case when small lattice polarons are driven by a strong external electric field [46]. Transient oscillations arising from the Jaynes-Cummings interaction can be manifested when the molecule or quantum dot with strong coupling between electronic and nuclei vibration degrees of freedom is placed in a resonator [47].

Here, we consider the transient dynamics of a molecule with strongly coupled vibron and exciton driven by a weak monochromatic wave, without the resonator and additional modulation of a driving signal. We demonstrate that strong exciton-vibron coupling, by itself, can result in nontrivial transient dynamics. We solve the Lindblad master equations in the global approach using eigenstates of the Hamiltonian of strongly coupled excitons and vibrons. We show that the transient dynamics of the system can be divided into three stages. In the first stage, oscillations of the polarization at the exciton eigenfrequency collapse due to the transition to the set of shifted Fock states of vibrons. In the second stage, revivals of these oscillations appear. At the final stage, collapses and revivals dissipates. We give theoretical estimates for the collapse and revival times and find the dependence of this time on the interaction constant between the vibron and exciton and the frequency of the vibron. We demonstrate that these collapses and revivals lead to the radiation spectrum exhibits a series of peaks near the exciton transition frequency with a distance equal to vibron frequency.

II. THE MODEL

For simplicity, we assume that the exciton corresponding to the excitation of an electron-hole pair interacts with one eigenmode of oscillations of the nuclei, hereinafter, vibron. Such a situation is realized, e.g., in semiconductor quantum dots [48–52] and organic molecules [53–55]. Among the electronic states, we consider one state in the valence band $|g\rangle$, which we will call the ground state, and one state in the conduction band $|e\rangle$, which we will call the excited state. We denote the exciton eigenfrequency as ω_σ. Such a two-level approximation is valid, in particular, when the excited state presents a group of closely lying levels and relaxation between the excited levels is high [56]. This is the case for some organic materials, e.g., MeLPPP [15,16]. If we suppose that the energy of the ground state is zero, then the exciton Hamiltonian takes the form $\hbar\omega_\sigma|e\rangle\langle e|$. Furthermore, we introduce operators of transitions from the excited state $|e\rangle$ to the ground state $|g\rangle$, $\hat{\sigma} = |g\rangle\langle e|$ and operator of inverse transition, $\hat{\sigma}^\dagger = |e\rangle\langle g|$. In such an approximation, the exciton Hamiltonian can be written as $\hbar\omega_\sigma\hat{\sigma}^\dagger\hat{\sigma}$. The operators $\hat{\sigma}$ and $\hat{\sigma}^\dagger$ satisfy the commutation relation $[\hat{\sigma}^\dagger, \hat{\sigma}] = \hat{\sigma}_z$, where the operator $\hat{\sigma}_z$ is the operator of the difference between the populations of the excited and ground states. Note that the mean value of the operator $\hat{\sigma}$ multiplied by the matrix element of the dipole moment $\mathbf{d}_{eg}$ and molecular concentration gives molecular polarization. Thus, the expected value of the operator $\hat{\sigma}$ can be called dimensionless polarization.

We also consider one vibrational mode of nuclei in the harmonic approximation. In this case, the Hamiltonian can be represented as $\hbar\omega_{\mathrm{v}}\hat{b}^\dagger\hat{b}$, where ω_{v} is the eigenfrequency of the vibron, and $\hat{b}^\dagger$ and $\hat{b}$ are the creation and annihilation operators of vibrons satisfying the commutation relation $[\hat{b}, \hat{b}^\dagger] = \hat{1}$. The interaction between the electronic and vibrational subsystems of molecules, i.e., the exciton and the vibron, can be represented in the form of the Fröhlich Hamiltonian $\sigma^\dagger\sigma(\hat{b}^\dagger + \hat{b})$ [14,26,34], where g is the interaction constant. The operator $\hat{b}^\dagger + \hat{b}$ is the nuclear displacement amplitude operator, and the operator $\hat{\sigma}^\dagger\hat{\sigma}$ is the population operator of the excited state of the exciton.

The Hamiltonian of the system has the form

$$\hat{H}_{\mathrm{mol}} = \hbar\omega_\sigma\hat{\sigma}^\dagger\hat{\sigma} + \hbar\omega_{\mathrm{v}}\hat{b}^\dagger\hat{b} + \hbar g\hat{\sigma}^\dagger\hat{\sigma}(\hat{b}^\dagger + \hat{b}). \tag{1}$$

We consider coherent pumping of exciton by a monochromatic electromagnetic (EM) wave. The EM wave is described in the classical approximation. In the dipole and rotating-wave approximations, the interaction Hamiltonian has the form

$$\hat{H}_{\mathrm{mol-field}} = \frac{\hbar\Omega}{2}(\hat{\sigma}e^{i\omega t} + \hat{\sigma}^\dagger e^{-i\omega t}), \tag{2}$$

where ω is the EM field frequency, and Ω is the Rabi interaction constant with the exciton dipole moment:

$$\Omega = \frac{-\mathbf{d}_{eg}\mathbf{E}(r)}{\hbar}. \tag{3}$$

Here $\mathbf{d}_{eg}$ is the transition matrix element between states $|e\rangle$ and $|g\rangle$, $\mathbf{E}(\mathbf{r})$ is the electric-field amplitude at the exciton location (we suppose that the length of exciton localization is much smaller than the EM wavelength). The total Hamiltonian of the system reads

$$\hat{H} = \hbar\omega_\sigma\hat{\sigma}^\dagger\hat{\sigma} + \hbar\omega_{\mathrm{v}}\hat{b}^\dagger\hat{b} + \hbar g\hat{\sigma}^\dagger\hat{\sigma}(\hat{b}^\dagger + \hat{b}) + \frac{\hbar\Omega}{2}(\hat{\sigma}e^{i\omega t} + \hat{\sigma}^\dagger e^{-i\omega t}). \tag{4}$$

To find an eigenstate, we note that the molecular Hamiltonian can be rewritten in the form

$$\hat{H}_{\mathrm{mol}} = \hbar\omega_\sigma(1-\alpha^2)\hat{\sigma}^\dagger\hat{\sigma} + \hbar\omega_{\mathrm{v}}\hat{\tilde{b}}^\dagger\hat{\tilde{b}}, \tag{5}$$

where

$$\hat{\tilde{b}} = \hat{b} + \alpha\hat{\sigma}^\dagger\hat{\sigma}, \quad \alpha = \frac{g}{\omega_{\mathrm{v}}} \tag{6}$$

is the shifted annihilation operator of vibrons. The eigenstates of the Hamiltonian (5) have the form

$$|g, n\rangle, \quad \omega_{gn} = \omega_{\mathrm{v}}(n + 1/2), \quad n = 0, 1, \ldots, \tag{7}$$

$$|e, \tilde{n}_\alpha\rangle, \quad \omega_{e\tilde{n}} = \omega_\sigma(1-\alpha^2) + \omega_{\mathrm{v}}(\tilde{n} + 1/2), \quad \tilde{n} = 0, 1, \ldots, \tag{8}$$

where we introduce the shifted Fock state [34,57] via the displacement operator $\hat{D}(\alpha) = \exp(\alpha\hat{b}^\dagger - \alpha^*\hat{b})$:

$$|\tilde{n}_\alpha\rangle = \hat{D}(\alpha)|n\rangle. \tag{9}$$

The matrix elements of expansion of the shifted Fock states over the Fock state are well known [57,58]:

$$\langle n_0|\tilde{n}_\alpha\rangle = (-\alpha^*)^{\tilde{n}_\alpha - n_0}\sqrt{\frac{n_0!}{\tilde{n}_\alpha!}}L_{n_0}^{(\tilde{n}_\alpha - n_0)}(|\alpha|^2)e^{-|\alpha|^2/2},$$

$$\text{when } \tilde{n}_\alpha \geqslant n_0,$$

$$\langle n_0|\tilde{n}_\alpha\rangle = (\alpha^*)^{n_0 - \tilde{n}_\alpha}\sqrt{\frac{\tilde{n}_\alpha!}{n_0!}}L_{\tilde{n}_\alpha}^{(n_0 - \tilde{n}_\alpha)}(|-\alpha|^2)e^{-|-\alpha|^2/2},$$

$$\text{when } \tilde{n}_\alpha < n_0, \tag{10}$$

and are related to the Frank-Condon factors [34]. Here L_m^n are associated Laguerre polynomials.

To describe relaxation processes, we use the Lindblad equation for the density matrix [20,59,60] in the global approach [38,40]. It can be derived from the von Neumann equation for the density matrix of the system and environment by eliminating environmental variables in the Born-Markov approximation [20,59,60]. The Lindblad equation has the form

$$\dot{\hat{\rho}} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] + L_{\text{diss}}[\hat{\rho}] + L_{\text{pump}}[\hat{\rho}] + L_{\text{deph}}[\hat{\rho}] + L_{\text{v}}[\hat{\rho}]. \tag{11}$$

The first term on the right side of Eq. (11) describes the Hermitian dynamics of the system. The rest of the terms describe the relaxation processes that occur when the system interacts with the environment (external reservoirs).

For further consideration, it is convenient to expand the density matrix over the eigenstates (7), (8):

$$\hat{\rho} = \hat{\rho}_{gg} + \hat{\rho}_{eg} + \hat{\rho}_{ge} + \hat{\rho}_{ee}, \tag{12}$$

where

$$\hat{\rho}_{gg} = \sum_{n_1,n_2}\rho_{g,n_1,g,n_2}|g, n_1\rangle\langle g, n_2|,$$

$$\hat{\rho}_{eg} = \sum_{\tilde{n}_{1\alpha},n_2}\rho_{e,\tilde{n}_{1\alpha},g,n_2}|e, \tilde{n}_{1\alpha}\rangle\langle g, n_2|,$$

$$\hat{\rho}_{ge} = \sum_{n_1,\tilde{n}_{2\alpha}}\rho_{g,n_1,e,\tilde{n}_{2\alpha}}|g, n_1\rangle\langle e, \tilde{n}_{2\alpha}|,$$

$$\hat{\rho}_{ee} = \sum_{\tilde{n}_{1\alpha},\tilde{n}_{2\alpha}}\rho_{e,\tilde{n}_{1\alpha},e,\tilde{n}_{2\alpha}}|e, \tilde{n}_{1\alpha}\rangle\langle e, \tilde{n}_{2\alpha}|, \tag{13}$$

where n is the number of vibrons in the ground state, and $\tilde{n}$ is the number of "shifted vibrons" in the excited state.

The Lindblad superoperators describing the relaxation of vibrons have the form

$$L_{\text{v}}[\hat{\rho}] = L_{\text{v}}[\hat{\rho}_{gg}] + L_{\text{v}}[\hat{\rho}_{ee}],$$

$$L_{\text{v}}[\hat{\rho}_{gg}] = \frac{\gamma_{\text{v}}(1 + n_{\text{v}})}{2}(2\hat{b}\hat{\rho}_{gg}\hat{b}^\dagger - \hat{b}^\dagger\hat{b}\hat{\rho}_{gg} - \hat{\rho}_{gg}\hat{b}^\dagger\hat{b})$$

$$+ \frac{\gamma_{\text{v}}n_{\text{v}}}{2}(2\hat{b}^\dagger\hat{\rho}_{gg}\hat{b} - \hat{b}\hat{b}^\dagger\hat{\rho}_{gg} - \hat{\rho}_{gg}\hat{b}\hat{b}^\dagger,$$

$$L_{\text{v}}[\hat{\rho}_{ee}] = \frac{\gamma_{\text{v}}(1 + n_{\text{v}})}{2}(2\hat{\tilde{b}}\hat{\rho}_{ee}\hat{\tilde{b}}^\dagger - \hat{\tilde{b}}^\dagger\hat{\tilde{b}}\hat{\rho}_{ee} - \hat{\rho}_{ee}\hat{\tilde{b}}^\dagger\hat{\tilde{b}})$$

$$+ \frac{\gamma_{\text{v}}n_{\text{v}}}{2}(2\hat{\tilde{b}}^\dagger\hat{\rho}_{ee}\hat{\tilde{b}} - \hat{\tilde{b}}\hat{\tilde{b}}^\dagger\hat{\rho}_{ee} - \hat{\rho}_{ee}\hat{\tilde{b}}\hat{\tilde{b}}^\dagger). \tag{14}$$

The term $L_{\text{v}}[\rho_{gg}]$ describes the transitions between the levels $|e, \tilde{n}\rangle$ with different $\tilde{n}$. The term $L_{\text{v}}[\rho_{ee}]$ describes the transitions between the levels $|g, n\rangle$. Here $n_{\text{v}} = [\exp(\hbar\omega_{\text{v}}/kT) - 1]^{-1}$ is the mean number of quanta in the reservoir taken at the phonon frequency. The ratio of transition rates with energy increasing to energy lowering is $\gamma_{\text{v}}n_{\text{v}}/\gamma_{\text{v}}(1 + n_{\text{v}}) = \exp(-\hbar\omega_{\text{v}}/kT)$, i.e., satisfies the Kubo-Martin-Schwinger condition [20].

The Lindblad superoperator describing phase destruction (dephasing) of excitons is

$$L_{\text{deph}}[\hat{\rho}] = \frac{\gamma_{\text{deph}}}{4}(\hat{\sigma}_z\hat{\rho}\hat{\sigma}_z - \hat{\rho}). \tag{15}$$

The Lindblad superoperator, which describes the relaxation of the exciton energy, takes the form

$$L_{\text{diss}}[\hat{\rho}] = \frac{\gamma_{\sigma_z}}{2}\sum_{\Delta\omega}(2\hat{\tilde{\sigma}}_{\Delta\omega}\hat{\rho}\hat{\tilde{\sigma}}^\dagger_{\Delta\omega} - \hat{\tilde{\sigma}}^\dagger_{\Delta\omega}\hat{\tilde{\sigma}}_{\Delta\omega}\hat{\rho} - \hat{\rho}\hat{\tilde{\sigma}}^\dagger_{\Delta\omega}\hat{\tilde{\sigma}}), \tag{16}$$

where $\Delta\omega = \omega_{e\tilde{n}} - \omega_{gn}$ and $\hat{\tilde{\sigma}}_{\Delta\omega} = \langle g, n|\hat{\sigma}|e, \tilde{n}\rangle|g, n\rangle\langle e, \tilde{n}|$. The Lindblad superoperator describing incoherent exciton pumping is

$$L_{\text{pump}}[\hat{\rho}] = \frac{\gamma_p}{2}\sum_{\Delta\omega}(2\hat{\tilde{\sigma}}^\dagger_{\Delta\omega}\hat{\rho}\hat{\tilde{\sigma}}_{\Delta\omega} - \hat{\tilde{\sigma}}_{\Delta\omega}\hat{\tilde{\sigma}}^\dagger_{\Delta\omega}\hat{\rho} - \hat{\rho}\hat{\tilde{\sigma}}_{\Delta\omega}\hat{\tilde{\sigma}}^\dagger). \tag{17}$$

In Appendix A we present the explicit form of equations for the density-matrix elements.

Furthermore, we investigate the dynamics and the spectrum of the expected value of polarization operator $\sigma(t) = \text{Tr}(\hat{\rho}(t)\hat{\sigma})$, i.e., the coherent part of the polarization. In Appendix B we show that, in the case when a large number N of molecules occupy subwavelength volume, the radiation spectrum is proportional to the Fourier spectrum of the coherent part of the polarization $\sigma(t)$ multiplied by N^2: $S \simeq N^2|\int_0^t d\tau\langle\hat{\sigma}(\tau)\rangle\exp(-i\omega\tau)|^2$.

III. THE DYNAMICS OF MOLECULAR POLARIZATION

A. Continuous-wave pumping

First, we consider the case when only a coherent external field excites the system, and there is no incoherent pumping, i.e., $\gamma_p = 0$. We find the dynamics of the system by numerical simulations of the master equation (11). We use the parameters typical for organic MeLPPP molecules [15,16], namely, $\omega_\sigma = 2.4$ eV, $\omega_{\text{v}} = 0.2$ eV, $\gamma_{\text{deph}} = 5 \times 10^{-2}$ eV, $\gamma_{\sigma_z} = 10^{-6}$ eV. We investigate the changing of the system dynamics with the increase of the Fröhlich interaction constant g by passing the value typical for MeLPPP, $g \simeq 0.5\omega_{\text{v}}$. As an initial condition, we consider the ground state of electronic subsystems and the thermal state of the vibron subsystem, $\hat{\rho}(0) = |g\rangle\langle g| \otimes (1 - e^{-\hbar\omega_{\text{v}}/kT})\sum_n e^{-\hbar\omega_{\text{v}}/kT}|n\rangle\langle n|$. In addition, we consider the case of large detuning, $\gamma_{\text{deph}}, \gamma_{\sigma_z}, \Omega \ll |\omega - \omega_\sigma| \ll \omega_\sigma, \omega$, which is typical for the nonresonant Raman scattering. In the case when there is no interaction between vibrons and excitons ($g = 0$), Eq. (11) describes the dynamics of excitons driven by monochromatic field. In such a case, the dynamics of molecular polarization, $\sigma(t) = \text{Tr}(\hat{\rho}(t)\hat{\sigma})$, can be divided [59] into damped Rabi oscillations at the exciton eigenfrequency and persistent driven oscillations at the frequency of the

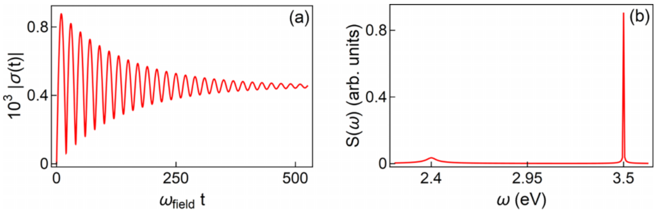

FIG. 1. (a) The temporal dependence of $|\sigma(t)| = |\mathrm{Tr}(\hat\rho(t)\hat\sigma)|$, $\gamma_{\sigma_z} = 1\times10^{-3}$ eV, $\gamma_{\rm deph} = 5\times10^{-2}$ eV, $\gamma_{\rm v} = 2\times10^{-4}$ eV, $\Omega = 10^{-3}$ eV, $\omega_{\rm field} = 3.5$ eV, $\omega_\sigma = 2.4$ eV, $\omega_{\rm v} = 0.2$ eV, $g = 0$ eV, $\tilde n = 10^{-3}$. (b) Spectrum of oscillations of $\sigma(t)$.

external field (Rayleigh response). These dynamics are presented in Fig. 1(a). The spectrum of the oscillations is the sum of Lorentzian line at the exciton eigenfrequency with the width equal to exciton transverse relaxation rates, and the δ function corresponding to Rayleigh response, see Fig. 1(b). The number of phonons remains unchanged, and there is no displacement of nuclei ($b = 0$). Note that the mean value of operator $\hat\sigma$ is proportional to the irradiated field [60], thus, the spectrum of oscillations $\langle\hat\sigma\rangle$ is proportional to the spectrum of irradiated field.

With the increase of g, dipole moment also exhibits Rabi oscillations but with beating at vibron frequency, see Fig. 2(a). The reason of this beating is that the electric field by itself results in oscillations between electronic ground and excited states. Because direct product of Fock vibron state and excited electronic state is not the molecular eigenstate, the system begins to oscillate at the eigenfrequencies described by Eq. (8). The difference between these eigenfrequencies is vibron eigenfrequency $\omega_{\rm v}$. The amplitude of vibrons oscillates at vibron eigenfrequency $\omega_{\rm v}$. In the spectrum, the multiple peaks near the exciton transition frequency ω_σ appear, see Fig. 2(b) (in this and subsequent figures, we do not show the δ function of Rayleigh response).

Further increasing of the coupling constant between phonons and the dipole moment g results in intensifying of beating of the dipole moment.

When the coupling constant between exciton and vibron g becomes larger than the vibron eigenfrequency $\omega_{\rm v}$, beating of exciton dipole moment transforms to repeating collapses and revivals, see Fig. 3(a). The spectrum of the system is the sum of the Rayleigh δ peak and multiple peaks at the exciton transition frequency, see Fig. 3(b).

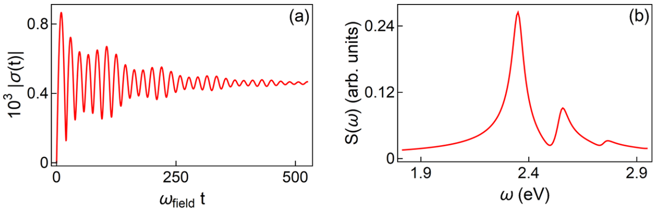

FIG. 2. (a) The temporal dependence of $|\sigma(t)| = |\mathrm{Tr}(\hat\rho(t)\hat\sigma)|$, $\gamma_{\sigma_z} = 1\times10^{-3}$ eV, $\gamma_{\rm deph} = 5\times10^{-2}$ eV, $\gamma_{\rm v} = 2\times10^{-4}$ eV, $\Omega = 10^{-3}$ eV, $\omega_{\rm field} = 3.5$ eV, $\omega_\sigma = 2.4$ eV, $\omega_{\rm v} = 0.2$ eV, $g = 0.1$ eV, $\tilde n = 10^{-3}$. (b) Spectrum of oscillations of $\sigma(t)$.

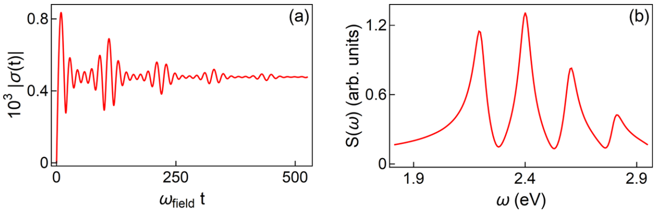

FIG. 3. (a) The temporal dependence of $|\sigma(t)| = |\mathrm{Tr}(\hat\rho(t)\hat\sigma)|$, $\gamma_{\sigma_z} = 1\times10^{-3}$ eV, $\gamma_{\rm deph} = 5\times10^{-2}$ eV, $\gamma_{\rm v} = 2\times10^{-4}$ eV, $\Omega = 10^{-3}$ eV, $\omega_{\rm field} = 3.5$ eV, $\omega_\sigma = 2.4$ eV, $\omega_{\rm v} = 0.2$ eV, $g = 0.2$ eV, $\tilde n = 10^{-3}$. (b) Spectrum of oscillations of $\sigma(t)$.

In all of these cases, beating of oscillations and collapses and revivals dissipate with the exciton dephasing rate. We verify this by changing dephasing rate and observing that beating and collapses and revivals relax with this rate.

We verify that, for the parameters which we use, $|\omega_\sigma - \omega| \gg \Omega$, the polarization $\sigma(t)$ linearly depends on the amplitude of the external field. Thus, the appearance of the collapses and revivals is the consequence of the strong exciton-vibron coupling.

In the Appendix C we show that, without the rotating-wave approximation, the system dynamics and spectrum do not change qualitatively.

B. Pulse pumping

Let us now consider the case when in addition to the coherent pump there is short pump pulse. We suppose that the rate of incoherent pumping is

$$\gamma_p = \gamma_p^0, \quad 0 \leqslant t \leqslant t_0, \quad \gamma_p = 0, \quad t \geqslant t_0. \tag{18}$$

The dynamics of the molecule polarization and its spectrum are shown in Figs. 4(a) and 4(b). During the pump pulse, the population of the excited state increases which results in saturation of excited-state population, see Fig. 4(c). After the pump pulse is turned off, population inversion gets smaller

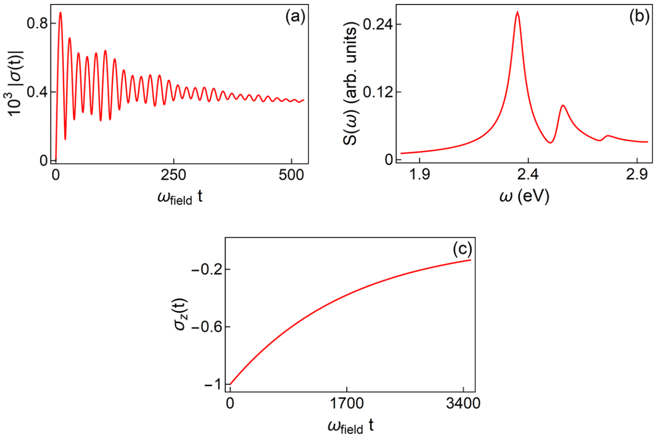

FIG. 4. (a) Temporal dynamics of $|\sigma(t)|$, $\gamma_{\sigma_z} = 10^{-3}$ eV, $\gamma_{\rm deph} = 5\times10^{-2}$ eV, $\gamma_{\rm v} = 2\times10^{-4}$ eV, $\Omega = 10^{-3}$ eV, $\omega_{\rm field} = 3.5$ eV, $\omega_\sigma = 2.4$ eV, $\omega_{\rm v} = 0.2$ eV, $g = 0.1$ eV, $t_0 = 2/\gamma_D$, $\tilde n = 10^{-3}$ (b) Spectrum of oscillation of $\sigma(t)$. (c) Temporal dynamics of $\sigma_z(t) = \mathrm{Tr}(\hat\rho(t)\hat\sigma_z)$.

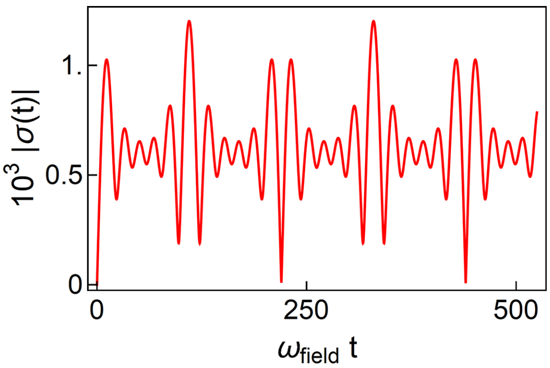

FIG. 5. Temporal dynamics of $|\sigma(t)|$, $\Omega = 10^{-3}$ eV, $\omega_{\text{field}} = 3.5$ eV, $\omega_\sigma = 2.4$ eV, $\omega_{\text{v}} = 0.2$ eV, $g = 0.2$ eV.

and the polarization starts to grow. During these processes, the polarization dynamics exhibit collapses and revivals similar to the case without of pulse pump. The only difference is during saturation the polarization amplitude decreases and amplitude of oscillations decreases too.

IV. ESTIMATION OF THE COLLAPSE AND REVIVALS TIMES

To estimate collapse and revival times, we first demonstrate that it is Hermitian part of the system dynamics which is responsible for the collapses and revivals. To do that, we write the Schrödinger equation for the wave function of excitons and vibrons, which has the form:

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{\hat{H}}|\psi\rangle, \tag{19}$$

where we expand the wave function over the eigenstates of $\hat{H}_{\text{mol}}$:

$$|\psi\rangle = \sum_n C_{g,n}(t)|g,n\rangle + \sum_{\tilde{n}_\alpha} C_{e,\tilde{n}_\alpha}(t)|e,\tilde{n}_\alpha\rangle. \tag{20}$$

The system Hamiltonian is determined by Eq. (4).

The dynamics of mean value of $\hat{\sigma}$ obtained from numerical simulations of Eqs. (19)–(20) are shown in Fig. 5. It is seen that Hermitian dynamics quantitatively reproduce the dynamics obtained from the Lindblad equation (11) at times smaller than inverse dephasing rate γ_σ. Namely, there is the collapses in the dynamics of molecule polarization and the revivals that occur at the same times as they occur when modeling the Lindblad equation (11). Thus, we can conclude that it is the Hermitian part of the dynamics that is responsible for formation of collapses and revivals and neglect dissipation processes to estimate collapse and revival times.

To estimate the collapse time, we use the following reasoning: The eigenstates of the system are described by Eqs. (7) and (8). Consider the case when the system is initially in the state $|g,0\rangle$. The electric field results in transitions to the state $|e,0\rangle$. This state is not an eigenstate of the system. As a result, the projection of the system state to the eigenstate, say, $|e,\tilde{n}_\alpha\rangle$, will oscillate with the frequency of this eigenstate and will have the amplitude $\langle\tilde{n}_\alpha|0\rangle$. In Fig. 6, we show the dependence of this matrix element in two cases: weak $g/\omega_{\text{v}} \ll 1$ and strong $g/\omega_{\text{v}} \gg 1$ exciton-vibron coupling. We see that the higher the value g/ω_{v}, the smoother the function $\langle\tilde{n}_\alpha|0\rangle$. Thus, in the case of strong exciton-vibron coupling, after the transition to the state $|e,0\rangle$, one has simultaneous excitations of many system eigenstates $|e,\tilde{n}_\alpha\rangle$. The projections of the system state to these eigenstates will oscillate with close eigenfrequencies $\omega_\sigma(1-\alpha^2) + \omega_{\text{v}}(\tilde{n}_\alpha + 1/2)$. The difference between these eigenfrequencies, ω_{v}, is much less than the eigenfrequencies themselves.

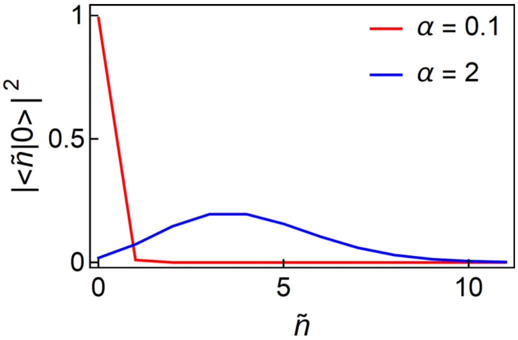

FIG. 6. Dependence of the matrix element $\langle\tilde{n}|n\rangle$ on $\tilde{n}$ for $n = 0$.

Thus, we can consider the shifted Fock states as an effective reservoir for the state $|e,0\rangle$ which the external field excites. Indeed, an analogous situation takes place if we consider one initially excited harmonic oscillator interacting with an interaction constant g with a set of a large number of harmonic oscillators with difference $\Delta\omega$ between their eigenfrequencies. The last will play the role of effective reservoir and will result in exponential relaxation of the oscillator energy with the rate $\pi g^2/\Delta\omega$ [61].

As a result, we can estimate the collapse time as an inverse rate of relaxation of oscillations to the reservoir of system eigenstates:

$$t_c \simeq \frac{\omega_{\text{v}}}{\pi g^2|M(\alpha)|^2} \sim (g\alpha|M(\alpha)|^2)^{-1}, \tag{21}$$

where $M(\alpha) = \max\langle 0|\tilde{n}_\alpha\rangle$ is the characteristic value of matrix elements of the transition described by Eq. (10).

To estimate the revival time, we should take into account that the effective reservoir of shifted vibron states has a discrete spectrum. It is known that, in such a case, the excitation, initially stored in the system and subsequently transferred into the reservoir, will return to the system after time $2\pi/\Delta\omega$ [62]. Thus, in the case considered, the revival time can be estimated as $2\pi/\omega_{\text{v}}$.

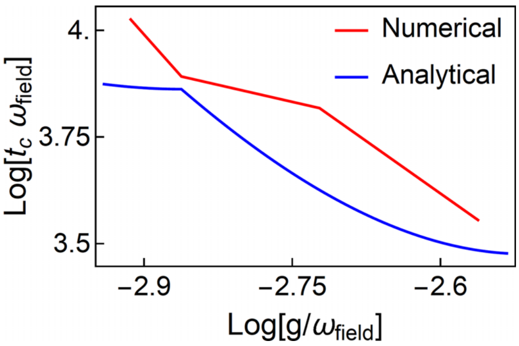

FIG. 7. The theoretical dependence of the collapse time on the Fröhlich constant g in a logarithmic scale, $\Omega = 10^{-3}$ eV, $\omega_{\text{field}} = 3.5$ eV, $\omega_\sigma = 2.4$ eV, $\omega_{\text{v}} = 0.2$ eV.

Figure 7 shows the dependence of the time of the first collapse as a function of the Fröhlich constant of interaction obtained from a numerical simulation and from analytical estimates. It is seen good agreement between them.

V. CONCLUSION

In this work, we consider the temporal dynamics of the molecule which electronic degrees of freedom strongly coupled with degrees of freedom of nuclei vibrations. We show that when the coupling constant is larger than the vibron frequency, transient oscillations of polarization exhibit collapses. The reason for the collapses is connected with structure of the eigenstates of the system. The eigenstates of the system can be divided into two subsets. The first one is the direct product of the ground electronic state and Fock states of nuclei vibrations. The second subset is the direct product of the excited electronic state and shifted Fock states of nuclei vibrations. The action of external monochromatic field on the molecular dipole moment by itself results in Rabi cycle between ground and excited electronic states during which the system changes the electronic state but does not change the vibrational state because we consider Raman-active molecules. As a result, after half of a Rabi cycle, starting from, e.g., the ground electronic state and the Fock vibrational state, the system occurs at an excited electronic state and still the Fock vibrational state. This state is not an eigenstate and the system begins to transit to the eigenstates of the second subset, e.g., to an excited electronic state and a shifted vibrational state. If the time of this transition is smaller than both inverse dephasing rate and inverse vibrational frequency, the collapse of the transition oscillations appear. Due to the frequency difference between the Fock vibrational states and shifted Fock vibrational states are equal to each other, the revival of transient oscillations appears. These collapses and revivals proceed until transient oscillations dissipate due to dephasing. They manifest in the spectrum of polarization oscillations as splitting of the spectral line in the vicinity of electronic transition frequency. Namely, the spectral line splits into multiple lines with width equal to the inverse collapse time and distance between them equals the vibron frequency. The obtained results provides an additional tool for measurement of the vibron frequency and constant of interaction between electronic and nuclei vibrational degrees of freedom.

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APPENDIX A: EQUATIONS FOR THE DENSITY MATRIX ELEMENTS

Using Eq. (11), we can write the equations for each matrix element (12) of the density matrix $\hat{\rho}$. They have the form

$$\dot{\rho}_{e,\tilde{n}_{1\alpha},e,\tilde{n}_{2\alpha}} = i\omega_{\mathrm{v}}(\tilde{n}_{1\alpha}-\tilde{n}_{2\alpha})\rho_{e,\tilde{n}_{1\alpha},e,\tilde{n}_{2\alpha}} - i\frac{\Omega}{2}e^{-i\omega t}\sum_{n_1}\langle\tilde{n}_{1\alpha}|n_1\rangle\rho_{g,n_1,e,\tilde{n}_{2\alpha}} + i\frac{\Omega}{2}e^{i\omega t}\sum_{n_2}\langle n_2|\tilde{n}_{2\alpha}\rangle\rho_{e,\tilde{n}_{1\alpha},g,n_2} \tag{A1}$$

$$-\gamma_{\sigma_z}\rho_{e,\tilde{n}_{1\alpha},e,\tilde{n}_{2\alpha}} + \gamma_p\sum_{n_1,n_2}\langle n_1|\tilde{n}_{1\alpha}\rangle\langle n_2|\tilde{n}_{2\alpha}\rangle\rho_{g,n_1,g,n_2} \tag{A2}$$

$$+\frac{\gamma_{\mathrm{v}}(\tilde{n}_0+1)}{2}(2\sqrt{(\tilde{n}_{1\alpha}+1)(\tilde{n}_{2\alpha}+1)}\rho_{e,\tilde{n}_{1\alpha}+1,e,\tilde{n}_{2\alpha}+1} - (\tilde{n}_{1\alpha}+\tilde{n}_{2\alpha})\rho_{e,\tilde{n}_{1\alpha},e,\tilde{n}_{2\alpha}}) \tag{A3}$$

$$+\frac{\gamma_{\mathrm{v}}\tilde{n}_0}{2}(2\sqrt{\tilde{n}_{1\alpha}\tilde{n}_{\alpha 2}}\rho_{e,\tilde{n}_{1\alpha}-1,e,\tilde{n}_{2\alpha}-1} - (\tilde{n}_{1\alpha}+\tilde{n}_{2\alpha}+2)\rho_{e,\tilde{n}_{1\alpha},e,\tilde{n}_{2\alpha}}), \tag{A4}$$

$$\dot{\rho}_{g,n,e,\tilde{n}_\alpha} = i\omega_\sigma\rho_{g,n,e,\tilde{n}_\alpha} + i\omega_{\mathrm{v}}(\tilde{n}_\alpha - n)\rho_{g,n,e,\tilde{n}_\alpha} - i\frac{\Omega}{2}e^{i\omega t}\sum_{\tilde{n}_{1\alpha}}\langle n|\tilde{n}_{1\alpha}\rangle\rho_{e,\tilde{n}_{1\alpha},e,\tilde{n}_\alpha} + i\frac{\Omega}{2}e^{i\omega t}\sum_{n_{2\alpha}}\langle n_2|\tilde{n}_\alpha\rangle\rho_{g,n,g,n_2}$$

$$-\frac{\gamma_p+\gamma_{\sigma_z}+\gamma_{\mathrm{deph}}}{2}\rho_{g,n,e,\tilde{n}_\alpha}, \tag{A5}$$

$$\dot{\rho}_{e,\tilde{n}_\alpha,g,n} = -i\omega_\sigma\rho_{e,\tilde{n}_\alpha,g,n} + i\omega_{\mathrm{v}}(n-\tilde{n}_\alpha)\rho_{e,\tilde{n}_\alpha,g,n} - i\frac{\Omega}{2}e^{-i\omega t}\sum_{n_1}\langle\tilde{n}_\alpha|n_1\rangle\rho_{g,n_1,g,n} + i\frac{\Omega}{2}e^{-i\omega t}\sum_{\tilde{n}_{2\alpha}}\langle\tilde{n}_{2\alpha}|n\rangle\rho_{e,\tilde{n}_\alpha,e,\tilde{n}_{2\alpha}}$$

$$-\frac{\gamma_p+\gamma_{\sigma_z}+\gamma_{\mathrm{deph}}}{2}\rho_{e,\tilde{n}_\alpha,g,n}, \tag{A6}$$

$$\dot{\rho}_{g,n_1,g,n_2} = i\omega_{\mathrm{v}}(n_1-n_2)\rho_{g,n_1,g,n_2} - i\frac{\Omega}{2}e^{i\omega t}\sum_{\tilde{n}_{1\alpha}}\langle n_1|\tilde{n}_{1\alpha}\rangle\rho_{e,\tilde{n}_{1\alpha},g,n_2} + i\frac{\Omega}{2}e^{-i\omega t}\sum_{\tilde{n}_{2\alpha}}\langle\tilde{n}_{2\alpha}|n_2\rangle\rho_{g,n_1,e,\tilde{n}_{2\alpha}}$$

$$-\gamma_p\rho_{g,n_1,g,n_2} + \gamma_{\sigma_z}\sum_{\tilde{n}_{1\alpha},\tilde{n}_{2\alpha}}\langle n_1|\tilde{n}_{1\alpha}\rangle\langle n_2|\tilde{n}_{2\alpha}\rangle\rho_{e,\tilde{n}_{1\alpha},e,\tilde{n}_{2\alpha}} + \frac{\gamma_{\mathrm{v}}(\tilde{n}_0+1)}{2}(2\sqrt{(n_1+1)(n_2+1)}\rho_{g,n_1+1,g,n_2+1}$$

$$-(n_1+n_2)\rho_{g,n_1,g,n_2}) + \frac{\gamma_{\mathrm{v}}\tilde{n}_0}{2}(2\sqrt{n_1n_2}\rho_{g,n_1-1,g,n_2-1} - (n_1+n_2+2)\rho_{g,n_1,g,n_2}). \tag{A7}$$

APPENDIX B: THE RADIATION SPECTRUM

In this Appendix, we derive the general expression for the radiation spectrum.

The radiation spectrum can be calculated (see Ref. [63]) as the number of radiated photons, $\langle n(\omega,\mu)\rangle$ for each free-space mode with wave vector $\mathbf{k}$ and polarization μ and multiply them by $\hbar\omega_{\mathbf{k}}$. To calculate the number of irradiated photons, we consider an ensemble of noninteracting molecules, each of which interacts with the external monochromatic wave and, in addition, with the free-space modes. The Hamiltonian of such system has the form

$$\hat{H}=\sum_{\mathbf{k},\mu}\hbar\omega_{\mathbf{k},\mu}\hat{a}^{\dagger}_{\mathbf{k},\mu}\hat{a}_{\mathbf{k},\mu}+\sum_{\mathbf{k},\mu,j}\Omega_{\mathbf{k},\mu,j}(\hat{a}^{\dagger}_{\mathbf{k},\mu}\hat{\sigma}_j+\hat{a}_{\mathbf{k},\mu}\hat{\sigma}_j)+\sum_j\hat{H}_{\text{mol},j}+\sum_j\hat{H}_{\text{mol-field},j}, \tag{B1}$$

where $\Omega_{\mathbf{k},\mu,j}=-\mathbf{d}_{eg}\mathbf{E}_{\mathbf{k},\mu}(\mathbf{r}_j)/\hbar$ is the Rabi interaction constant between the molecular dipole moment and the electric field of the free-pace mode with wave vector $\mathbf{k}$ and polarization μ, $\mathbf{E}_{\mathbf{k},\mu}(\mathbf{r}_j)=\sqrt{2\pi\hbar\omega_{\mathbf{k}}/V}\exp(i\mathbf{k}\mathbf{r}_j)\mathbf{e}_{\mathbf{k},\mu}$ (V is the quantization volume, $\mathbf{e}_{\mathbf{k},\mu}$ is the polarization vector). The Hamiltonians $\hat{H}_{\text{mol},j}$ and $\hat{H}_{\text{mol-field},j}$ for each jth molecule are given by Eqs. (1) and (2).

We can solve this problem into two steps that are used for calculating the spectrum (see, e.g., Ref. [64]). In the first step, we exclude free-space mode variables using the Born-Markov approximation. At this step, for each jth molecule we obtain the Lindblad master equation (11).

In the second step, supposing that the dynamics of each molecule is determined by the Lindblad superoperator, we find the number of irradiated photons using Heisenberg equation of motion. The Heisenberg equation for the operators $\hat{a}_{\mathbf{k},\mu}$ has the form

$$\frac{d\hat{a}_{\mathbf{k},\mu}}{dt}=\frac{i}{\hbar}[\hat{H},\hat{a}_{\mathbf{k},\mu}]=-i\omega_{\mathbf{k},\mu}\hat{a}_{\mathbf{k},\mu}-i\sum_j\Omega_{\mathbf{k},\mu,j}\hat{\sigma}_j(t). \tag{B2}$$

Supposing that the dynamics of the operator $\hat{\sigma}_j(t)$ is known from Eq. (11), we can formally integrate Eq. (B2) and obtain

$$\hat{a}_{\mathbf{k},\mu}(t)=\hat{a}_{\mathbf{k},\mu}(0)\exp[-i\omega_{\mathbf{k},\mu}t]-i\sum_j\Omega_{\mathbf{k},\mu,j}\int_0^t d\tau\,\hat{\sigma}_j(\tau)\exp[-i\omega_{\mathbf{k},\mu}(t-\tau)]. \tag{B3}$$

The first term is the initial value of the operator $\hat{a}^{\dagger}_{\mathbf{k},\mu}$ which determines the initial number of photons. The second term is responsible for the irradiated photons which we are interested in. Using the second part of the last equation, we can write the following equation for the number of irradiated photons:

$$n_{\mathbf{k},\mu}(t)=\sum_{j_1,j_2}\Omega^*_{\mathbf{k},\mu,j_2}\Omega_{\mathbf{k},\mu,j_1}\int_0^t d\tau_2\int_0^t d\tau_1\langle\hat{\sigma}^{\dagger}_{j_2}(\tau_2)\hat{\sigma}_{j_1}(\tau_1)\exp[-i\hat{\omega}_{\mathbf{k},\mu}(\tau_2-\tau_1)]\rangle. \tag{B4}$$

This equation can be rewritten if we divide the total response of molecule polarization $\hat{\sigma}$ into two parts. The first one is the coherent response on the external field, $\langle\hat{\sigma}\rangle$. The second part describes quantum fluctuations, $\Delta\hat{\sigma}=\hat{\sigma}-\langle\hat{\sigma}\rangle$, $\langle\Delta\hat{\sigma}\rangle=0$. Substituting $\hat{\sigma}=\langle\hat{\sigma}\rangle+\Delta\hat{\sigma}$ into the Eq. (B4), we obtain

$$n_{\mathbf{k},\mu}(t)=\sum_{j_1,j_2}\Omega^*_{\mathbf{k},\mu,j_2}\Omega_{\mathbf{k},\mu,j_1}\int_0^t d\tau_2\int_0^t d\tau_1\big\langle\hat{\sigma}^{\dagger}_{j_2}(\tau_2)\big\rangle\big\langle\hat{\sigma}_{j_1}(\tau_1)\big\rangle\exp[-i\hat{\omega}_{\mathbf{k},\mu}(\tau_2-\tau_1)] \tag{B5}$$

$$+\sum_{j_1,j_2}\Omega^*_{\mathbf{k},\mu,j_2}\Omega_{\mathbf{k},\mu,j_1}\int_0^t d\tau_2\int_0^t d\tau_1\big\langle\Delta\hat{\sigma}^{\dagger}_{j_2}(\tau_2)\Delta\hat{\sigma}_{j_1}(\tau_1)\big\rangle\exp[-i\hat{\omega}_{\mathbf{k},\mu}(\tau_2-\tau_1)]$$

$$=\left|\sum_j\Omega_{\mathbf{k},\mu,j}\int_0^t d\tau\,\langle\hat{\sigma}_j(\tau)\rangle\exp(-i\hat{\omega}_{\mathbf{k},\mu}\tau)\right|^2$$

$$+\sum_j|\Omega_{\mathbf{k},\mu,j}|^2\int_0^t d\tau_2\int_0^t d\tau_1\big\langle\Delta\hat{\sigma}^{\dagger}_j(\tau_2)\Delta\hat{\sigma}_j(\tau_1)\big\rangle\exp[-i\hat{\omega}_{\mathbf{k},\mu}(\tau_2-\tau_1)]. \tag{B6}$$

At the last step we use that, for noninteracting and initially non-correlated atoms, $\langle\Delta\hat{\sigma}_{j_1}\Delta\hat{\sigma}_{j_2}\rangle=\langle\Delta\hat{\sigma}_{j_1}\rangle\langle\Delta\hat{\sigma}_{j_2}\rangle=0$, $j_1\neq j_2$. As a result, we have

$$S(\omega)=S_{\text{coh}}(\omega)+S_{\text{fluct}}(\omega), \tag{B7}$$

where the coherent part is

$$S_{\text{coh}}(\omega)=\left|\sum_j\Omega_{\mathbf{k},\mu,j}\int_0^t d\tau\,\langle\hat{\sigma}_j(\tau)\rangle\exp(-i\hat{\omega}_{\mathbf{k},\mu}\tau)\right|^2, \tag{B8}$$

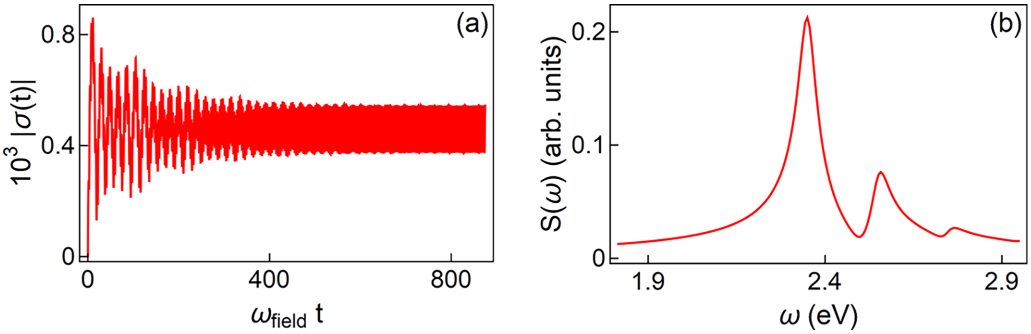

FIG. 8. (a) The temporal dependence of $|\sigma(t)| = |\mathrm{Tr}(\hat{\rho}(t)\hat{\sigma})|$ calculated without the rotating-wave approximation, $\gamma_{\sigma_z} = 1 \times 10^{-3}$ eV, $\gamma_{\text{deph}} = 5 \times 10^{-2}$ eV, $\gamma_{\text{v}} = 2 \times 10^{-4}$ eV, $\Omega = 10^{-3}$ eV, $\omega_{\text{field}} = 3.5$ eV, $\omega_\sigma = 2.4$ eV, $\omega_{\text{v}} = 0.2$ eV, $g = 0.1$ eV, $\tilde{n} = 10^{-3}$. (b) Spectrum of oscillations of $\sigma(t)$.

and the fluctuation part is

$$S_{\text{fluct}}(\omega) = \hbar\omega \sum_j |\Omega_{\mathbf{k},\mu,j}|^2 \int_0^t d\tau_2 \int_0^t d\tau_1 \langle \Delta\hat{\sigma}_j^\dagger(\tau_2)\Delta\hat{\sigma}_j(\tau_1)\rangle \exp[-i\hat{\omega}_{\mathbf{k},\mu}(\tau_2 - \tau_1)]. \tag{B9}$$

Suppose that the sample of the molecules are in subwavelength volume such that $\Omega_{\mathbf{k},\mu,j} = \exp(i\mathbf{k}\mathbf{r}_j)\Omega_0 \simeq \Omega_0$. The first term is proportional to the square of number of molecules, N^2, while the second one is proportional to the number of molecules, N. In the case of large number of molecules, the coherent part of the spectrum is much larger than the fluctuation part, $S_{\text{coh}} \gg S_{\text{fluct}}$.

Thus, in the case of noninteracting molecules in subwavelength volume, the radiation spectrum can be calculated using the response of one molecule as follows:

$$S(\omega) \simeq N^2|\Omega_0|^2 \left| \int_0^t d\tau \langle \hat{\sigma}(\tau)\rangle \exp(-i\omega_{\mathbf{k},\mu}\tau) \right|^2. \tag{B10}$$

APPENDIX C: THE INFLUENCE OF THE ROTATING-WAVE APPROXIMATION ON THE RADIATION SPECTRUM

In this Appendix, we calculate the system dynamics by taking into account non-RWA terms that have been neglected in the main text. Namely, we assume that the Hamiltonian $\hat{H}_{\text{mol-field}}$ of molecule-field interaction has the form

$$\hat{H}_{\text{mol-field}} = \hat{\Omega}(\hat{\sigma} + \hat{\sigma}^\dagger)[\exp(-i\omega t) + \exp(i\omega t)]. \tag{C1}$$

Figures 8(a) and 8(b) show the dynamics of $\sigma(t)$ and the spectrum. It is seen that, in the dynamics, high-frequency oscillations appear. However, the spectrum in the frequency range corresponding to collapses and revivals does not change significantly [cf. Figs. 8(b) and 2(b)]. This is because the terms that oscillate at the frequencies $\omega_\sigma + \omega$ do not influence on the frequency range near ω_σ where collapses and revivals manifest. Thus, the predicted phenomenon is present without the rotating-wave approximation.

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