Research article

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Ultrastrong coupling effects in molecular cavity QED

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Abstract: The spectrum and energy dynamics for a system that comprises a molecule interacting with a cavity photon is analyzed, taking into account the effect of both molecular vibrations and counter-rotating terms (CR) in the dipole Hamiltonian. The CR terms do not have a strong effect on the spectrum even for moderately large values of the exciton-photon interaction. However, it is shown that the polariton subspace is governed by an effective Quantum-Rabi Hamiltonian, where polaritons act as a two-level system and the phonons play the role of cavity photons. The effect of the CR terms is amplified in the dynamics: as the vibrations reduce the effective photon-exciton coupling, small Bloch-Siegert energy shifts can bring the system out of resonance.

Keywords: ultrastrong coupling; molecule; cavity quantum electrodynamics; Rabi oscillations.

1 Introduction

Cavity quantum electrodynamics (CQED), that is, the behavior of matter with a discrete quantum level structure interacting with a confined electromagnetic field, has been a blooming topic of research in the last three decades [1]. One attractive possibility is to strongly couple the constituents in order to create hybrid quasiparticles, which inherit both the intrinsic nonlinearities of a quantum system and the speed of photons. Different material platforms have been considered as the discrete-level system (which can usually be described as an effective two-level system, 2LS), such as quantum dots [2], NV centers in diamond [3], and superconducting systems [4]. Recently, organic molecules have also been added to this list. Notably, placing a macroscopic set of molecules in an extended cavity has been shown to modify their chemical reaction rates [5], exciton transport [6, 7], and even the electronic conductivity [8]. The case of few-molecules in cavities has also been reached [9], even going down to a single molecule in the case of plasmonic cavities [10, 11]. Remarkably, these last cases reported coupling rates of the order of 1/10 of the excitation bare energies, indicating that ultrastrong effects may be relevant (see [12, 13] for recent reviews on the ultrastrong coupling regime). Molecules are also being considered as effective 2LS in open 1D waveguides, both in the optical [14] and microwave [15] regimes, with potential applications in quantum information. It is clear that, despite the similarities with other 2LS, molecules also present peculiarities associated with their manifold of vibrational excitations, which need to be taken into consideration.

In this article we analyze the dynamics of the simplest system in molecular CQED: a single molecule interacting with a single cavity mode. As a difference from other works, we concentrate on analyzing ultrastrong coupling effects that may arise in these systems.

2 One molecule in one cavity

2.1 The model

We consider one molecule inside a cavity (see Figure 1A for a schematic diagram). This system can be described as the single-molecule version of the Holstein-Tavis-Cummings Hamiltonian, which has been analyzed in depth in the past for collections of molecules [16–19] (throughout this article, we denote this single-molecule case as the

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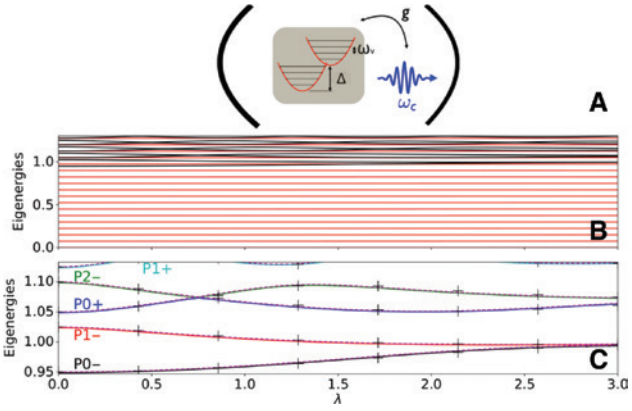

Figure 1: Energy levels in molecular cavity QED.
(A) Schematic representation of the energy scales in the problem of a molecule in a cavity. (B) Lower eigen energies as a function of the Huang-Rhys factor. Red lines correspond to the vibrational ladder of the photon-exciton ground-state, while black lines correspond to the 1 excitation light-matter (polariton) sector. The parameters used are $\omega_c = \Delta = 1$, $\omega_v = 0.075$, and $g = 0.05$. (C) Zoom of panel (B) in the polariton sector. Solid lines were obtained with the HQR model, data points marked with crosses were obtained with the HJC Hamiltonian (neglecting the CR terms), and the discontinuous lines are obtained with the effective QR model described by Eq. (3).

Holstein-Jaynes-Cummings (HJC) case). However, this Hamiltonian is obtained after neglecting the counter-rotating (CR) terms that arise when quantizing the dipole Hamiltonian [1, 13]. This is correct in the usual case where the molecule-photon interaction is weak, but as the coupling increases when the photon modal volume decreases, the CR terms may be relevant when considering ultrasmall plasmonic cavities. We thus retain the CR terms and propose the Holstein-Quantum-Rabi (HQR) Hamiltonian:

$$H = \omega_c a^+ a + \Delta \sigma^+ \sigma^- + \underbrace{g(\sigma^+ + \sigma^-)(a^+ + a)}_{\text{Rabi exciton-phonon}} + \underbrace{\omega_v (b^+ b + \lambda \sigma^+ \sigma^- (b^+ + b + \lambda))}_{\text{Holstein exciton-phonon}}, \quad (1)$$

where the operators a^+, σ^+, and b^+ create one cavity photon (with energy ω_c), one exciton in the molecule (with energy Δ), and one molecular vibrational quantum (with energy ω_v), respectively, while their adjoint operators (a, σ^-, and b) annihilate the corresponding excitations. The operators a and b are bosonic, while the σ's are Pauli matrices operating in the molecular ground state-exciton two-level manifold.

The Holstein exciton-phonon interaction takes into account that the molecule vibrates differently in the ground and excited states, and it is characterized by the Huang-Rhys factor λ^2. The coefficient g sets the exciton-photon interaction strength and depends on both the molecular transition dipole moment and the photon modal volume. When g is small enough compared to both ω_c and Δ, the CR term $H_{CR} = g(\sigma^+ a^+ + \sigma^- a^-)$ can be safely neglected, arriving at the HJC model. On the contrary, for large enough g, the CR term is relevant to the dynamics of the system (situation termed as "ultrastrong coupling regime" or USC). In CQED, the rule of thumb is that reaching the USC requires $g \gtrsim 0.1\ \Delta$ [12, 13, 20]; here we will show that this condition is modified in molecular CQED.

Notice that the diamagnetic term ($A^2 \sim (a + a^+)^2$) has not been included in the Hamiltonian (1), as we assume that its effect has already been taken into account in the values of ω_c and g [17].

Hamiltonian (1) is expressed in the base of vibrational levels of the electronic ground state $\{n\}$. It is possible to go into a representation where vibrations in the electronic ground state are expressed in the base $\{n\}$ while the vibrations in the exciton sector are expressed in their own eigenfunctions: the displaced oscillators $\{\tilde{n}\}$. In this case, the base vectors are $\{|\downarrow, i, n\rangle, |\uparrow, i, \tilde{n}\rangle\}$, where $\downarrow$, $\uparrow$ refers to the electronic degree of freedom and i is the number of photons. This basis change is implemented by a polaron transformation, which takes $b \to b - \lambda \sigma^+ \sigma^-$ via the unitary transformation $H \to U_P^\dagger H U_P$, with $U_P = \exp(-\lambda \sigma^+ \sigma^- (b^+ - b))$. After standard manipulations, we obtain a Hamiltonian that is exactly equivalent to Hamiltonian (1):

$$H = \omega_c a^+ a + \Delta \sigma^+ \sigma^- + \omega_v b^+ b + g(D(\lambda)\sigma^+ + D(\lambda)^\dagger \sigma^-)(a^+ + a). \quad (2)$$

In this representation, the vibrations "dress" the exciton-photon coupling through the Frank-Condon factors $\langle n | D(\lambda) | \tilde{m} \rangle \equiv \langle n | e^{\lambda(b^+ - b)} | \tilde{m} \rangle$ [21].

Although the motivation behind the presentation of the HQR Hamiltonian is the application to molecular CQED, note that it could more generally apply to cases where a 2LS is coupled both to a cavity photon and to another bosonic degree of freedom, a situation that may occur in circuit QED [22]. With this in mind, in what follows we present results over a wide range of Huang-Rhys factors (which in molecules typically range from 0 to ~2 [23, 24]).

2.2 The spectrum

In this article we focus on the modification of the dynamics of a 2LS in a cavity due to the presence of vibrational modes. We thus consider the cavity to be in resonance with the zero-phonon excitonic transition ($\omega_c = \Delta$, which is taken as the energy unit). Figure 1B renders the numerically computed spectrum for the case $g = 0.05$

(the chosen values for ω_c and g representative for vibrations in organic molecules [25] and ultrasmall plasmonic cavities [10, 11], respectively). Results for both HQR and HJC models are shown, demonstrating that the CR terms have only a minimal impact in the eigen energies for that value of g. The spectrum shows a series of vibrational modes associated with the exciton-photon ground state (with energies virtually independent of λ) and another set associated with the vibrational dressed polaritonic states. At $\lambda = 0$, when $|m\rangle = |\tilde{m}\rangle$, this set comprises m–phonon replicas of the polaritonic states $|P_{m\pm}\rangle = |\pm\rangle \otimes |m\rangle = 2^{-1/2}\{|\downarrow, 1\rangle \pm |\uparrow, 0\rangle\} \otimes |m\rangle$ (in the Rabi model, polaritons may have a more complex structure, but for the considered values of g, this "Jaynes-Cummings" expression is an excellent approximation). For finite λ, these vibrational states couple and the eigenstates do not have a well-defined number of phonons. Notably, as shown in Figure 1C, some eigenstates trend toward degeneracy at large λ (e.g. the two lowest polaritonic states in Figure 1C, arising from $|P_{0-}\rangle$ and $|P_{1-}\rangle$). In order to understand this feature, which as we will show has consequences on the Rabi oscillation, we assume that $\omega_c = \Delta$, and (i) neglect the CR terms in the HQR Hamiltonian in Eq. (2), (ii) project the Hamiltonian on the polariton basis on the Jaynes-Cummings light-matter interaction $|\pm\rangle$, and (iii) perform a polaron transformation with $U_P = \exp(-\lambda(b^+ - b)/2)$. After this, we obtain that the polaritonic sector is governed by an effective Quantum-Rabi (QR) Hamiltonian

$$H = \hat{\Delta}\sigma_P^+\sigma_P^- + \omega_v b^+ b + \hat{g}(\sigma_P^+ + \sigma_P^-)(b^+ + b) + \epsilon, \tag{3}$$

where the σ_P operators work in the two-level subspace spanned by the exciton-photon polaritons, $\hat{\Delta} = 2g$, $\hat{g} = \lambda\omega_v/2$, and $\epsilon = \omega_c + \omega_v\lambda^2/4 - g$ is just an energy shift of all eigen energies. We emphasize that Eq. (3) has been derived assuming the resonant condition $\omega_c = \Delta$, as we wanted to stress that in the Jaynes-Cummings polariton sector the system behaves according to the QR Hamiltonian (or, in other words, it could be used as a "quantum simulator" for this Hamiltonian). The validity of this effective Hamiltonian can be seen in Figure 1C: the approximate spectrum is very close to those obtained with both HQR and HJC models. Thus, the dynamics in the polaritonic subspace mimic that of CQED, with the polaritons playing the part of the 2LS and the phonons the part of the cavity photons! The effective description also unveils another feature that was not evident in the HJC one: at photon-exciton resonance, the number of excitations in Hamiltonian (3) is not conserved, but they uncouple in sectors with odd and even numbers of excitations. The only exception is near degeneracies, for instance, the crossing between P_{0+} and P_{2-} at $\lambda \approx 0.74$. While both HJC and effective Rabi models predict a crossing of levels (notice that those levels have different parity), the full HQR model produces an anti-crossing with a small gap (not shown). This gap originates from the CR terms, which in the effective Rabi model induce additional parity-breaking terms. This ultrastrong coupling effect is small in the spectrum but, as will be shown later, affects the dynamics.

Thus, away from these degeneracy points, the dynamics in the polariton subspace is governed by an effective QR Hamiltonian, which can even reach the deep-ultrastrong coupling regime $\hat{g} \gtrsim \hat{\Delta}$ (a parameter regime that has proven difficult to access experimentally), even when g is small enough for the CR terms in the original Hamiltonian to be negligible. The analogy also explains why the evolution of the energy levels with λ strongly resembles that in the QR model with coupling strength g. It must be stressed nonetheless that the effective QR Hamiltonian applies to the dynamics of excited states but, additionally, the system presents a manifold of energy states associated with the molecular ground state. Obviously, this manifold should be taken into account in the presence of decay channels for the polaritons.

2.3 Dynamics: ultrastrong effects

We consider the situation where one photon enters the system, in resonance with the zero-phonon exciton, and study the subsequent dynamics. In this work we assume that the decay rates are small enough to be safely neglected in the timescales we examine; the effect of losses will be analyzed in a subsequent publication. It can be anticipated, nevertheless, that the high losses present in today's room-temperature plasmonic cavities would have to be drastically reduced in order to observe any ultrastrong coupling effects. This can perhaps be achieved by lowering the temperature, considering metallodielectric cavities with high dielectric index, or using quantum circuits [22].

Figure 2 renders, for different values of λ and g, the time evolution of the photon number $P(t) \equiv \langle a^+a\rangle(t)$ (the exciton number $E(t) = \langle\sigma^+\sigma^-\rangle(t)$ is complementary to $P(t)$, as their sum is 1). Each panel shows the comparison between the calculations using the full HQR and the HJC models. In the $\lambda = 0$ case, the vibrational degrees of freedom decouple and, for the considered initial condition, the system is always in the zero-vibration state. Thus, the molecule behaves as a 2LS and the system maps into traditional CQED, where ultrastrong coupling effects are negligible for $g = 0.05$ (Figure 2B) and very small even for

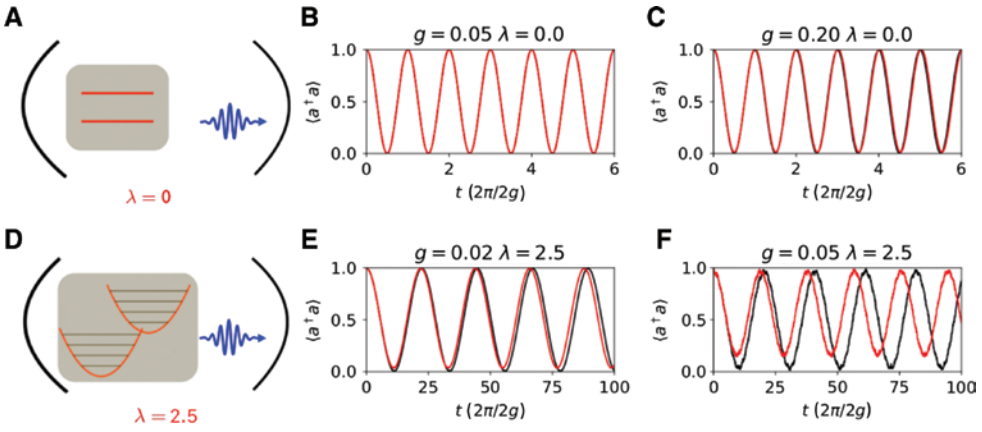

Figure 2: Time evolution of the average number of photons, $P(t)$, for different values of λ and g.
The photon and the zero-phonon exciton are considered to be in resonance, $\omega_c = \Delta$, and $\omega_v = 0.075$. Each panel shows the comparison between the full HQR model (red curves) and the one without the CR terms (Holstein-Jaynes-Cummings model, black curves). Top panels (A–C) are for $\lambda = 0$, and bottom ones (D–F) are for $\lambda = 2.5$. The case $g = 0.05$ is rendered for both values of λ, while the other panels are representative of the values g needed for ultrastrong coupling effects to appear for each λ.

$g = 0.2$ (Figure 2C). As shown in the figure, the frequency of the Rabi oscillations Ω_R strongly decreases with λ. This occurs because the oscillations mainly involve the two lowest polaritonic states, whose energy decreases with λ (as shown in Figure 1C). But, notably, the influence of the CR terms on the dynamics is strongly enhanced for larger values of λ, as shown by the incompleteness of Rabi oscillations in the lower panels of Figure 2. This is highlighted in Figure 3, which renders the comparison between the time-averaged values for $P(t)$, $E(t)$, and $V(t) \equiv \langle b^\dagger b \rangle(t)$ when the CR terms have been either considered or neglected, as a function of λ. In the last ("Jaynes-Cummings") case,

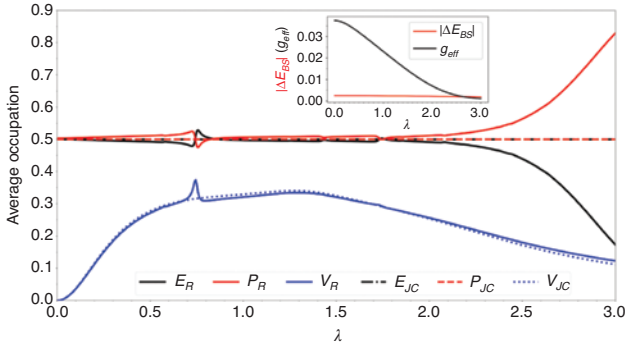

Figure 3: Time-averaged number of excitons (E), photons (P), and molecular vibrations (V) as a function of λ.
Continuous lines are computed using the Holstein-Quantum-Rabi model, while dashed lines were computed by neglecting the counter-rotating terms (HJC model). The inset shows the Bloch-Siegert correction to the photon energy, $\Delta E_{BS}(|\downarrow, 1, 0\rangle)$, and the effective value of g (i.e. half their energy difference between the two lowest polaritons). The parameters used are $\omega_c = \Delta = 1$, $\omega_v = 0.075$, and $g = 0.05$.

$P_{JC} = E_{JC} = 1/2$ for all λ. The presence of CR terms change the occupations in two ways. First, they "dress" the bare energies of the states ("Bloch-Siegert" effect). This can be taken into account considering H_{CR} as a perturbation to the HJC Hamiltonian. Within second order, the Bloch-Siegert corrections to the bare eigen energies are

$$\Delta E_{BS}(|\downarrow, 1, 0\rangle) = g^2 \sum_{\tilde{n}} \frac{|\langle \uparrow, 2, \tilde{n}|\sigma^+ a^+|\downarrow, 1, 0\rangle|^2}{\omega_c - (\Delta + 2\omega_c + \tilde{n}\omega_v)}$$
$$\approx -\frac{2g^2}{\omega_c + \Delta + \lambda^2 \omega_v}, \quad \Delta E_{BS}(|\uparrow, 0, \tilde{0}\rangle) = 0, \tag{4}$$

where, in the approximation to $\Delta E_{BS}(|\downarrow, 1, 0\rangle)$, we have used the following properties of the Frank-Condon factors: (i) $\langle \tilde{n}|0\rangle$ is peaked at $\tilde{n} = \lambda^2$ and (ii) $\sum_{\tilde{n}} |\langle \tilde{n}|m\rangle|^2 = 1$. The important point is that the Bloch-Siegert corrections dress the exciton and photon states differently. This "ultrastrong" mechanism can be incorporated into an effective Jaynes-Cummings model by "renormalizing" the photon frequency $\omega_c \to \omega_c + \Delta E_{BS}(|\downarrow, 1, 0\rangle)$, which clearly affects whether the photon is in resonance with the exciton or not. This shift, combined with the strong renormalization of the effective coupling that occurs at large λ, brings the exciton and photon out of resonance. This is illustrated in the inset to Figure 3. Assuming the bare resonant condition $\omega_c = \Delta$, the system essentially remains at resonance for values of λ such that $|\Delta E_{BS}(|\downarrow, 1, 0\rangle)| < g_{eff}$, thus developing complete Rabi oscillations. But these cease to happen when $|\Delta E_{BS}(|\downarrow, 1, 0\rangle)|$ and g_{eff} are comparable (for $\lambda \gtrsim 2.5$ in the inset to Figure 3, computed for $g = 0.05$). As $g_{eff} \sim g$, while $\Delta E_{BS} \sim g^2$, the BS corrections are more relevant for larger exciton-photon interactions but, admittedly, this effect plays a role only for large values of λ. It is worth

noting that the CR parity-breaking terms we mentioned when discussing the effective Hamiltonian (3) cancel when the "renormalized" cavity is in resonance with the 2LS, i.e. when $\omega_c + \Delta E_{BS} = \Delta$. In that case, Hamiltonian (3) is virtually exact in the polariton subspace, for all values of g, ω_v, and λ.

The second way in which the CR terms modify the occupations occurs at smaller values of λ. It works via mixing states which would be orthogonal within the HJC Hamiltonian but anti-cross when the CR terms are considered (which, as mentioned before and shown in Figure 1, occurs for the states P_{0+} and P_{2-} at $\lambda \approx 0.74$). This mixing allows P_{0+} to couple to P_{2-}, thus enhancing the average number of phonons P (see the peak in P in Figure 3, at $\lambda \approx 0.74$).

3 Conclusions and outlook

We have analyzed the CQED setup where a molecule plays the role of a 2LS, in the case where the bare photon and exciton are in resonance. We have shown that, due to the presence of molecular vibrations, the CR terms in the photon-exciton coupling may influence the Rabi oscillations at much smaller coupling strengths that usually are required in other CQED setups. We have also shown that even when the CR terms are negligible, the polariton energy sector is described by an effective QR Hamiltonian where the two polariton states play the role of the 2LS and molecular vibrations play the role of photons. Future work should analyze how these effects are affected by the presence of different decay channels, how these ultrastrong coupling effects scale with the number of molecules, and what their possible influence would be on the properties of dark modes.

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References

[1] Haroche S, Raimond JM. Exploring the quantum: atoms, cavities, and photons. Oxford, Oxford University Press, 2006.
[2] Zrenner A, Beham E, Stufler S, Findeis F, Bichler M, Abstreiter G. Coherent properties of a two-level system based on a quantum-dot photodiode. Nature 2002;418:612–4.
[3] Jelezko F, Gaebel T, Popa I, Gruber A, Wrachtrup J. Observation of coherent oscillations in a single electron spin. Phys Rev Lett 2004;92:076401.
[4] Schoelkopf RJ, Girvin SM. Wiring up quantum systems. Nature 2008;451:664–9.
[5] Hutchison JA, Schwartz T, Genet C, Devaux E, Ebbesen TW. Modifying chemical landscapes by coupling to vacuum fields. Angew Chem Int Ed 2012;51:1592–6.
[6] Feist J, Garcia-Vidal FJ. Extraordinary exciton conductance induced by strong coupling. Phys Rev Lett 2015;114:196402.
[7] Schachenmayer J, Genes C, Tignone E, Pupillo G. Cavity-enhanced transport of excitons. Phys Rev Lett 2015;114:196403.
[8] Orgiu E, George J, Hutchison JA, et al. Conductivity in organic semiconductors hybridized with the vacuum field. Nat Mater 2015;14:1123EP.
[9] Zengin G, Wersäll M, Nilsson S, Antosiewicz TJ, Käll M, Shegai T. Realizing strong light-matter interactions between single-nanoparticle plasmons and molecular excitons at ambient conditions. Phys Rev Lett 2015;114:157401.
[10] Chikkaraddy R, de Nijs B, Benz F, et al. Single-molecule strong coupling at room temperature in plasmonic nanocavities. Nature 2016;535:127–30.
[11] Haran G, Chuntonov L. Artificial plasmonic molecules and their interaction with real molecules. Chem Rev 2018;118:5539–80. PMID: 29781601.
[12] Forn-Daz P, Lamata L, Rico E, Kono J, Solano E. Ultrastrong coupling regimes of light-matter interaction. Rev Mod Phys 2019;91:025005.
[13] Kockum AF, Miranowicz A, De Liberato S, Savasta S, Nori F. Ultrastrong coupling between light and matter. Nat Rev Phys 2019;1:19–40.
[14] Faez S, Türschmann P, Haakh HR, Götzinger S, Sandoghdar V. Coherent interaction of light and single molecules in a dielectric nanoguide. Phys Rev Lett 2014;113:213601.
[15] Jenkins M, Hümmer T, Martnez-Pérez MJ, Garca-Ripoll J, Zueco D, Luis F. Coupling single-molecule magnets to quantum circuits. New J Phys 2013;15:095007.
[16] del Pino J, Feist J, Garcia-Vidal FJ. Signatures of vibrational strong coupling in raman scattering. J Phys Chem C 2015;119:29132–7.
[17] Ćwik JA, Kirton P, De Liberato S, Keeling J. Excitonic spectral features in strongly coupled organic polaritons. Phys Rev A 2016;93:033840.
[18] Herrera F, Spano FC. Cavity-controlled chemistry in molecular ensembles. Phys Rev Lett 2016;116:238301.
[19] Neuman T, Esteban R, Giedke G, Schmidt MJ, Aizpurua J. Quantum description of surface-enhanced resonant Raman scattering within a hybrid-optomechanical model. Phys Rev A 2019;100:043422.
[20] Niemczyk T, Deppe F, Huebl H, et al. Circuit quantum electrodynamics in the ultrastrong-coupling regime. Nat Phys 2010;6:772–6.
[21] Brandes T. Phonons in electronic transport in nanoscale systems. Lecture Notes Caltech NEMS Summer School, 2007.
[22] Hu L, Ma Y-C, Xu Y, et al. Simulation of molecular spectroscopy with circuit quantum electrodynamics. Sci Bull 2018;63:293–9.
[23] Sanchez-Carrera R, Delgado MCR, Ferran CC, et al. Optical absorption and emission properties of end-capped oligothienoacenes: A joint theoretical and experimental study. Org Electron 2010;11:1701–12.
[24] Herrera F, Spano FC. Absorption and photoluminescence in organic cavity qed. Phys Rev A 2017;95:053867.
[25] Wu N, Feist J, Garcia-Vidal FJ. When polarons meet polaritons: exciton-vibration interactions in organic molecules strongly coupled to confined light fields. Phys Rev B 2016;94:195409.