Quantum Coherent Control of a Single Molecular-Polariton Rotation

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We present a combined analytical and numerical study for coherent terahertz control of a single molecular polariton, formed by strongly coupling two rotational states of a molecule with a single-mode cavity. Compared to the bare molecules driven by a single terahertz pulse, the presence of a cavity strongly modifies the postpulse orientation of the polariton, making it difficult to obtain its maximal degree of orientation. To solve this challenging problem toward achieving complete quantum coherent control, we derive an analytical solution of a pulse-driven quantum Jaynes-Cummings model by expanding the wave function into entangled states and constructing an effective Hamiltonian. We utilize it to design a composite terahertz pulse and obtain the maximum degree of orientation of the polariton by exploiting photon blockade effects. This Letter offers a new strategy to study rotational dynamics in the strong-coupling regime and provides a method for complete quantum coherent control of a single molecular polariton. It, therefore, has direct applications in polariton chemistry and molecular polaritonics for exploring novel quantum optical phenomena.

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Since the pioneering experimental work by Ebbesen and collaborators in 2012 [1], strong light-matter interactions between an internal mode of molecules and a cavity-photon mode have attracted substantial attention in chemistry and physics [2–8]. It promptly established an emerging field within chemistry called polariton chemistry [9–14], bringing together quantum optics and chemical physics. Considerable experimental and theoretical works have demonstrated that strong light-matter coupling can significantly modify the physical and chemical properties of molecules [15–20]. Experimentally, it has become possible to achieve vibrational-strong coupling (VSC) of a single molecule with nanocavities even at room temperature [21,22]. The formation of vibrational polaritons as the quantum superpositions of molecular vibrations and cavity-photon modes offers an alternative approach for selective activation of chemical bonds and an efficient pathway for energy transfer between molecules [23–28].

The rotational degree of freedom of molecules can provide physical insights into light-matter interactions beyond the VSC limit. This Letter explores the rotational-strong coupling (RSC) and focuses on quantum control of molecular rotation [29–32]. Recent experiments have shown how to orient single polar molecules on a surface with maximum precision using the electric field of a scanning turning microscope [33] and how to control the orientation of molecules inside a cavity for enhancing the VSC [34]. However, the generation of postpulse orientation of a single molecule inside a cavity remains unexplored, which is related to a phenomenon known as field-free orientation [35]. In the absence of a cavity, there has been significant progress for generating postpulse orientation of molecules using resonant terahertz pulses [35–48] or nonresonant optical pulses [49–51]. It is crucial to show how cavity quantum electrodynamics (cQED) effects modify such a phenomenon as a direct consequence of RSC.

In this Letter, we theoretically explore the realization of the maximal postpulse orientation of a single polariton irradiated by pulsed terahertz fields, which is of much current interest to the existing techniques on molecular orientation and the field of single-molecule strong coupling in cavities. We examine an archetypal model of RSC for two rotational states of a single molecule inside a single-mode cavity. Previously, by combining a long nonresonant laser pulse and a weak static electric field to mix the lowest two rotational states with equal weights, the maximal two-state-postpulse orientation has been demonstrated experimentally for ultracold carbonyl sulfide (OCS) molecules without a cavity [52]. Here, we show that this orientation maximum is reachable for the bare molecule using a single terahertz pulse without using a static electric field. Furthermore, the orientation features are strongly modified when placing the

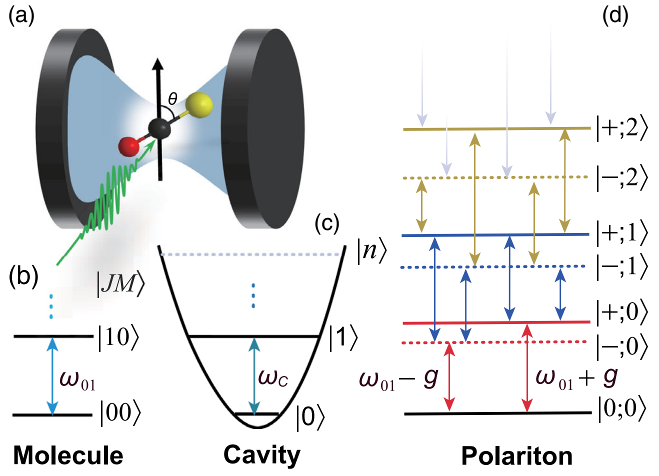

FIG. 1. (a) Schematic of a pulse-driven molecular polariton and the corresponding energy levels. A single molecule with rotational states $|JM\rangle$ at a rotational frequency ω_{01} in (b) is strongly coupled with a single-mode cavity with photon states $|n\rangle$ at a frequency ω_c in (c), resulting in entangled states $|0;0\rangle$ and $|\pm;n\rangle$ in (d). θ denotes the angle between the molecular axis and the driving field's polarization vector.

molecule into a cavity, showing a direct signature of hybrid entangled states. By expanding the time-dependent wave function into entangled states and using an effective Hamiltonian, we derive an analytical solution of a pulse-driven quantum Jaynes-Cummings (JC) model [53] to describe the molecular-polariton dynamics without the rotating wave approximation (RWA). We then utilize it to design a complete quantum coherent control scheme, which can achieve the orientation maximum of the polariton by controlling the amplitude and phase of a composite terahertz pulse while exploiting quantum blockade effects.

We consider a single polar molecule initially in the absolute-ground state strongly coupled with a single-mode cavity of a frequency ω_c and driven by a linearly polarized terahertz pulse $\mathcal{E}(t)$, as illustrated in Fig. 1(a). By setting the laser field's polarization vector $\hat{\mathbf{e}}$ along the cavity one, the total Hamiltonian of the molecule in the presence of the cavity and pulsed fields can be described in the dipole gauge by ($\hbar = 1$) [54–56]

$$\hat{H}_{\rm tot}(t) = B\hat{J}^2 + \omega_c\hat{a}^\dagger\hat{a} - \sqrt{\frac{\omega_c}{2\epsilon_0 V}}\hat{\boldsymbol{\mu}}\cdot\hat{\mathbf{e}}(\hat{a}+\hat{a}^\dagger) - \hat{\boldsymbol{\mu}}\cdot\hat{\mathbf{e}}\mathcal{E}(t), \tag{1}$$

where the first term is the field-free rigid-rotor Hamiltonian with the angular momentum operator $\hat{J}$ and rotational constant B, and the second one denotes the cavity field Hamiltonian with $\hat{a}^\dagger$ ($\hat{a}$) being the creation (annihilation) photon operators. The last two terms in Eq. (1) describe the interactions of the molecule with a cavity and a laser field, respectively, where ϵ_0, V, and $\hat{\boldsymbol{\mu}}$ represent the electric constant, volume of the electromagnetic mode, and dipole operator of the molecule.

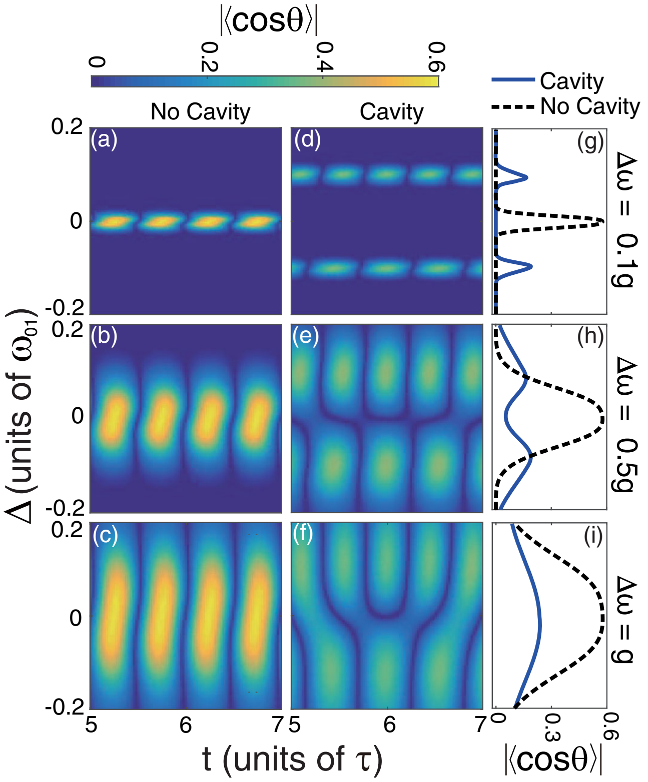

FIG. 2. The dependence of the numerically calculated time-dependent degree of orientation $|\langle\cos\theta\rangle(t)|$ on the laser frequency detuning Δ with time in units of the full revival period τ of the bare molecule. The comparisons without [(a)–(c)] and with [(d)–(f)] a cavity are calculated with three different pulse bandwidths $\Delta\omega = 0.1g$ (top), $0.5g$ (middle), and $1.0g$ (bottom) while keeping other parameters unchanged. (g)–(i) The simulations of $\langle\cos\theta\rangle(t)$ versus Δ at a given time $t = 6.75\tau$.

In the absence of the second and third terms in Eq. (1), postpulse orientation of the bare molecule can be generated by applying resonant terahertz laser pulses [47,48]. By designing a single terahertz pulse to satisfy the condition $|\mu_{01}\int_{t_0}^{t_f}\mathcal{E}(t)\exp[i\omega_{01}t]dt| = |\theta_{01}(t_f)| = \pi/4$ with $\mu_{01} = \langle 00|\hat{\boldsymbol{\mu}}\cdot\hat{\mathbf{e}}|10\rangle$ and $\omega_{01} = 2B$, while keeping its bandwidth narrow enough, we obtain a coherent superposition of rotational states $|00\rangle$ and $|10\rangle$ with equal weights without populating higher rotational states. The corresponding postpulse orientation reaches the maximum of $\langle\cos\theta\rangle_{\max} = \sqrt{3}/3 \approx 0.5774$ with the revival period of $\tau = \pi/B$, which can be modified by applying a weak static field [57]. In the presence of strong molecule-cavity coupling, the third term in Eq. (1) mixes the bare molecular and photon states into hybrid entangled states in Figs. 1(b)–1(d).

To examine how the cQED affects the postpulse orientation of the bare molecule, we consider OCS molecules at ultralow temperatures as an example with $B = 0.202\,86\ \mathrm{cm}^{-1}$ and $\mu = 0.715$ D. Figure 2 shows

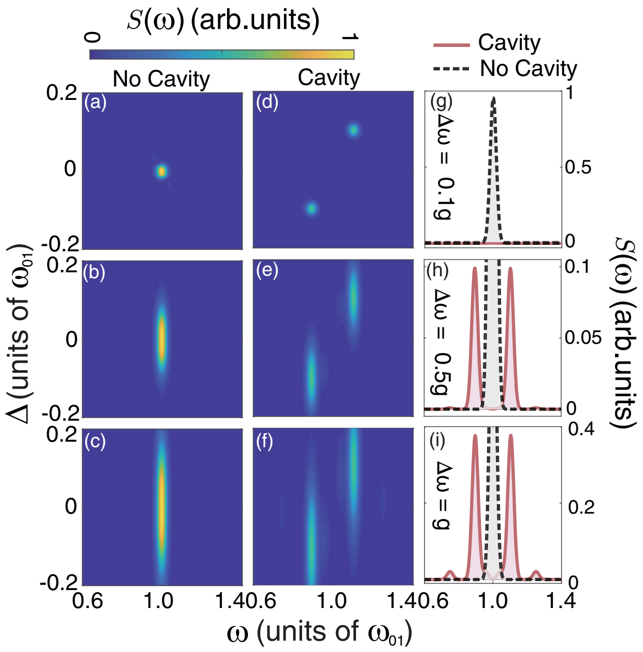

FIG. 3. The corresponding Fourier transform spectra $S(\omega)$ of $\langle\cos\theta\rangle(t)$ in Fig. 2. The comparisons without [(a)–(c)] and with [(d)–(f)] a cavity are calculated at three different laser bandwidths $\Delta\omega = 0.1g$ (top), $0.5g$ (middle), and $1.0g$ (bottom). (g)–(i) The simulations of $S(\omega)$ at detuning $\Delta = 0$.

the comparisons of the time-dependent degree of orientation $\langle\cos\theta\rangle(t)$ without and with a cavity. We consider the cavity mode in resonance with the transition between $|00\rangle$ and $|10\rangle$ with $\omega_c = \omega_{01}$ and set the strength of the polariton interaction $g = \sqrt{\omega_c/(2\epsilon_0 V)}\langle 00|\mu\cos\theta|10\rangle = 0.1\omega_{01}$. A Gaussian-profile pulse $\mathcal{E}(t) = \mathcal{E}_0 f(t)\cos(\omega_0 t + \phi_0)$ is used, where $f(t) = \exp[-t^2/2\tau_0^2]$ and $\mathcal{E}_0 = \sqrt{2/\pi}A_0/(\mu_{01}\tau_0)$ with the duration τ_0, center frequency ω_0, and absolute phase ϕ_0. This choice leads to $|\theta_{01}(t_f)| = A_0$ at the frequency ω_0, independent of duration τ_0. We examine the differences with the use of the pulse at three different bandwidths $\Delta\omega = 1/\tau_0 = 0.1g, 0.5g$, and $1.0g$ while fixing $A_0 = \pi/4$ and $\phi_0 = 0$. At each given $\Delta\omega$, we perform the simulations by scanning the frequency detuning $\Delta = \omega_0 - \omega_{01}$, from $-0.2\omega_{01}$ to $0.2\omega_{01}$.

Figure 2 shows that the polariton's postpulse orientation phenomena are very distinct from the bare molecule one. For the case $\omega_0 = \omega_{01}$, the orientation maximum 0.5774 appears in the bare molecule for different pulse bandwidths. For the polariton, however, the postpulse orientation is affected and even disappears using a narrow-bandwidth pulse. As $|\Delta|$ becomes large, the orientation maximum of the bare molecule decreases, whereas the polariton one becomes visible. Interestingly, the oscillation period of the polariton orientation becomes longer (shorter) for the negative (positive) detuning compared to the bare molecule. It implies that the manipulation of the molecule-driving pulse can selectively control the rotation speed of the molecule in a cavity.

To understand the cQED effect in Fig. 2, we perform an analysis using the hybrid entangled states [53,58]. We treat the first three terms in Eq. (1) under the JC model Hamiltonian $\hat{H}_{\mathrm{JC}} = \omega_{01}|10\rangle\langle 10| + \omega_c\hat{a}^\dagger\hat{a} + g(|00\rangle\langle 10|\hat{a}^\dagger + \hat{a}|10\rangle\langle 00|)$. By diagonalizing the Hamiltonian $\hat{H}_{\mathrm{JC}}$ at the resonant cavity-molecule coupling $\omega_c = \omega_{01}$, we obtain the polariton's eigenenergies $\omega_{0,0} = 0$ and $\omega_{\pm,n} = \omega_c(n+1)\pm g\sqrt{n+1}$, associated with the vacuum ground state $|0;0\rangle = |00\rangle|0\rangle$ and maximally entangled states $|\pm;n\rangle = \sqrt{2}/2\,(|00\rangle|n+1\rangle \pm |10\rangle|n\rangle)$. The pulsed-driven polariton's Hamiltonian in terms of hybrid entangled states reads

$$\hat{H}_{\mathrm{p}}(t) = \sum_{n=0}^{\infty}\sum_{\ell=\pm}\omega_{\ell,n}|\ell;n\rangle\langle\ell;n| - \mathcal{E}(t) \times \sum_{\ell=\pm}\tilde{\mu}_0(|\ell;0\rangle\langle 0;0| + |0;0\rangle\langle\ell;0|) - \mathcal{E}(t)\sum_{n=1}^{\infty}\sum_{\ell,\ell'=\pm}\tilde{\mu}_\ell(|\ell;n\rangle\langle\ell';n-1| + |\ell';n-1\rangle\langle\ell;n|), \tag{2}$$

where $\tilde{\mu}_0 = \pm\sqrt{2}/2\mu_{01}$ and $\tilde{\mu}_\pm = \pm 1/2\mu_{01}$ denote the transition dipole moments between entangled states with $\mu_{01} = \langle 00|\mu\cos\theta|10\rangle = \sqrt{3}/3\mu$. The RSC splits the excited states $|\pm;n\rangle$ by the Rabi splitting $2\sqrt{n+1}g$ and modifies the dipole moments, as shown in Figs. 1(b)–1(d).

Figure 3 shows the Fourier-transform spectra of the calculated time-dependent degree of orientation in Fig. 2, i.e., $S(\omega) = |\int_{t_0}^{\infty}dt\langle\cos\theta\rangle(t)\exp(i\omega t)|$, which can be used to retrieve the transitions between the involved dressed states. For a resonant molecule-driving $\omega_0 = \omega_{01}$ with a narrow bandwidth $\Delta\omega = 0.1g$ in Figs. 3(a), 3(d), and 3(g), the vacuum Rabi splitting blocks one-photon transition from $|0;0\rangle$ to $|\pm,0\rangle$, leading to the disappearance of the orientation in Fig. 2(d) for $\Delta = 0$. By tuning ω_0 away from ω_{01}, the two states $|\pm;0\rangle$ can be excited independently, resulting in an orientation enhancement at $\Delta = g$ and $-g$ in Fig. 2. For the molecule driving with broad bandwidths of $\Delta\omega = 0.5g$ and $1.0g$, the spectra in Figs. 3(e), 3(f), 3(h), 3(i) consist of symmetric doublet peaks around the bare-molecule resonances. The first doublet peaks at $\omega_{01}\pm g$ in Figs. 3(e) and 3(h) imply that the laser field described by the second term in Eq. (2) drives the transitions from $|0;0\rangle$ to $|\pm;0\rangle$ in Fig. 1(d) simultaneously. The higher-lying doublet peaks become visible in Figs. 3(f) and 3(i), corresponding to the further transitions from $|\pm;0\rangle$ to $|\pm;1\rangle$. The corresponding orientation phenomena become much more complex in Figs. 2(e) and 2(f) than the bare two-state molecule in Figs. 2(b) and 2(c). It opens an important question of whether there exists a theoretical orientation

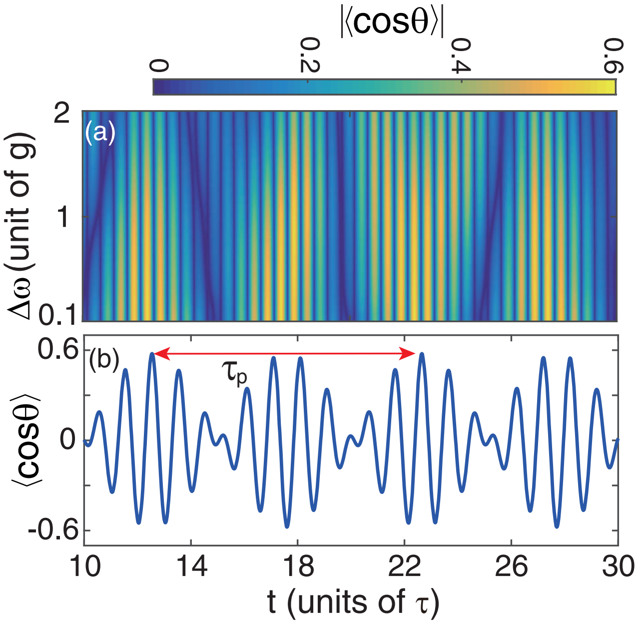

FIG. 4. The numerically calculated postpulse orientation of the polariton driven by an optimized laser pulse. (a) The time-dependent degree of orientation $|\langle\cos\theta\rangle(t)|$ versus the bandwidth $\Delta\omega$ of the laser pulses, (b) $\langle\cos\theta\rangle(t)$ at a narrow bandwidth of $\Delta\omega = 0.1g$. The red arrows indicate the revival period τ_p of the polariton.

maximum and how to achieve it for such a molecular rotational polariton.

To address this challenging question, we expand the time-dependent wave function $|\psi(t)\rangle$ into the hybrid entangled states

$$|\psi(t)\rangle = \sum_{\ell=0,\pm} C_{\ell,0} e^{-i\omega_{\ell,0}t}|\ell;0\rangle + \sum_{n'=1}^{\infty}\sum_{\ell'=\pm} C_{\ell',n'} e^{-i\omega_{\ell',n'}t}|\ell';n'\rangle, \tag{3}$$

where $C_{\ell,0}$ denote the complex coefficients of the lowest three states $|0;0\rangle$ and $|\pm;0\rangle$, and $C_{\pm,n}$ correspond to the complex coefficients of the higher-lying doublet states $|\pm;n\rangle$ with $n > 0$. Based on the method of Lagrange multipliers [59,60], we conclude that the orientation maximum of the polariton is $\langle\cos\theta\rangle_{\max} = \sqrt{3}/3$, the same as for the bare molecule [57]. In this Letter, we achieve this maximum by generating a coherent superposition of the lowest three states with $|C_{0,0}|^2 = 0.5$, $|C_{+,0}|^2 = |C_{-,0}|^2 = 0.25$, while satisfying a phase relation of $\omega_{-,0}\arg[C_{+,0}] - \omega_{+,0}\arg[C_{-,0}] = 2g\pi$. This implies that $|C_{\pm,n'}| = 0$ in the second term in Eq. (3) by blocking the transitions driven by the third term in Eq. (2).

Since the usual pulse area theorem with the RWA [61,62] fails to include the pulse-phase information explicitly, we derive an analytical solution of the time-dependent wave function within the pulse-driven quantum JC model described by Eq. (2) without the RWA, which remains challenging in quantum optics [63–69]. We consider the model including the lowest three states $|0;0\rangle$ and $|\pm;0\rangle$ and the second higher-lying doublet states $|\pm;1\rangle$. We describe the transitions between the five states using an effective three-level model with sublevels [57] and involving the first-order Magnus expansion of the unitary operator [47,48,70–72]. The corresponding time-dependent wave function for the polariton starting from $|0;0\rangle$ reads [57]

$$\begin{aligned}|\psi^{(1)}(t)\rangle =& \frac{|\theta_1(t)|^2 + |\theta_0(t)|^2\cos\theta(t)}{\theta^2(t)}|0;0\rangle\\ &+ \frac{i\sin\theta(t)}{\theta(t)}\sum_{\ell=\pm}\theta_{l,0}(t)e^{i\omega_{l,0}t}|\ell;0\rangle\\ &+ \frac{\cos\theta(t)-1}{\theta^2(t)}\sum_{\ell=\pm}\sum_{s=\pm}\theta_{s,0}(t)\theta_{s,\ell,1}(t)e^{i\omega_{\ell,1}t}|\ell;1\rangle,\end{aligned} \tag{4}$$

where we define $\theta_0(t) = \sqrt{|\theta_{+,0}(t)|^2 + |\theta_{-,0}(t)|^2}$ with $\theta_{\pm,0}(t) = \tilde{\mu}_0\int_{t_0}^{t} dt'\,\mathcal{E}(t')\exp(-i\omega_{\pm,0}t')$, and $\theta(t) = \sqrt{|\theta_0(t)|^2 + |\theta_1(t)|^2}$ with $\theta_1(t) = \sqrt{|\theta_{+,1}(t)|^2 + |\theta_{-,1}(t)|^2}$, by setting $\theta_{\ell',1}(t) = \sqrt{|\theta_{+,\ell',1}(t)|^2 + |\theta_{-,\ell',1}(t)|^2}$ with $\theta_{s,\pm,1} = \tilde{\mu}_s\int_{t_0}^{t} dt'\,\mathcal{E}(t')\exp[i(\omega_{s,0} - \omega_{\pm,1})t']$.

Based on Eq. (4), we conclude that the transitions to $|\pm,1\rangle$ can be perfectly blocked as long as $\mathcal{E}(t)$ satisfies the condition $|\theta_{\pm,1}(t_f)| = 0$, reducing Eq. (4) into a V-type-three-level solution [70]. It provides an alternative strategy to achieve the theoretical orientation maximum $\sqrt{3}/3$ by designing $\mathcal{E}(t)$ to satisfy the following conditions [57]:

$$|\theta_{\pm,0}(t_f)| = \frac{\sqrt{2}\pi}{8}, \tag{5a}$$

$$\omega_{-,0}\arg[\theta_{+,0}(t_f)] - \omega_{+,0}\arg[\theta_{-,0}(t_f)] = \pm g\pi. \tag{5b}$$

The amplitude condition by Eq. (5a) ensures optimal population distributions with 0.5 in $|0;0\rangle$ and 0.25 in $|\pm,0\rangle$. The phase condition by Eq. (5b) enables that the faster coherence between $|0;0\rangle$ and $|+;0\rangle$ constructively interferes with the slower one between $|0;0\rangle$ and $|-;0\rangle$.

We perform numerical simulations to determine the orientation maximum of the polariton. A composite laser field $\mathcal{E}(t) = \mathcal{E}_0 f(t)\sum_{\ell=\pm}\cos(\omega_{\ell,0}t + \phi_{\ell,0})$ is applied in Eq. (2) with choices of $\mathcal{E}_0 = \sqrt{2/\pi}A_1/(\tilde{\mu}_0\tau_0)$, $A_1 = \sqrt{2}\pi/8$, $\phi_{-,0} = 0$ and $\phi_{+,0} = \pi/9$, which satisfies both the amplitude and phase conditions in Eq. (5). Figure 4 shows the dependence of $\langle\cos\theta\rangle(t)$ on the pulse bandwidth $\Delta\omega$. The degree of orientation in the narrow-bandwidth regime can reach the maximum, i.e., 0.5774, and decreases in the

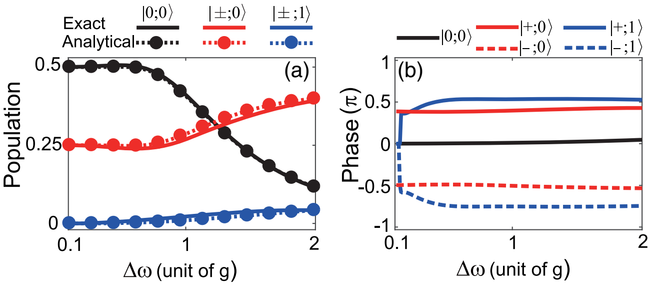

FIG. 5. The final populations (a) and phases (b) in states $|0;0\rangle$, $|\pm;0\rangle$ and $|\pm;1\rangle$ versus the bandwidth $\Delta\omega$ of two laser pulses. The exactly solved numerical results (solid line) are compared with the analytical ones (dashed lines) in (a).

broad-bandwidth regime. As shown in Figs. 4(a) and 4(b), the orientation dynamics exhibits much more complex revival behaviors than the bare two-state molecule. The revival period of the polariton is significantly prolonged to $\tau_p = 10\tau$, in agreement with the theoretical value [57].

Figure 5 shows the final populations and phases in states $|0;0\rangle$, $|\pm;0\rangle$, and $|\pm;1\rangle$ versus the bandwidth $\Delta\omega$ of the composite laser fields. Exact numerical results using the wave function in Eq. (3) are compared with the analytical theoretical ones in Eq. (4). In the narrow bandwidth regime, the final populations as expected are localized in the lowest three states $|0;0\rangle$ and $|\pm;0\rangle$ with optimal distributions, where the photon blockade effects take place without populating $|\pm;1\rangle$. As the bandwidth increases, the population transfers to $|\pm;1\rangle$ in Fig. 5(a) become visible, and the phase values of the lowest three states in Fig. 5(b) deviate slightly from the theoretical values that keep unchanged in the narrow bandwidth regime. This implies that the condition $|\theta_{\pm,1}(t_f)| = 0$ breaks down in the broad bandwidth regime, resulting in the dependence of orientation on the bandwidth in Fig. 4. The slight differences between the exactly and analytically calculated results in Fig. 5(a) may come from the transitions via higher-order Magnus terms, ignored in the analytical solution in Eq. (4) [47,48].

To conclude, we contributed theoretical proof to complete quantum coherent control of rotational dynamics at a single molecular-polariton level. As a proof of principle, we performed simulations by considering a single-mode cavity in resonance with the lowest two rotational states of a single molecule driven by a terahertz pulse with a narrow bandwidth. Our results illustrated that the presence of the cavity reduces the theoretical orientation maximum of the polariton and modifies its revival period. We derived an analytical solution of the pulse-driven quantum Jaynes-Cummings model by describing the polariton in terms of hybrid entangled states and utilized it to design the molecule-driving fields. We demonstrated that the theoretical orientation maximum of the polariton could be revived to the same value as the bare molecule by controlling the amplitude and phase parameters of a composite terahertz field.

To the best of our knowledge, this is the first exploration of the postpulse orientation of molecules in a cavity, providing a direct signature of the RSC. This Letter offers a strategy for complete quantum coherent control of strongly coupled molecule-cavity systems, a long-standing goal in chemistry and physics [73–75]. A natural extension of the present Letter would be to explore novel quantum optical phenomena of the molecular polariton in the ultrastrong, even deep-strong coupling regimes [76,77]. It would also be interesting to extend the present method to a multimolecule Jaynes-Cumming model [76–79], significantly reducing the requirement of the coupling strength of the cavity to each molecule. The experimental implementation of coherent control of molecular rotation in cavities requires the state of the art of microcavity techniques, for which molecule-cavity strong and ultrastrong coupling in the terahertz regime has been observed recently in different experiments [80,81].

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[1] J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, and T. W. Ebbesen, Modifying chemical landscapes by coupling to vacuum fields, Angew. Chem., Int. Ed. **51**, 1592 (2012).
[2] G. Zengin, M. Wersäll, S. Nilsson, T. J. Antosiewicz, M. Käll, and T. Shegai, Realizing Strong Light-Matter Interactions between Single-Nanoparticle Plasmons and

Molecular Excitons at Ambient Conditions, Phys. Rev. Lett. **114**, 157401 (2015).

[3] M. Kowalewski, K. Bennett, and S. Mukamel, Cavity femtochemistry: Manipulating nonadiabatic dynamics at avoided crossings, J. Phys. Chem. Lett. **7**, 2050 (2016).

[4] J. Flick, M. Ruggenthaler, H. Appel, and A. Rubio, Atoms and molecules in cavities, from weak to strong coupling in quantum-electrodynamics (QED) chemistry, Proc. Natl. Acad. Sci. U.S.A. **114**, 3026 (2017).

[5] T. Szidarovszky, G. J. Halász, A. G. Császár, L. S. Cederbaum, and Á. Vibók, Direct signatures of light-induced conical intersections on the field-dressed spectrum of Na_2, J. Phys. Chem. Lett. **9**, 2739 (2018).

[6] T. Szidarovszky, G. J. Halász, A. G. Császár, L. S. Cederbaum, and Á. Vibók, Conical intersections induced by quantum light: Field-dressed spectra from the weak to the ultrastrong coupling regimes, J. Phys. Chem. Lett. **9**, 6215 (2018).

[7] A. Mandal, S. M. Vega, and P. Huo, Polarized Fock states and the dynamical Casimir effect in molecular cavity quantum electrodynamics, J. Phys. Chem. Lett. **11**, 9215 (2020).

[8] S. Hughes, A. Settineri, S. Savasta, and F. Nori, Resonant Raman scattering of single molecules under simultaneous strong cavity coupling and ultrastrong optomechanical coupling in plasmonic resonators: Phonon-dressed polaritons, Phys. Rev. B **104**, 045431 (2021).

[9] R. F. Ribeiro, L. A. Martínez-Martínez, M. Du, J. Campos-Gonzalez-Angulo, and J. Yuen-Zhou, Polariton chemistry: Controlling molecular dynamics with optical cavities, Chem. Sci. **9**, 6325 (2018).

[10] X. Yu, Y. Yuan, J. Xu, K.-T. Yong, J. Qu, and J. Song, Strong coupling in microcavity structures: Principle, design, and practical application, Laser Photonics Rev. **13**, 1800219 (2019).

[11] M. Hertzog, M. Wang, J. Mony, and K. Börjesson, Strong light-matter interactions: A new direction within chemistry, Chem. Soc. Rev. **48**, 937 (2019).

[12] T. S. Haugland, E. Ronca, E. F. Kjønstad, A. Rubio, and H. Koch, Coupled Cluster Theory for Molecular Polaritons: Changing Ground and Excited States, Phys. Rev. X **10**, 041043 (2020).

[13] S. Latini, D. Shin, S. A. Sato, C. Scäfer, U. De Giovannini, and Hübener, A. Rubio, The ferroelectric photo ground state of SrTiO3: Cavity materials engineering, Proc. Natl. Acad. Sci. U.S.A. **118**, e2105618118 (2021).

[14] F. J. Garcia-Vidal, C. Ciuti, and T. W. Ebbesen, Manipulating matter by strong coupling to vacuum fields, Science **373**, 6551 (2021).

[15] J. Galego, F. J. Garcia-Vidal, and J. Feist, Cavity-Induced Modifications of Molecular Structure in the Strong-Coupling Regime, Phys. Rev. X **5**, 041022 (2015).

[16] J. F. Triana and J. L. Sanz-Vicario, Revealing the Presence of Potential Crossings in Diatomics Induced by Quantum Cavity Radiation, Phys. Rev. Lett. **122**, 063603 (2019).

[17] F. Herrera and J. Owrutsky, Molecular polaritons for controlling chemistry with quantum optics, J. Chem. Phys. **152**, 100902 (2020).

[18] M.-L. Hu, Z.-J. Yang, X.-J. Du, and J. He, Towards strong linear and nonlinear light-matter interactions in hybrid nanostructures of a single molecule and a plasmonic nanocavity, Phys. Rev. B **104**, 064311 (2021).

[19] A. Pscherer, M. Meierhofer, D. Q. Wang, H. Kelkar, D. Martín-Cano, T. Utikal, S. Götzinger, and V. Sandoghdar, Single-Molecule Vacuum Rabi Splitting: Four-Wave Mixing and Optical Switching at the Single-Photon Level, Phys. Rev. Lett. **127**, 133603 (2021).

[20] J. F. Triana and J. L. Sanz-Vicario, Polar diatomic molecules in optical cavities: Photon scaling, rotational effects, and comparison with classical fields, J. Chem. Phys. **154**, 094120 (2021).

[21] R. Chikkaraddy, B. de Nijs, F. Benz, S. J. Barrow, O. A. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, and J. J Baumberg, Single-molecule strong coupling at room temperature in plasmonic nanocavities, Nature (London) **535**, 127 (2016).

[22] O. S. Ojambati, R. Chikkaraddy, W. D. Deacon, M. Horton, D. Kos, V. A. Turek, U. F. Keyser, and J. J. Baumberg, Quantum electrodynamics at room temperature coupling a single vibrating molecule with a plasmonic nanocavity, Nat. Commun. **10**, 1049 (2019).

[23] A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A. Vergauwe, J. George, T. Chervy, A. Shalabney, E. Devaux, C. Genet, J. Moran, and T. W. Ebbesen, Tilting a ground-state reactivity landscape by vibrational strong coupling, Science **363**, 615 (2019).

[24] T. E. Li, J. E. Subotnik, and A. Nitzan, Cavity molecular dynamics simulations of liquid water under vibrational ultrastrong coupling, Proc. Natl. Acad. Sci. U.S.A. **117**, 18324 (2020).

[25] B. Xiang, R. F. Ribeiro, M. Du, L. Chen, Z. Yang, J. Wang, J. Yuen-Zhou, and W. Xiong, Intermolecular vibrational energy transfer enabled by microcavity strong light-matter coupling, Science **368**, 665 (2020).

[26] X.-Y. Li, A. Mandal, and P. Huo, Cavity frequency-dependent theory for vibrational polariton chemistry, Nat. Commun. **12**, 1315 (2021).

[27] K. Nagarajan, A. Thomas, and T. W. Ebbesen, Chemistry under vibrational strong coupling, J. Am. Chem. Soc. **143**, 16877 (2021).

[28] B. Xiang and W. Xiong, Molecular vibrational polariton: Its dynamics and potentials in novel chemistry and quantum technology, J. Chem. Phys. **155**, 050901 (2021).

[29] H. Stapelfeldt and T. Seideman, Colloquium: Aligning molecules with strong laser pulses, Rev. Mod. Phys. **75**, 543 (2003).

[30] Y. Ohshima and H. Hasegawa, Coherent rotational excitation by intense nonresonant laser fields, Int. Rev. Phys. Chem. **29**, 619 (2010).

[31] S. Fleischer, Y. Khodorkovsky, E. Gershnabel, Y. Prior, and I. Sh. Averbukh, Molecular alignment induced by ultrashort laser pulses and its impact on molecular motion, Isr. J. Chem. **52**, 414 (2012).

[32] C. P. Koch, M. Lemeshko, and D. Sugny, Quantum control of molecular rotation, Rev. Mod. Phys. **91**, 035005 (2019).

[33] G. J. Simpson, V. García-López, A D. Boese, J. M. Tour, and L. Grill, How to control single-molecule rotation, Nat. Commun. **10**, 4631 (2019).

[34] M. Hertzog, P. Rudquist, J. A. Hutchison, J. George, T. W. Ebbesen, and K. Börjesson, Voltage-controlled switching of strong light–matter interactions using liquid crystals, Chem. Eur. J. **23**, 18166 (2017).

[35] M. Machholm and N. E. Henriksen, Field-Free Orientation of Molecules, Phys. Rev. Lett. **87**, 193001 (2001).

[36] D. Daems, S. Guérin, D. Sugny, and H. R. Jauslin, Efficient and Long-Lived Field-Free Orientation of Molecules by a Single Hybrid Short Pulse, Phys. Rev. Lett. **94**, 153003 (2005).

[37] E. Gershnabel, I. S. Averbukh, and R. J. Gordon, Orientation of molecules via laser-induced anti-alignment, Phys. Rev. A **73**, 061401(R) (2006).

[38] C.-C. Shu, K.-J. Yuan, W.-H. Hu, and S.-L. Cong, Carrier-envelope phase-dependent field-free molecular orientation, Phys. Rev. A **80**, 011401(R) (2009).

[39] C.-C. Shu, K.-J. Yuan, W.-H. Hu, and S.-L. Cong, Field-free molecular orientation with terahertz few-cycle pulses, J. Chem. Phys. **132**, 244311 (2010).

[40] S. Fleischer, Y. Zhou, R. W. Field, and K. A. Nelson, Molecular Orientation and Alignment by Intense Single-Cycle THz Pulses, Phys. Rev. Lett. **107**, 163603 (2011).

[41] K. Kitano, N. Ishii, and J. Itatani, High degree of molecular orientation by a combination of THz and femtosecond laser pulses, Phys. Rev. A **84**, 053408 (2011).

[42] S. Fleischer, R. W. Field, and K. A. Nelson, Commensurate Two-Quantum Coherences Induced by Time-Delayed THz Fields, Phys. Rev. Lett. **109**, 123603 (2012).

[43] C.-C. Shu and N. E. Henriksen, Field-free molecular orientation induced by single-cycle THz pulses: The role of resonance and quantum interference, Phys. Rev. A **87**, 013408 (2013).

[44] K. N. Egodapitiya, S. Li, and R. R. Jones, Terahertz-Induced Field-Free Orientation of Rotationally Excited Molecules, Phys. Rev. Lett. **112**, 103002 (2014).

[45] R. Damari, S. Kallush, and S. Fleischer, Rotational Control of Asymmetric Molecules: Dipole-versus Polarizability-Driven Rotational Dynamics, Phys. Rev. Lett. **117**, 103001 (2016).

[46] L. Xu, I. Tutunnikov, E. Gershnabel, Y. Prior, and I. S. Averbukh, Long-Lasting Molecular Orientation Induced by a Single Terahertz Pulse, Phys. Rev. Lett. **125**, 013201 (2020).

[47] C.-C. Shu, Q.-Q. Hong, Y. Guo, and N. E. Henriksen, Orientational quantum revivals induced by a single-cycle terahertz pulse, Phys. Rev. A **102**, 063124 (2020).

[48] Q.-Q. Hong, L.-B. Fan, C.-C. Shu, and N. E. Henriksen, Generation of maximal three-state field-free molecular orientation with terahertz pulses, Phys. Rev. A **104**, 013108 (2021).

[49] S. De, I. Znakovskaya, D. Ray, F. Anis, Nora G. Johnson, I. A. Bocharova, M. Magrakvelidze, B. D. Esry, C. L. Cocke, I. V. Litvinyuk, and M. F. Kling, Field-Free Orientation of CO Molecules by Femtosecond Two-Color Laser Fields, Phys. Rev. Lett. **103**, 153002 (2009).

[50] I. Znakovskaya, M. Spanner, S. De, H. Li, D. Ray, P. Corkum, I. V. Litvinyuk, C. L. Cocke, and M. F. Kling, Transition between Mechanisms of Laser-Induced Field-Free Molecular Orientation, Phys. Rev. Lett. **112**, 113005 (2014).

[51] K. Lin, I. Tutunnikov, J. J. Qiang, J. Y. Ma, Q. Y. Song, Q. Y. Ji, W. B. Zhang, H. X. Li, F. H. Sun, X. C. Gong, H. Li, P. F. Lu, H. P. Zeng, Y. Prior, I. S. Averbukh, and J. Wu, All-optical field-free three-dimensional orientation of asymmetric-top molecules, Nat. Commun. **9**, 5134 (2018).

[52] S. Trippel, T. Mullins, N. L. M. Müller, J. S. Kienitz, R. González-Férez, and J. Küpper, Two-State Wave Packet for Strong Field-Free Molecular Orientation, Phys. Rev. Lett. **114**, 103003 (2015).

[53] E. T. Jaynes and F. W. Cummings, Comparison of quantum and semiclassical radiation theories with application to the beam maser, Proc. IEEE **51**, 89 (1963).

[54] F. Yoshihara, T. Fuse, S. Ashhab, K. Kakuyanagi, S. Saito, and K. Semba, Superconducting qubit–oscillator circuit beyond the ultrastrong-coupling regime, Nat. Phys. **13**, 44 (2017).

[55] O. D. Stefano, A. Settineri, V. Macrì, L. Garziano, R. Stassi, S. Savasta, and F. Nori, Resolution of gauge ambiguities in ultrastrong-coupling cavity quantum electrodynamics, Nat. Phys. **15**, 803 (2019).

[56] M. A. D. Taylor, A. Mandal, W. Zhou, and P. Huo, Resolution of Gauge Ambiguities in Molecular Cavity Quantum Electrodynamics, Phys. Rev. Lett. **125**, 123602 (2020).

[57] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.130.043604 for the details for deriving the maximum degree of orientation, Eq. (4), and Eq. (5).

[58] B. W. Shore and P. L. Knight, The Jaynes-Cummings model, J. Mod. Opt. **40**, 1195 (1993).

[59] D. Sugny, A. Keller, O. Atabek, D. Daems, C. M. Dion, S. Guérin, and H. R. Jauslin, Reaching optimally oriented molecular states by laser kicks, Phys. Rev. A **69**, 033402 (2004).

[60] S. Wang and N. E. Henriksen, Optimal field-free molecular orientation with nonresonant two-color adiabatic-turn-on and sudden-turn-off laser pulses, Phys. Rev. A **102**, 063120 (2020).

[61] M. F. Ciappina, J. A. Pérez-Hernández, A. S. Landsman, T. Zimmermann, M. Lewenstein, L. Roso, and F. Krausz, Carrier-Wave Rabi-Flopping Signatures in High-Order Harmonic Generation for Alkali Atoms, Phys. Rev. Lett. **114**, 143902 (2015).

[62] K. A. Fischer, L. Hanschke, M. Kremser, J. J. Finley, K. Müller, and J. Vučković, Pulsed Rabi oscillations in quantum two-level systems: Beyond the area theorem, Quantum Sci. Technol. **3**, 014006 (2018).

[63] I. Schuster, A. Kubanek, A. Fuhrmanek, T. Puppe, P. W. H. Pinkse, K. Murr, and G. Rempe, Nonlinear spectroscopy of photons bound to one atom, Nat. Phys. **4**, 382 (2008).

[64] F. Deppe, M. Mariantoni, E. P. Menzel, A. Marx, S. Saito, K. Kakuyanagi, H. Tanaka, T. Meno, K. Semba, H. Takayanagi, E. Solano, and R. Gross, Two-photon probe of the Jaynes–Cummings model and controlled symmetry breaking in circuit QED, Nat. Phys. **4**, 686 (2008).

[65] Y.-X. Liu, J. Q. You, L. F. Wei, C. P. Sun, and F. Nori, Optical Selection Rules and Phase-Dependent Adiabatic State Control in a Superconducting Quantum Circuit, Phys. Rev. Lett. **95**, 087001 (2005).

[66] J. M. Fink, M. Göppl, M. Baur, R. Bianchetti, P. J. Leek, A. Blais, and A. Wallraff, Climbing the Jaynes–Cummings ladder and observing its nonlinearity in a cavity QED system, Nature (London) **454**, 315 (2008).

[67] L. S. Bishop, J. M. Chow, J. Koch, A. A. Houck, M. H. Devoret, E. Thuneberg, S. M. Girvin, and R. J. Schoelkopf, Nonlinear response of the vacuum Rabi resonance, Nat. Phys. **5**, 105 (2009).

[68] C. Hamsen, K. N. Tolazzi, T. Wilk, and G. Rempe, Two-Photon Blockade in an Atom-Driven Cavity QED System, Phys. Rev. Lett. **118**, 133604 (2017).

[69] X. Gu, A. F. Kockum, A. Miranowicz, Y.-X. Liu, and F. Nori, Microwave photonics with superconducting quantum circuits, Phys. Rep. **718–719**, 1 (2017).

[70] G. Shchedrin, C. O'Brien, Y. Rostovtsev, and M. O. Scully, Analytic solution and pulse area theorem for three-level atoms, Phys. Rev. A **92**, 063815 (2015).

[71] Y. Guo, C.-C. Shu, D. Dong, and F. Nori, Vanishing and Revival of Resonance Raman Scattering, Phys. Rev. Lett. **123**, 223202 (2019).

[72] C.-C. Shu, Y. Guo, K.-J. Yuan, D. Dong, and A. D. Bandrauk, Attosecond all-optical control and visualization of quantum interference between degenerate magnetic states by circularly polarized pulses, Opt. Lett. **45**, 960 (2020).

[73] P. Brumer and M. Shapiro, Control of unimolecular reactions using coherent light, Chem. Phys. Lett. **126**, 541 (1986).

[74] J. Zhang, Y.-X. Liu, R. B. Wu, K. Jacobs, and F. Nori, Quantum feedback: Theory, experiments, and applications, Phys. Rep. **679**, 1 (2017).

[75] A. Devolder, P. Brumer, and T. V. Tscherbul, Complete Quantum Coherent Control of Ultracold Molecular Collisions, Phys. Rev. Lett. **126**, 153403 (2021).

[76] A. F. Kockum, A. Miranowicz, S. D. Liberato, S. Savasta, and F. Nori, Ultrastrong coupling between light and matter, Nat. Rev. Phys. **1**, 19 (2019).

[77] P. Forn-Díaz, L. Lamata, E. Rico, J. Kono, and E. Solano, Ultrastrong coupling regimes of light-matter interaction, Rev. Mod. Phys. **91**, 025005 (2019).

[78] J. Seke and F. Rattay, Influence of the Fock-state field on the many-atom radiation processes in a damped cavity, Phys. Rev. A **39**, 171 (1989).

[79] J. Seke, Many-atom Jaynes-Cummings model without rotating-wave approximation, Quantum Opt. **3**, 127 (1991).

[80] R. Damari, O. Weinberg, D. Krotkov, N. Demina, K. Akulov, A. Golombek, T. Schwartz, and S. Fleischer, Strong coupling of collective intermolecular vibrations in organic materials at terahertz frequencies, Nat. Commun. **10**, 3248 (2019).

[81] E. Mavrona, S. Rajabali, F. Appugliese, J. Andberger, M. Beck, G. Scalari, and J. Faist, THz ultrastrong coupling in an engineered Fabry-Perot cavity, ACS Photonics **8**, 2692 (2021).