

Supplemental Material for “Quantum Coherent Control of a Single-Molecular Polariton Rotation”

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Abstract

To help readers understand how we obtain the key equations in the main text, we provide further details in this Supplemental Material, organized as follows. In Sec. [I](#), we derive the control condition for generating the maximum degree of orientation for a two-state molecule in the absence (presence) of a weak static field. In Sec. [II](#), we derive the maximum post-pulse orientation for a single molecular polariton. An analytical solution is derived in Sec. [III](#) for describing the pulsed-driven molecular polariton. Finally, we show the optimal amplitude and phase conditions in Sec. [IV](#) for analytically designing molecule-driving pulses.

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I. THE MAXIMUM DEGREE OF ORIENTATION FOR A TWO-LEVEL SYSTEM

A. A TWO-STATE SYSTEM

In this section, we provide further details about the theoretical maximum orientation of a two-state system driven by a pulsed terahertz field $\mathcal{E}(t)$ through its dipole moment μ [1, 2]. The molecular Hamiltonian reads $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$ with the field-free Hamiltonian $\hat{H}_0 = B\hat{J}^2$ and the time-dependent interaction potential $\hat{V}(t) = -\mu\mathcal{E}(t)\cos\theta$, where \hat{J} is an angular momentum operator and θ denotes the angle between the rotor axis and the polarization direction of the control field. The time-dependent two-state wave packet after the laser pulse excitation is given by

$$|\psi_{J_0M}(t)\rangle = C_0(t_f)e^{-iE_0t}|00\rangle + C_1(t_f)e^{-iE_1t}|10\rangle, \quad (\text{S1})$$

where the rotational eigenstates $|JM\rangle$ satisfy $\hat{H}_0|JM\rangle = E_J|JM\rangle$, with eigenenergies $E_J = BJ(J+1)$, and C_J are the expansion coefficients of $|JM\rangle$.

The degree of orientation after the rotational excitation with the selection rule $\Delta J = \pm 1$ can be written as

$$\langle\psi(t)|\cos\theta|\psi(t)\rangle = 2|C_0(t)||C_1(t)|M_{01}\cos(\omega_{01}t - \phi_{01}), \quad (\text{S2})$$

where $M_{J',J} = \langle J'M|\cos\theta|JM\rangle$, the transition frequency is defined by $\omega_{01} = E_1 - E_0 = 2B$, and the relative phase is $\phi_{01} = \arg[C_1(t)] - \arg[C_0(t)]$.

Based on the method of Lagrange multipliers [3, 4], the maximum degree of orientation with the two-state subspace can be obtained from

$$L(|C_0|, |C_1|, \lambda) = f - \lambda g, \quad (\text{S3})$$

where $f = 2|C_0||C_1|M_{10}$ corresponds to the amplitude of the orientation at the full revivals and $g = |C_0|^2 + |C_1|^2 - 1 = 0$ is a constraint. The extremum of f subject to g can be obtained by satisfying $\nabla L = 0$. We have

$$\begin{aligned} M_{01}|C_1| - \lambda|C_0| &= 0, \\ M_{01}|C_0| - \lambda|C_1| &= 0. \end{aligned} \quad (\text{S4})$$

By multiplying each equation in (S4) by $|C_0|$ and $|C_1|$, respectively, we have

$$f - \lambda(|C_0|^2 + |C_1|^2) = f - \lambda = 0. \quad (\text{S5})$$

The degree of orientation f reaches its maximum when $|C_0|^2 = |C_1|^2 = \sqrt{2}/2$. For molecules initially in the ground rotational state with $J = 0, M = 0$, we can calculate the maximum orientation $f = M_{10} = 1/\sqrt{3}$.

To derive how a control field can result in this orientation maximum, we write the Hamiltonian in the interaction picture without using the rotating wave approximation (RWA)

$$H_I = \begin{pmatrix} 0 & -\mu_{01}\mathcal{E}(t)e^{i\omega_{01}t} \\ -\mu_{01}\mathcal{E}(t)e^{-i\omega_{01}t} & 0 \end{pmatrix}, \quad (\text{S6})$$

where $\mu_{01} = \langle 00|\hat{\mu} \cdot \hat{\mathbf{e}}|10\rangle$. To obtain an analytical solution of $|\psi(t)\rangle_I$, we expand the unitary operator $U(t, t_0)$ by using the Magnus expansion [1, 2, 5]

$$U(t, t_0) = \exp \left[\sum_{n=1}^{\infty} \hat{S}^{(n)}(t) \right], \quad (\text{S7})$$

where the first leading term is given by $\hat{S}^{(1)}(t) = -i \int_{t_0}^t dt_1 H_I(t_1)$. The corresponding time-dependent wave function $|\psi(t)\rangle_I = U(t, t_0)|00\rangle$ starting from the ground rotational state $|00\rangle$ is given by

$$|\psi(t)\rangle_I = i \frac{|\theta_{01}(t)|}{\theta_{01}^*(t)} \sin |\theta_{01}(t)| |10\rangle + \cos |\theta_{01}(t)| |00\rangle. \quad (\text{S8})$$

where $|\theta_{01}(t)| = \left| \mu_{01} \int_{t_0}^t \mathcal{E}(t') e^{i\omega_{01}t'} dt' \right|$. Note that $|\theta_{01}(t)|$ coincides with the pulse area for a resonant pulse with the RWA. Based on the above analysis, the maximum degree of orientation requires that $\theta_{01}(t)$ satisfies the following relations:

$$\begin{aligned} |C_0(t_f)| &= |\cos |\theta_{01}(t)|| = \frac{\sqrt{2}}{2}, \\ |C_1(t_f)| &= \left| i \frac{|\theta_{01}(t)|}{\theta_{01}^*(t)} \sin |\theta_{01}(t)| \right| = \frac{\sqrt{2}}{2}. \end{aligned} \quad (\text{S9})$$

This implies that the amplitude of the control field should satisfy the condition $|\theta_{01}(t_f)| = \pi/4$.

As used in the main text, we consider a Gaussian-profile pulse $\mathcal{E}(t) = \mathcal{E}_0 \exp[-t^2/2\tau_0^2] \cos(\omega_0 t + \phi_0)$ with $\mathcal{E}_0 = \sqrt{2/\pi}\pi/(4\mu_{01}\tau_0)$, center frequency $\omega_0 = \omega_{01}$, and absolute phase $\phi_0 = 0$. This choice leads to $|\theta_{01}(t_f)| = \pi/4$, independent of duration τ_0 . We apply a THz pulse to a multi-state molecule by including higher rotational states of $J > 1$. Figure S1 shows the final population distribution of rotational states as a function of the THz pulse's bandwidth $\Delta\omega = 1/\tau$. It is clear that a coherent superposition of rotational states $|00\rangle$ and $|10\rangle$ with equal weights can be obtained

when the bandwidth of the THz pulse is narrow enough. In the present work, we apply the THz pulses with a narrow bandwidth of $\Delta\omega \leq 2g$, where the effect of higher rotational states of $J > 1$ can be ignored, as shown in Fig. S1.

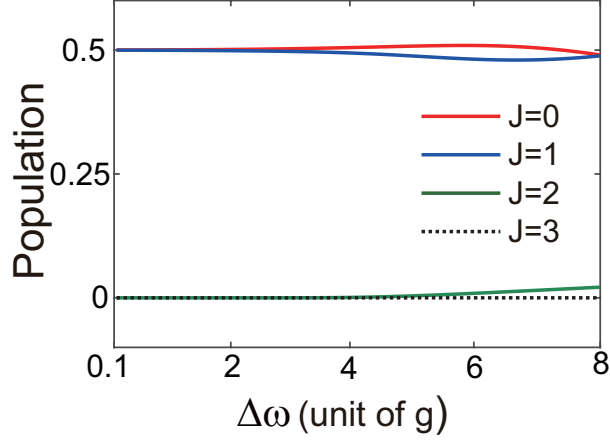


FIG. S1. The final population distribution of rotational states $J = 0$ (red solid line), $J = 1$ (blue dotted line), $J = 2$ (green solid line), and $J = 3$ (gray dotted line) as a function of the THz pulse's bandwidth $\Delta\omega = 1/\tau$.

B. A TWO-STATE SYSTEM IN THE PRESENCE OF A STATIC FIELD

To understand how a static field modifies the rotational dynamics, here we show how to generate the maximum degree of orientation for a two-state molecule driven by a THz pulse $\mathcal{E}(t)$ combined with a weak static field $\epsilon(t) = \epsilon_0$. The Hamiltonian of a two-state molecule in the presence of a weak static field can be described by

$$\hat{H}_0 = \begin{pmatrix} 0 & \mu_{01}\epsilon_0 \\ \mu_{01}\epsilon_0 & E_1 \end{pmatrix}.$$

By diagonalizing the Hamiltonian H_0 , we obtain two eigenenergies $E_{\pm} = (E_1 \pm \Delta_0)/2$ with $\Delta_0 = \sqrt{E_1^2 + 4\mu_{01}^2\epsilon_0^2}$. The corresponding eigenfunctions $|E_{\pm}\rangle$ can be analyzed by replacing the definition of $|\theta_{01}(t)\rangle$ in Eq. (S8) with $\mathcal{E}(t) = \epsilon_0$ and $t_0 \rightarrow -\infty$, i.e., $\theta_{01}(t) = \mu_{01} \int_{-\infty}^t \epsilon_0 e^{i\omega_{01}t'} dt'$. We can obtain two eigenfunctions $|E_+\rangle = |10\rangle$ and $|E_-\rangle = |00\rangle$ in the long-time limit. This implies that a weak static field does not modify the eigenfunctions of bare molecules, but the corresponding transition frequency $\omega_{+-} = \omega_{01} + \Delta_0$ is blue shifted Δ_0 from ω_{01} . As a result, the control condition for generating the maximum degree of orientation by a THz pulse becomes

$$|\theta_{+-}(t_f)\rangle = \left| \mu_{01} \int_{t_0}^{t_f} \mathcal{E}(t') e^{i\omega_{+-}t'} dt' \right| = \frac{\pi}{4}. \quad (\text{S10})$$

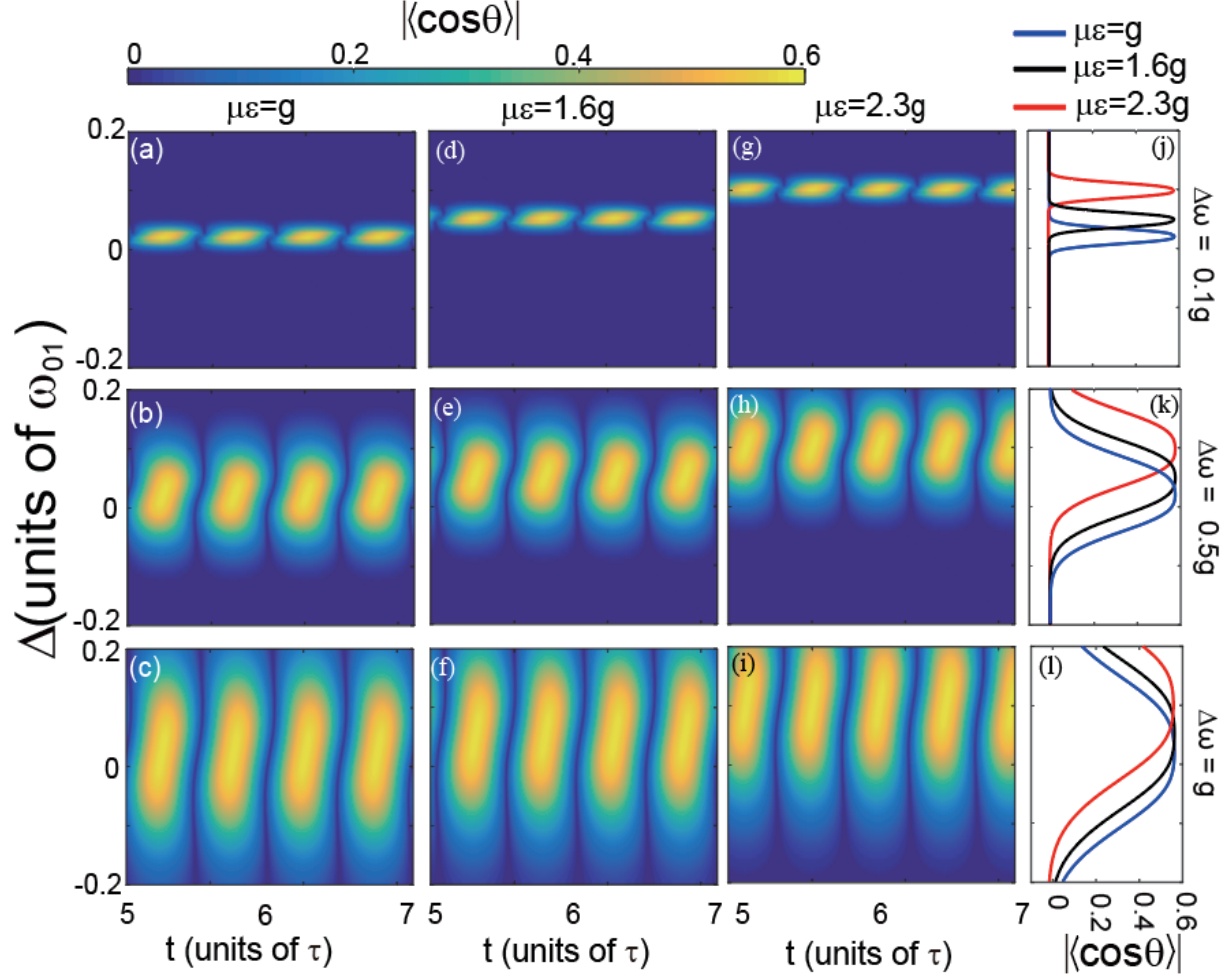


FIG. S2. The same simulations as those in Fig. 2 of the main text for a two-state molecule driven by a THz pulse combined with a static field at three different strengths with $\Omega_0 = \mu_{01}\epsilon_0 = g$ (a)-(c), $1.6g$ (d)-(f) and $2.3g$ (g)-(i).

The revival period is modified to $\tau = 2\pi/\omega_{+-}$, shorter than that of the bare molecule.

Figure S2 shows the same simulations as those in Fig. 2 of the main text for a two-state molecule driven by a THz pulse in the presence of a weak static field at three different values of the Rabi frequency $\Omega_0 = \mu_{01}\epsilon_0 = g, 1.6g$ and $2.3g$. We can see that the maximum orientation disappears at $\Delta = 0$ with $\omega_0 = \omega_{01}$, but occurs at $\Delta = \Delta_0$ with $\omega_0 = \omega_{+-}$, in good agreement with the above theoretical analysis. This blue-shift phenomenon is similar to that observed in Fig. 2 of the main text. We can see that the blue shift depends on the value of Rabi frequency Ω_0 . A static field with $\Omega_0 = 2.3g$ results in a blue shift $\Delta_0 = g$, the same as the energy shift of the state $|+; 0\rangle$ caused by the cavity.

II. THE MAXIMUM DEGREE OF ORIENTATION OF A SINGLE MOLECULAR POLARITON

In this section, we provide the details for deriving the maximum degree of orientation of a single molecular polariton. The time-dependent wave function of the molecular polariton driven by the control field is given by

$$|\psi(t)\rangle = \sum_{l=0,\pm} C_{l,0} e^{-i\omega_{l,0}t} |l; 0\rangle + \sum_{n'=1}^{\infty} \sum_{l'=\pm} C_{l',n'} e^{-i\omega_{l',n'}t} |l'; n'\rangle \quad (\text{S11})$$

with eigenstates $|l; n\rangle$ and eigenfrequencies $\omega_{0,0} = 0$ and $\omega_{\pm,n} = \omega_c(n+1) \pm g\sqrt{n+1}$. The expansion coefficients $C_{l,n}$ can be calculated numerically by $C_{l,n} = \langle l; n | \hat{U}(t, t_0) | 0; 0 \rangle$ for the system initially in the vacuum ground state $|0; 0\rangle$.

The degree of orientation for the molecular polariton after the rotational excitation with the selection rule $\Delta J = \pm 1$ can be written as

$$\begin{aligned} \langle \cos \theta \rangle = & 2 \sum_{l=\pm} |C_{0,0}| |C_{l,0}| \cos(-\omega_{l,0}t + \phi_{l,0}) M_{l,0} \\ & + 2 \sum_{n'=1}^{\infty} \sum_{l',s'=\pm} |C_{s',n'-1}| |C_{l',n'}| \cos((\omega_{s',n'-1} - \omega_{l',n'})t + \phi_{s'l'n'}) M_{s',n'-1,l',n'}, \end{aligned} \quad (\text{S12})$$

with $M_{s',n'-1,l',n'} = \langle s'; n' - 1 | \cos \theta | l'; n' \rangle$, and $\phi_{s'l'n'} = \arg[C_{s',n'}(t)] - \arg[C_{l',n'}(t)]$. Based on the method of Lagrange multipliers, the maximum degree of orientation can be estimated by

$$L(|C_{0,0}|, |C_{-,0}|, |C_{+,0}|, \dots, |C_{-,n}|, |C_{+,n}|, \lambda) = f - \lambda g, \quad (\text{S13})$$

where

$$\begin{aligned} f = & 2|C_{0,0}| |C_{-,0}| M_{-,0} + 2|C_{0,0}| |C_{+,0}| M_{+,0} \\ & + 2 \sum_{n=1}^{\infty} \sum_{s,l=\pm} |C_{s,n-1}| |C_{l,n}| M_{s,n-1,l,n}, \end{aligned} \quad (\text{S14})$$

and $g = |C_{0,0}|^2 + \sum_{n=0}^{\infty} \sum_{l=\pm} |C_{l,n}|^2 - 1 = 0$. The extremum of f subject to g can be obtained by satisfying $\nabla L = 0$; then we have

$$\begin{aligned} |C_{-,0}| M_{-,0} + |C_{+,0}| M_{+,0} - \lambda |C_{0,0}| &= 0, \\ |C_{0,0}| M_{-,0} + |C_{-,1}| M_{-,0,-1} + |C_{+,1}| M_{-,0,+1} - \lambda |C_{-,0}| &= 0, \\ |C_{0,0}| M_{+,0} + |C_{-,1}| M_{+,0,-1} + |C_{+,1}| M_{+,0,+1} - \lambda |C_{+,0}| &= 0, \\ \sum_{s=\pm} |C_{s,n-1}| M_{s,n-1,l,n} + |C_{s,n+1}| M_{s,n,l,n+1} - \lambda |C_{l,n}| &= 0. \end{aligned} \quad (\text{S15})$$

By multiplying each equation in (S15) by $C_{0,0}, C_{-,0}, \dots, C_{-,n}, C_{+,n}$, respectively, we have

$$f - \lambda(|C_{0,0}|^2 + |C_{-,0}|^2 + \dots + |C_{-,n}|^2 + |C_{+,n}|^2) = f - \lambda = 0. \quad (\text{S16})$$

The maximum degree of orientation f corresponds to the maximum value of λ governed by Eq.(S16). By analyzing Eqs.(S12)-(S15), the maximum degree of orientation f can be achieved by satisfying conditions either with $|C_{0,0}|^2 = |C_{-,0}|^2 + |C_{+,0}|^2$ or $|C_{-,n-1}|^2 + |C_{+,n-1}|^2 = |C_{-,n}|^2 + |C_{+,n}|^2$. We can calculate the matrix elements $M_{-,0} = M_{+,0} = (\sqrt{2}/2)M_{1,0}$ and $M_{l,n-1,s,n} = (1/2)M_{1,0}$. Thus, the maximum degree of orientation can be obtained

$$\lambda = \sqrt{M_{-,0}^2 + M_{+,0}^2} = \sqrt{\frac{1}{3}}, \quad (\text{S17})$$

with $|C_{0,0}| = \sqrt{2}/2, |C_{-,0}| = |C_{+,0}| = 1/2$, or

$$\lambda = \sqrt{\sum_{s,l=\pm} M_{l,n-1,s,n}^2} = \sqrt{\frac{1}{3}}, (n = 1, 2, 3, \dots). \quad (\text{S18})$$

with $|C_{l,n-1}| = |C_{s,n}| = 1/2$, with $l, s = \pm, n = 1, 2, 3, \dots$. As mentioned in the main text, this work demonstrates how to achieve the orientation maximum for the first case with $|C_{0,0}|^2 = 0.5$, $|C_{+,0}|^2 = |C_{-,0}|^2 = 0.25$ while satisfying a phase relation of $\omega_{-,0} \arg[C_{+,0}] - \omega_{+,0} \arg[C_{-,0}] = 2g\pi$. The corresponding revival period τ_p can be derived by calculating the least common multiple of $2\pi/(\omega_{\pm,0})$.

III. ANALYTICAL SOLUTION OF THE PULSED-DRIVEN MOLECULAR POLARITON

We now provide the details of how to derive the analytical solution of the time-dependent wave function for describing the molecular polariton driven by a pulsed control field $\mathcal{E}(t)$. The time-dependent Hamiltonian of the molecular polariton in the presence of the control field reads

$$\begin{aligned} H_p = & \sum_{n=0} \sum_{l=\pm} \omega_{l,n} |l; n\rangle \langle l; n| - \mathcal{E}(t) \sum_{l=\pm} \tilde{\mu}_0 (|l; 0\rangle \langle 0; 0| + |0; 0\rangle \langle l; 0|) \\ & - \mathcal{E}(t) \sum_{n=1}^{\infty} \sum_{l,l'=\pm} \tilde{\mu}_l (|l; n\rangle \langle l'; n-1| + |l'; n-1\rangle \langle l; n|), \end{aligned} \quad (\text{S19})$$

where $\tilde{\mu}_0 = \pm \sqrt{2}/2\mu_{01}$ and $\tilde{\mu}_{\pm} = \pm 1/2\mu_{01}$ denotes the transition dipole moments between entangled states with $\mu_{01} = \langle 00 | \mu \cos \theta | 10 \rangle = \sqrt{3}/3$. Without using the RWA, the corresponding

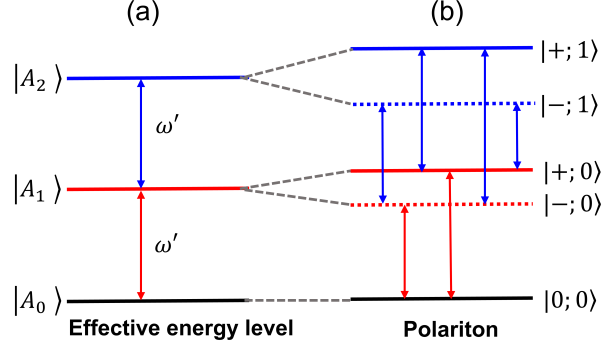


FIG. S3. Schematic of energy levels of the effective Hamiltonian and the polariton.

Hamiltonian in the interaction picture reads

$$H_I = \begin{pmatrix} 0 & B_{-,0}^* & B_{+,0}^* & 0 & 0 & \cdots & 0 & 0 & 0 & 0 \\ B_{-,0} & 0 & 0 & B_{-,-,1}^* & B_{-,+,1}^* & \cdots & 0 & 0 & 0 & 0 \\ B_{+,0} & 0 & 0 & B_{+,-,1}^* & B_{+,+,1}^* & \cdots & 0 & 0 & 0 & 0 \\ 0 & B_{-,-,1} & B_{+,-,1} & 0 & 0 & \cdots & 0 & 0 & 0 & 0 \\ 0 & B_{-,+,1} & B_{+,+,1} & 0 & 0 & \cdots & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & B_{-,-,n}^* & B_{-,+,n}^* \\ 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & B_{+,-,n}^* & B_{+,+,n}^* \\ 0 & 0 & 0 & 0 & 0 & \cdots & B_{-,-,n} & B_{-,+,n} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \cdots & B_{-,+,n} & B_{+,+,n} & 0 & 0 \end{pmatrix}, \quad (\text{S20})$$

where $B_{\pm,0} = \tilde{\mu}_0 \mathcal{E}(t) \exp(-i\omega_{\pm,0}t)$, and $B_{s,\pm,n} = \tilde{\mu}_s \mathcal{E}(t) \exp[i(\omega_{s,n} - \omega_{\pm,n})t]$.

We now derive an analytical solution of the time-dependent wave function within a pulse-driven quantum JC model described by Eqs.(S19) and (S20) without the rotating-wave approximation. However, it remains challenging to derive a general solution. As highlighted in the main text, we consider a five-level model including the lowest three states $|0; 0\rangle$ and $|\pm; 0\rangle$ and the second higher-lying doublet states $|\pm; 1\rangle$. The time-dependent wave function $|\psi(t)\rangle$ of the hybrid entangled states is given by

$$|\psi(t)\rangle = \sum_{\ell=0,\pm} C_{\ell,0} e^{-i\omega_{\ell,0}t} |\ell; 0\rangle + \sum_{\ell'=\pm} C_{\ell',1} e^{-i\omega_{\ell',1}t} |\ell'; 1\rangle, \quad (\text{S21})$$

where $C_{\ell,0}$ denote the complex coefficients of the lowest three states $|0; 0\rangle$ and $|\pm; 0\rangle$, and $C_{\pm,1}$ correspond to the complex coefficients of the higher-lying doublet states $|\pm; 1\rangle$.

It is still difficult to directly derive an analytical solution for such a five-level system. To solve this problem, we use an effective three-level system in Fig. S3 (a) to describe the transitions from the vacuum ground state $|0; 0\rangle$ to the excited doublet states $|\pm; 0\rangle$ and $|\pm; 1\rangle$. The Hamiltonian of the three-level system that consists of states $|A_0\rangle$, $|A_1\rangle$ and $|A_2\rangle$ can be written as

$$H_{\text{eff}}(t) = \sum_{q=0}^2 q\omega' |A_q\rangle\langle A_q| - \mathcal{E}'(t)\mu'_{01}(|A_0\rangle\langle A_1| + |A_1\rangle\langle A_0|) - \mathcal{E}'(t)\mu'_{12}(|A_1\rangle\langle A_2| + |A_2\rangle\langle A_1|), \quad (\text{S22})$$

where μ'_{01} and μ'_{12} denote the effective transition dipole moments between the states with a transition frequency ω' , and $\mathcal{E}'(t)$ describes an effective control field. The corresponding Hamiltonian in the interaction picture is given by

$$H_{\text{eff}}^I(t) = - \begin{pmatrix} 0 & \mu'_{01}\mathcal{E}'(t)e^{-i\omega't} & 0 \\ \mu'_{01}\mathcal{E}'(t)e^{i\omega't} & 0 & \mu'_{12}\mathcal{E}'(t)e^{-i\omega't} \\ 0 & \mu'_{12}\mathcal{E}'(t)e^{i\omega't} & 0 \end{pmatrix}. \quad (\text{S23})$$

The time dependent wave function of the system starting from a given initial state $|A_0\rangle$ is given by $|\psi_{\text{eff}}(t)\rangle_I = U_{\text{eff}}(t, t_0)|A_0\rangle$ with $U_{\text{eff}}(t_0, t_0) = I$. To obtain an analytical solution of $|\psi_{\text{eff}}(t)\rangle_I$, we expand the unitary operator $U_{\text{eff}}(t, t_0)$ by using Magnus expansion

$$U_{\text{eff}}(t, t_0) = \exp \left[\sum_{n=1}^{\infty} \hat{S}^{(n)}(t) \right], \quad (\text{S24})$$

where the first three leading terms can be given by means of the Baker-Campbell-Hausdorff formula as $\hat{S}^{(1)}(t) = -i \int_{t_0}^t dt_1 H_I(t_1)$, $\hat{S}^{(2)}(t) = (-i)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 [H_I(t_1), H_I(t_2)]$, $\hat{S}^{(3)}(t) = (-i)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_1} dt_3 \{H_I(t_1), [H_I(t_2), H_I(t_3)]\}$. We now consider the case by solely involving the first-order term in the Magnus expansion

$$\begin{aligned} \hat{S}^{(1)}(t) &= -i \int_{t_0}^t dt_1 H_{\text{eff}}^I(t_1) \\ &= i \begin{pmatrix} 0 & \theta_0^*(t) & 0 \\ \theta_0(t) & 0 & \theta_1^*(t) \\ 0 & \theta_1(t) & 0 \end{pmatrix}, \end{aligned} \quad (\text{S25})$$

where we take $\theta_0(t) = \left| \mu'_{01} \int_{t_0}^t dt' \mathcal{E}'(t') e^{i\omega't'} \right| = \sqrt{|\theta_{-,0}(t)|^2 + |\theta_{+,0}(t)|^2}$, and $\theta_1(t) = \left| \mu'_{12} \int_{t_0}^t dt' \mathcal{E}'(t') e^{i\omega't'} \right| = \sqrt{|\theta_{-,1}(t)|^2 + |\theta_{+,1}(t)|^2}$. By diagonalizing the matrix $\hat{S}^{(1)}(t)$, the unitary operator corresponding to the first-order term $\hat{S}^{(1)}(t)$ becomes

$$U^{(1)}(t, t_0) = \sum_{l=0,-,+} \exp[i\lambda_l(t)] |\lambda_l\rangle\langle\lambda_l| \quad (\text{S26})$$

where $\lambda_0(t) = 0$, $\lambda_{\pm}(t) = \pm\theta(t) = \pm\sqrt{\theta_0^2(t) + \theta_1^2(t)}$ are the eigenvalues of $\hat{S}^{(1)}(t)$, and the corresponding eigenstates are

$$\begin{aligned} |\lambda_0\rangle &= \frac{|\theta_1(t)|}{\theta(t)} \left(|A_0\rangle - \frac{\theta_0(t)}{\theta_1(t)} |A_2\rangle \right), \\ |\lambda_{-}\rangle &= \frac{|\theta_0(t)|}{\sqrt{2}\theta(t)} \left(|A_0\rangle - \frac{\theta(t)}{\theta_0^*(t)} |A_1\rangle + \frac{\theta_1(t)}{\theta_0^*(t)} |A_2\rangle \right), \\ |\lambda_{+}\rangle &= \frac{|\theta_0(t)|}{\sqrt{2}\theta(t)} \left(|A_0\rangle + \frac{\theta(t)}{\theta_0^*(t)} |A_1\rangle + \frac{\theta_1(t)}{\theta_0^*(t)} |A_2\rangle \right). \end{aligned} \quad (\text{S27})$$

The corresponding wave functions in terms of the first-order Magnus expansion can be obtained by using $|\psi_{eff}(t)\rangle_I = U_{eff}^{(1)}(t, t_0)|A_0\rangle$, i.e.,

$$\begin{aligned} |\psi_{eff}(t)\rangle_I &= \frac{[|\theta_1(t)|^2 + |\theta_0(t)|^2 \cos \theta(t)]}{\theta^2(t)} |A_0\rangle \\ &\quad + \frac{i\theta_0(t) \sin \theta(t)}{\theta(t)} |A_1\rangle \\ &\quad + \frac{\theta_0(t)\theta_1(t)}{\theta^2(t)} [\cos \theta(t) - 1] |A_2\rangle. \end{aligned} \quad (\text{S28})$$

This solution can be used to calculate the final population distributions in the states $|A_0\rangle$, $|A_1\rangle$ and $|A_2\rangle$, which correspond to the total populations in the vacuum ground state $|0; 0\rangle$, the first doublet states $|\pm; 0\rangle$ and the second doublet states $|\pm; 1\rangle$. Since the vacuum ground state is a singlet state, the time evolution of this state is the same as the state $|A_0\rangle$. To obtain the population distributions (expansion coefficients) of $|\pm; 0\rangle$ and $|\pm; 1\rangle$, we split the states $|A_1\rangle$ and $|A_2\rangle$ into $|\pm; 0\rangle$ and $|\pm; 1\rangle$, respectively, as shown in Fig. S3(b). By making resolution of $\theta_0(t)$ and $\theta_1(t)$ into complex pulse areas $\theta_{\pm,0}(t)$ and $\theta_{\pm,\pm,1}(t)$ in Eq. (S28), we can obtain the time-dependent wave function in the interaction picture as

$$\begin{aligned} |\psi^{(1)}(t)\rangle_I &= \frac{|\theta_1(t)|^2 + |\theta_0(t)|^2 \cos \theta(t)}{\theta^2(t)} |0; 0\rangle + \frac{i \sin \theta(t)}{\theta(t)} \sum_{\ell=\pm} \theta_{\ell,0}(t) |\ell; 0\rangle \\ &\quad + \frac{\cos \theta(t) - 1}{\theta^2(t)} \sum_{\ell=\pm} \sum_{s=\pm} \theta_{s,0}(t) \theta_{s,\ell,1}(t) |\ell; 1\rangle. \end{aligned} \quad (\text{S29})$$

As demonstrated in the main text, we see that this analytical solution can reproduce population distributions in the five states with high accuracy.

IV. THE OPTIMAL AMPLITUDE AND PHASE CONDITIONS FOR ANALYTICALLY DESIGNING MOLECULE-DRIVING PULSES

By blocking optical transitions from $|\pm, 0\rangle$ to $|\pm, 1\rangle$ with $|\theta_{\pm,1}(t_f)| = 0$ in Eq. (S29), the five-level system reduces to a three-level one, consisting of the lowest three states $|0; 0\rangle$, $|\pm; 0\rangle$. The time-dependent wave function in Eq. (S29) becomes

$$|\psi(t)\rangle_I = \cos(\theta_0(t))|0; 0\rangle + \frac{i\theta_{-,0}}{\theta_0(t)} \sin(\theta_0(t))|-, 0\rangle + \frac{i\theta_{+,0}}{\theta_0(t)} \sin(\theta_0(t))|+, 0\rangle. \quad (\text{S30})$$

Note that Eq. (S30) can be directly derived by using a V-type three-level system [5], consisting of the states $|0; 0\rangle$ and $|\pm; 0\rangle$. Based on the above analysis, the maximum degree of orientation in Sec. II requires that $|\theta_{\pm,0}|$ satisfies the following relations:

$$\begin{aligned} |C_{0,0}(t_f)| &= |\cos(\theta_0(t_f))| = \frac{\sqrt{2}}{2}, \\ |C_{-,0}(t_f)| &= \left| \frac{i\theta_{-,0}(t_f)}{\theta_0(t_f)} \sin(\theta_0(t_f)) \right| = \frac{1}{2}, \\ |C_{+,0}(t_f)| &= \left| \frac{i\theta_{+,0}(t_f)}{\theta_0(t_f)} \sin(\theta_0(t_f)) \right| = \frac{1}{2}. \end{aligned} \quad (\text{S31})$$

From Eq. (S31), we can derive

$$\frac{|\theta_{-,0}(t_f)|}{|\theta_{+,0}(t_f)|} = 1. \quad (\text{S32})$$

Thus the amplitude condition for generating the maximum orientation is

$$|\theta_{-,0}(t_f)| = |\theta_{+,0}(t_f)| = \frac{\sqrt{2}\pi}{8}. \quad (\text{S33})$$

To meet the relation $\omega_{-,0}\phi_{+,0} - \omega_{+,0}\phi_{-,0} = 2gk\pi$, $\theta_{-,0}(t_f)$ and $\theta_{+,0}(t_f)$ in Eq. (S30) are required to satisfy the phase condition

$$\omega_{-,0} \arg[\theta_{+,0}(t_f)] - \omega_{+,0} \arg[\theta_{-,0}(t_f)] = \pm g\pi + 2gk\pi. \quad (\text{S34})$$

As shown in the main text, the theoretical maximum degree of orientation can be realized by analytically designing a composite pulse that satisfies the amplitude and phase conditions by Eqs. (S33) and (S34), while blocking optical transitions by controlling its bandwidth.

We also examined the effects of other states by including higher photon states of $n > 1$ and higher rotational states of $J > 1$ into the calculations. Figure S4 shows the populations of other states versus the bandwidth of the THz pulses used in Fig. 5 of the main text by excluding the populations of the lowest five states $|0; 0\rangle$, $|\pm; 0\rangle$ and $|\pm; 1\rangle$. We can see that the calculations by

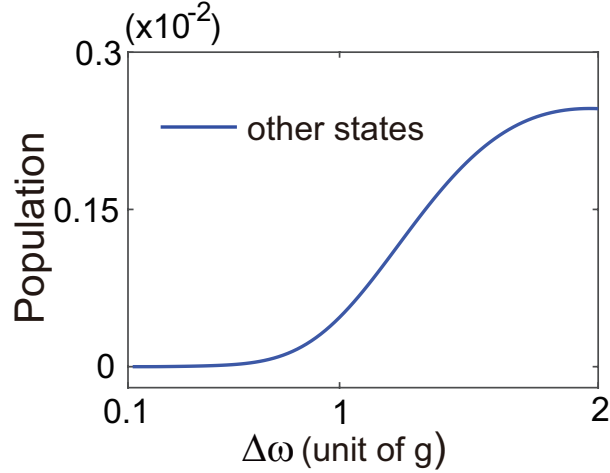


FIG. S4. The populations of other states versus the bandwidth of the THz pulses used in Fig. 5 of the main text by excluding the populations of the lowest five states $|0; 0\rangle$, $|\pm; 0\rangle$ and $|\pm; 1\rangle$.

considering $n = 1$ and $J = 1$ are sufficient for describing, with a high precision, the polariton dynamics in the present work.

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