

High-intensity optical-field population transfer between eigenstates

Dai Ikeda^{1,2,*} and Yasuhiro Ohshima^{3,†}

¹*Department of Chemistry, School of Science, [Tokyo Institute of Technology](#), 2-12-1-W4-9, Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

²*Department of Integrated Sciences, Graduate School of Arts and Sciences, [The University of Tokyo](#), Komaba, Meguro-ku, Tokyo 153-8902, Japan
and Komaba Institute for Science, [The University of Tokyo](#), Komaba, Meguro-ku, Tokyo 153-8902, Japan*

³*Department of Chemistry, School of Science, [Institute of Science Tokyo](#), 2-12-1-W4-9, Ookayama, Meguro-ku, Tokyo 152-8550, Japan*



(Received 26 March 2026; revised 30 July 2026; accepted 8 September 2026; published 15 September 2026)

Two types of coherent population transfer are developed using nonresonant intense ultrashort optical pulses. Transition-restricted wave-packet interference (WPI) achieves almost complete population transfer to the nearest state from the initial state. High-intensity optical-field population transfer between eigenstates (HOPE) also enables state-selective excitation of higher-lying states, exhibiting features of ac Stark-induced multiphoton Rabi oscillation and multipulse WPI. Experimentally, rotational excitation of nitric oxide from $J = 1/2$ to $J = 3/2$ via restricted WPI, and to $J = 5/2$, $7/2$, and $9/2$ via HOPE, was demonstrated with respective efficiencies of 90%, 85%, 70%, and 17%.

DOI: [10.1103/sy5j-g2cq](https://doi.org/10.1103/sy5j-g2cq)

I. INTRODUCTION

Creation of atomic or molecular ensembles, where the population is concentrated in a single or restricted quantum state(s), plays a crucial role across a wide range of fields, including ultracold photoassociation [1], state-selected collision experiments [2–5], and spectroscopic research [6]. Coherent population transfer, enabling highly efficient (de)excitation into target quantum states, is the best approach that achieves desired ensembles. One of the most widely adopted schemes for population transfer is Rabi oscillation, which originated from the early work employing spatially modulated magnetic fields [7]. This concept later became prevalent in the optical regime and has recently been observed even in the extreme ultraviolet region [8,9]. Beyond single-photon coupling, two-photon Rabi oscillations have also been reported [10,11]. Rabi oscillations, typically modeled as the dynamics of a two-level system, are powerful tools in simple quantum systems such as qubits [12]. Adiabatic passage using narrow-band, coherent radiation sources provides more robust alternatives. Stimulated Raman adiabatic passage (STIRAP) is one of the most widely used methods based on adiabatic passage, but it requires an appropriate intermediate state and two single-longitudinal-mode frequency-tunable lasers [1,6,13–17]. Stark-induced adiabatic Raman

*Contact author: dai-ikeda@g.ecc.u-tokyo.ac.jp

†Contact author: ohshima@chem.sci.isct.ac.jp

passage (SARP), which utilizes nonresonant Raman processes, avoids the need for real intermediate states and reduces the required number of frequency-tunable lasers [4,5,18–20]. While STIRAP and SARP are both two-photon Raman processes, there have been reported several rapid adiabatic passage approaches that rely on one-photon absorption [2,3,21]. Multiphoton schemes for Rabi oscillations and adiabatic passages have been explored theoretically [22–24], with only a few experimental demonstrations of nonlinear population transfer [25,26]. One of the key limitations in achieving population transfer to arbitrary eigenstates is the selection rules governed in one- and two-photon transitions. In addition, each transfer step usually requires one or two frequency-tunable radiation sources.

Ultrafast lasers are another class of coherent light sources and powerful tools for coherent excitation in multilevel systems [27,28]. They have significant potential for excitation to higher-lying states with a single laser pulse. The broadband nature of ultrashort pulses enables coherent mixing of multiple eigenstates to create a quantum wave packet and offers the possibility to tailor the contributions of individual states in constructing the wave packet. Optical centrifuges [29,30] are powerful tools for generating molecular ensembles containing ultrahigh- J rotational states; however, their primary aim is rotational ladder climbing rather than concentrating the population in a single target state. For population transfer, two main approaches are available: wave-packet interferometry (WPI) [31–33] and pulse-shaping control [34–36]. These methods have been extensively studied, particularly for impulsive Raman excitation of rotational states, whose transition energies (typically less than a few tens of cm^{-1}) lie within the bandwidth of ultrashort laser pulses. The latter method has achieved an excitation efficiency of nearly 60% in nitric oxide (NO) for population transfer from the rotational level $J = 1/2$ to $5/2$, as shown in Ref. [36]. Our group has also obtained the result showing a comparable excitation efficiency for the same transition in NO using WPI [33]. However, complete population transfer remains challenging for both approaches due to scattered population distribution caused by the broadband nature of ultrashort pulses.

Here, we demonstrate two types of coherent population transfer: transition-restricted WPI and a new method, high-intensity optical-field population transfer between eigenstates (HOPE). These approaches are applicable to multilevel quantum systems and enable an efficient, state-selective transfer. Numerical calculations illustrate the concepts and underlying mechanisms. Both methods rely on nonresonant Raman interactions enabled by sufficiently intense optical fields. HOPE is conceptually related to spectral focusing [37] and the constant-frequency optical centrifuge [38], in that these methods also use chirped-pulse pairs to generate frequency differences. However, the former has mainly been used for spectroscopic applications and the latter has mainly been used for low-acceleration rotational excitation of molecules in helium droplets: Neither of them has taken state-population control into account. Experimentally, we employ a femtosecond-derived pair of broadband, chirped ps pulses with tunable delay, whose high pulse energy and broad bandwidth facilitate access to a wide range of eigenstates.

II. THEORETICAL FRAMEWORK

A. Transition-restricted wave-packet interferometry

The strategy of the transition-restricted WPI is quite simple. When we adopt impulsive excitation by a single optical pulse, the generated wave packet usually consists of multiple eigenstates in case its pulse width is short enough. The state distribution can be controlled via interference between two identical wave packets created by a pair of short pulses by changing the mutual delay between the pulses. In general, complete concentration of population into a single eigenstate is hardly achieved in the WPI involving multiple eigenstates (see the Supplemental Material [39] for more details). However, if we properly adjust the pulse width and the field intensity, each of the two wave packets is composed of only two eigenstates, i.e., the initial and its nearest-neighbor states, with equal populations (1:1). Then, in the WPI within a two-level system, the excitation probability can be continuously tuned from 0% to 100% by varying the delay for the pulse pair, as a result of destructive-constructive interference.

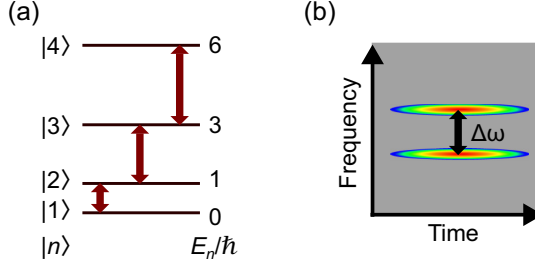


FIG. 1. (a) Energy-level diagram for a model system, where allowed Raman coupling pathways are indicated as double-sided arrows. (b) Schematic two-dimensional (2D) map along time and frequency for induced Raman excitation pulses, applied to the system shown in panel (a).

B. High-intensity optical-field population transfer between eigenstates

Next, we explore whether complete population transfer to higher-lying states can be realized even without direct coupling between the initial and target states, by numerically solving the time-dependent Schrödinger equation (TDSE) for a model system. We adopt atomic units throughout to describe the theoretical approach. The system consists of four states, $|n\rangle = |1\rangle, |2\rangle, |3\rangle$, and $|4\rangle$, with their eigenenergies arbitrarily set to 0, 1, 3, and 6, respectively, as shown in Fig. 1(a). Here, we consider induced Raman scattering (IRS) processes driven by linearly polarized pulses, where excitation is mediated by the polarizability (induced-dipole) interaction, $\hat{V} = -\frac{1}{2}\alpha_{ZZ}[E_Z(t)]^2$, where α_{ZZ} is the system polarizability and $E_Z(t)$ is the optical field along the space-fixed Z direction. We arbitrarily set the transition matrix elements for the polarizability $\langle n|\alpha_{ZZ}|m\rangle$ to be 1 for $m = n \pm 1$, while 0 for others.

The electric field in the IRS process consists of two components, pump and Stokes, i.e., $E_Z(t) = E_P(t) + E_S(t)$, where $E_{P/S}(t)$ is the pump (P) or Stokes (S) field. Here, we assume both fields share the same amplitude E_0 and the same envelope function (assumed here as of a Gaussian form with the pulse duration of τ), as shown in Fig. 1(b), and both the angular frequencies ω_P and ω_S are far from one-photon resonance. Then, the interaction term is recast into $\hat{V} = -\frac{1}{4}\alpha_{ZZ}[F(t)]^2$, by averaging the rapidly oscillating term, where $F(t) = E_0 \exp[-(t/\tau)^2] \cos(\Delta\omega t/2)$ is the slowly varying field amplitude with $\Delta\omega \equiv \omega_P - \omega_S$.

We investigate the dependence of the final populations on the field amplitude E_0 and the angular-frequency difference $\Delta\omega$, as shown in Fig. 2. Here, the initial population was assumed to be concentrated in the lowest state $|1\rangle$. In the 2D maps, blue and yellow areas correspond to the conditions achieving the populations ≈ 0 and 1, respectively. Interestingly, most of blue “islands” in the map for state $|1\rangle$ [panel (a)] match with yellow islands out of the three maps [panels (b)–(d)]. This means the population from the initial state is almost exclusively transferred to each of the three upper states at certain values of E_0 and $\Delta\omega$. Conditions for the efficient population transfer appear as vertical arrays of yellow islands in panels (b)–(d). For instance, state $|2\rangle$ exhibits population modulation (between 0 and 1) against E_0 for $\Delta\omega = 1.00$, as shown in the right-hand plot of panel (b). This is a clear manifestation of two-photon Rabi oscillation. Since the interaction term $\hat{V}$ is proportional to the square of the field amplitude, the oscillation frequency becomes faster for larger E_0 . Importantly, similar oscillations also appear in states $|3\rangle$ and $|4\rangle$, despite the absence of direct coupling with the initial state. Right-hand plots of panels (c) and (d) exhibit such oscillatory behavior of populations in $|3\rangle$ and $|4\rangle$ at $\Delta\omega = 1.53$ and 2.22, respectively. These resonance angular frequencies are approximated by

$$\Delta\omega \approx \frac{\Delta\omega_{m,n}}{N}, \quad (1)$$

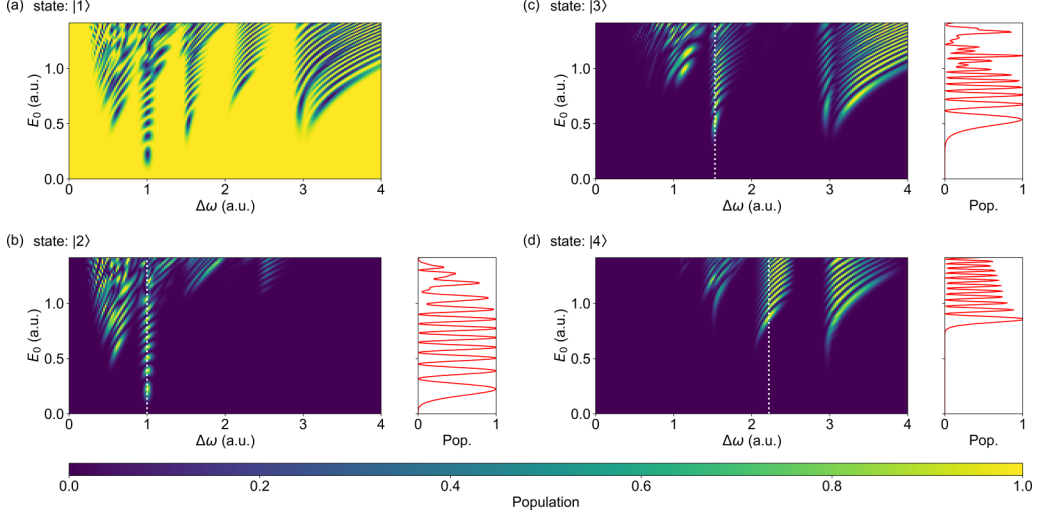


FIG. 2. 2D maps of the state populations as functions of the field amplitude E_0 and the angular-frequency difference $\Delta\omega$ for (a) state $|1\rangle$, (b) state $|2\rangle$, (c) state $|3\rangle$, and (d) state $|4\rangle$, respectively. The pulse duration is fixed at $\tau = 50$. The line cuts at fixed values of $\Delta\omega$ (1, 1.53, and 2.22), indicated by the white dotted lines, are shown in the right-hand plots for (b) state $|2\rangle$, (c) state $|3\rangle$, and (d) state $|4\rangle$.

where $\Delta\omega_{m,n}$ is an angular-frequency difference between states m and n , and N is a positive integer. This behavior can be interpreted as a resonance between the Floquet states $|\alpha, q\rangle = |m, 0\rangle$ and $|n, N\rangle$, where α and q are atomic/molecular and Floquet indices, respectively. Such population transfer is analogous to an effective N -photon resonance in dipole-driven systems under strong-field interaction [40]. The resonances for states $|3\rangle$ and $|4\rangle$ are deviated from Eq. (1), in particular, for higher E_0 . This behavior can be attributed to the ac Stark shift.

To gain an intuitive picture of the population-transfer mechanism, we examine the population dynamics. Figure 3 represents time dependence of state populations as well as the amplitude of the optical field exerted on the system. Panels (a)–(c) correspond to the cases where $\Delta\omega$ and E_0 are optimized to achieve complete population transfer (i.e., with $>99\%$ efficiency) from the initial state $|1\rangle$ to the target states $|2\rangle$, $|3\rangle$, and $|4\rangle$, respectively. The field amplitudes are sinusoidally modulated over a Gaussian envelope. They can be regarded as trains of equidistant subpulses, whose peak heights are smoothly changed. The mutual intervals between the subpulses are $2\pi/\Delta\omega$. The state populations exhibit stepwise changes in accordance with the pulse-train intervals. This behavior is explained as a result of sequential interferences between wave packets created by single subpulses. In particular, Fig. 3(b) clarifies the dynamics of population transfer from $|1\rangle$ to nondirectly coupled $|3\rangle$. At early stage, population of $|2\rangle$ gradually builds up, and when its population reaches to some extent, $|3\rangle$ starts growing due to the coherent coupling with $|2\rangle$. The intervals between the subpulses match with 2π changes of relative phases between $|1\rangle$ and $|3\rangle$, resulting in the accumulation of the population of $|3\rangle$ by constructive interferences and reaching to the complete population transfer.

III. APPLICATION TO ROTATIONAL EXCITATION OF NITRIC OXIDE

A. Numerical simulation

To experimentally demonstrate the HOPE scenario proposed above, we take NO molecules as the target system. The rotational energy-level diagram of NO in its $X^2\Pi_{1/2}$ lowest vibronic level is shown in Fig. 4(a). The preceding consideration with the simple model adopted the pump and Stokes fields as Fourier-transform-limited (FTL) Gaussian pulses with variable frequency difference. Since such a pulse pair is practically demanding to prepare, we implement a pair of chirped pulses

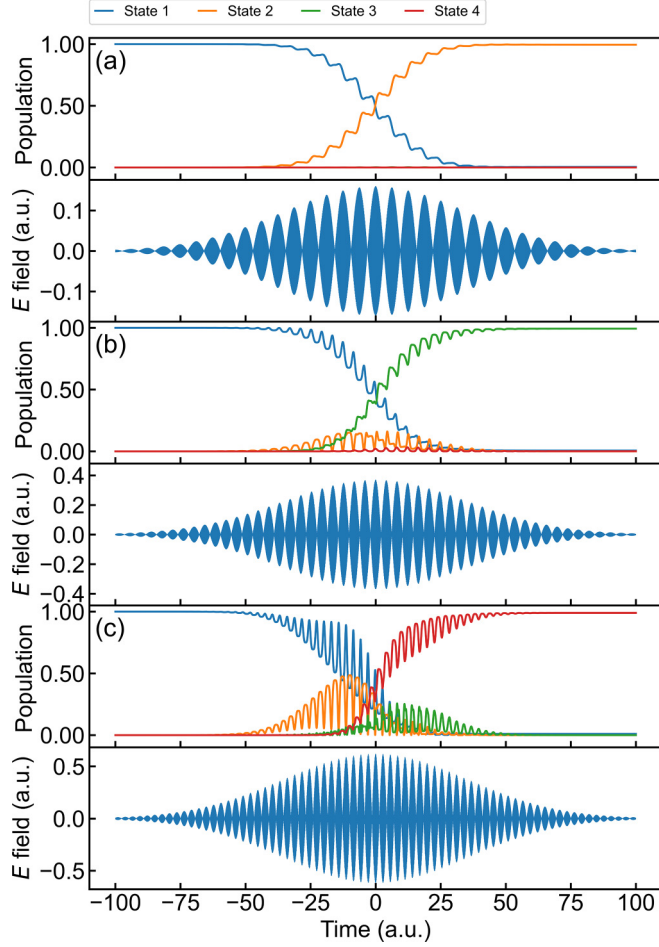


FIG. 3. Time variations of the state populations and the field amplitude for (a) $\Delta\omega = 1.00$, (b) $\Delta\omega = 1.53$, and (c) $\Delta\omega = 2.22$. The pulse duration τ is 50.

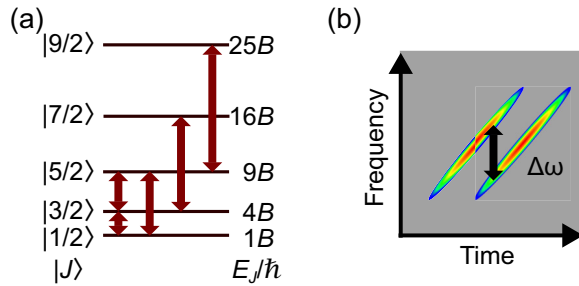


FIG. 4. (a) Rotational energy levels of NO in the $X^2\Pi_{1/2}$ manifold, with allowed Raman coupling pathways. Here, B is the effective rotational constant. (b) Schematic time-frequency 2D map for a pair of chirped pulses, applied to control the rotational dynamics of NO.

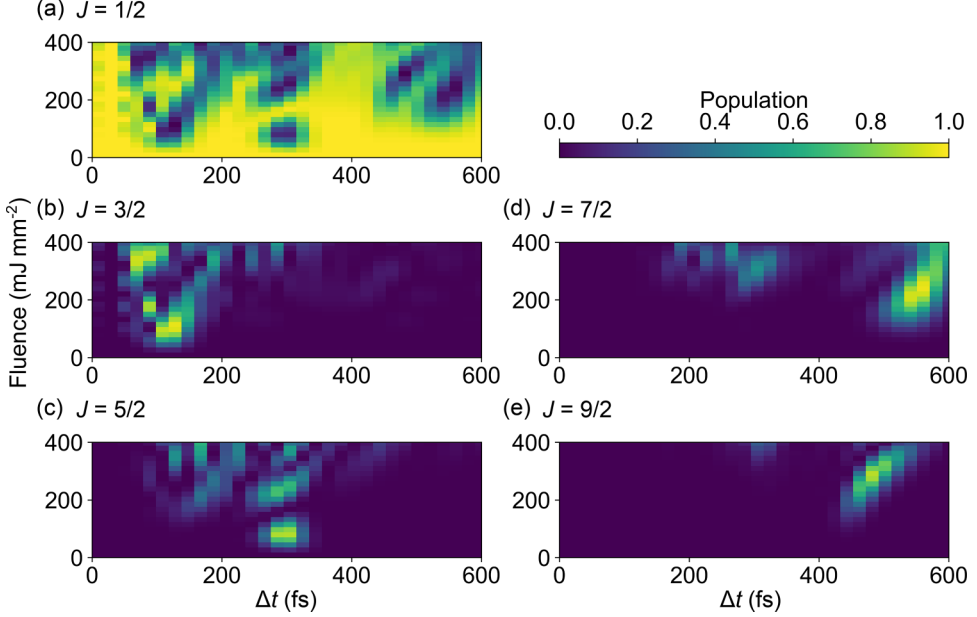


FIG. 5. 2D maps of the state populations in NO ($X^2\Pi_{1/2}$) as functions of the laser-pulse fluence and the interpulse delay Δt for (a) $J = 1/2$, (b) $J = 3/2$, (c) $J = 5/2$, (d) $J = 7/2$, and (e) $J = 9/2$. The central frequency was set at 379 THz (790 nm), and the spectral bandwidth (intensity FWHM) was 12.3 THz, corresponding to a 36-fs FTL pulse. The stretched pulse duration was set to 9 ps.

with variable mutual delay, as shown in Fig. 4(b). In a linearly chirped pulse, its instantaneous optical frequency is given as $\nu(t) \equiv \omega(t)/2\pi = \nu_0 + k(t - t_0)$, where ν_0 , t_0 , and k are the center frequency, the time offset, and the chirp rate, respectively. When an FTL Gaussian pulse is chirped, the magnitude of k is represented as

$$|k| = \frac{4 \ln 2}{2\pi} \frac{\sqrt{\tau_{\text{str}}^2 - \tau_{\text{FTL}}^2}}{\tau_{\text{str}}^2 \tau_{\text{FTL}}}, \quad (2)$$

with τ_{str} and τ_{FTL} being the stretched and FTL pulse durations, respectively. The frequency difference between a pair of chirped pulses with mutual delay Δt is given as $\Delta\nu(t) = k\Delta t$, which is constant against t . The effective difference wave number (in cm^{-1} unit) is

$$\Delta\tilde{\nu} = \frac{\Delta\nu}{100c} = \frac{k\Delta t}{100c}, \quad (3)$$

where c is the speed of light. Then, once the chirp rate k is appropriately set by adjusting the stretched pulse duration τ_{str} as given in Eq. (2), the difference wave number can be tuned by simply changing the interpulse delay Δt .

To determine the appropriate laser parameters, we conducted TDSE calculations on the rotational dynamics in NO ($X^2\Pi_{1/2}$) [39]. The nonresonant polarizability interaction in this molecular system governs the rotational selection rules for IRS as $\Delta J = \pm 1$ and ± 2 . It is noted that $\Delta J = \pm 2$ pathways dominate those for $\Delta J = \pm 1$ as J becomes larger [33]. The laser field was modeled as a pair of chirped Gaussian pulses with an adjustable interpulse delay Δt . The FTL and stretched pulse durations were set to 36 fs and 9 ps, respectively, to meet the experimental constraints. The corresponding chirp rate was $1.36 \times 10^{-6} \text{ fs}^{-2}$. The results are shown in Fig. 5, where the initial population was set concentrated in the lowest $J = 1/2$ state. Similar to Fig. 2 for the model system, yellow islands appear in the maps for all the excited rotational levels [panels (b)–(e)]. This verifies

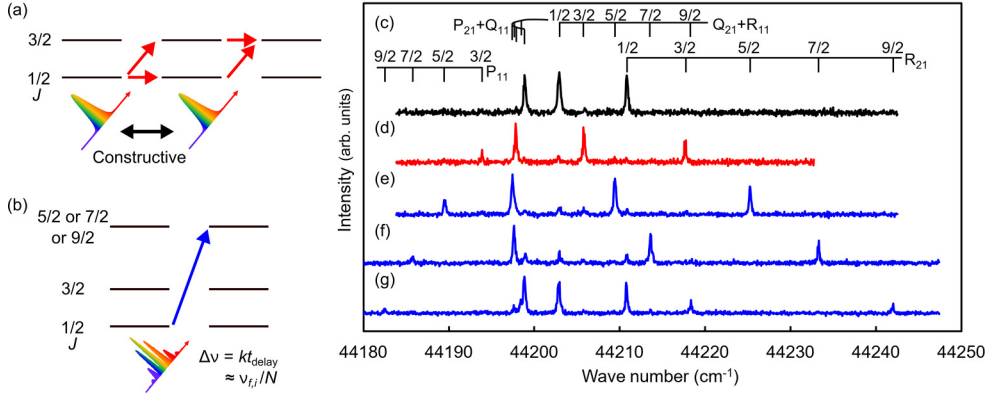


FIG. 6. Excitation schemes for (a) transition-restricted WPI and (b) HOPE. R2PI spectra of the 0–0 band of the $A^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$ transition in NO: (c) without excitation pulses, (d) with transition-restricted WPI to $J = 3/2$, (e) with HOPE to $J = 5/2$, (f) with HOPE to $J = 7/2$, and (g) with HOPE to $J = 9/2$. The rotational assignments are based on Refs. [43,44]. The optical parameters set at recording of the spectra are given in the text.

the high population transferability even into $J = 7/2$ and $9/2$, which are not directly connected via IRS pathways to the initial state. The oscillatory behavior against the laser fluence is partly evident in the map for $J = 5/2$ [panel (c)] at the delay of 290 fs. By consulting the maps, we selected the optimum values for the stretched pulse durations, fluences, and delays. Specifically, optimum delays for $J = 3/2, 5/2, 7/2$, and $9/2$ are $\sim 110, 290, 550$, and 480 fs, respectively. The corresponding difference wave numbers $\Delta\tilde{\nu}$ are calculated to be 5.0, 13.2, 25.0, and 21.8 cm^{-1} from Eq. (3). They follow the resonance condition given in Eq. (1), i.e., $\Delta\tilde{\nu} = (E_J - E_{1/2})/N$, where $E_J = B(J + 1/2)^2$ is the rotational term value for J , with $B = 1.696 \text{ cm}^{-1}$ being the effective rotational constant of NO in the $X^2\Pi_{1/2}$ manifold [41]. The Floquet index difference N is 2 for $J = 9/2$ while 1 for other J .

B. Experimental method and results

The experimental approach in the present study is similar to those adopted in our previous studies, where nonresonant intense ultrashort pulse(s) induces coherent rotational excitation and the resultant state distribution is probed by recording resonance-enhanced two-photon ionization (R2PI) spectrum [33]. Specifically, a near-infrared excitation pulse ($\approx 790 \text{ nm}$) and a counterpropagating ultraviolet probe pulse ($\approx 226 \text{ nm}$) were tightly focused onto a supersonic molecular beam of NO diluted in helium. The linearly polarized excitation pulse was delivered from a commercial femtosecond amplifier, and its duration was adjusted using the built-in pulse compressor. The pulse durations were characterized using second-harmonic-generation frequency-resolved optical gating (SHG-FROG) [39], and the FROG traces were retrieved using the common pulse retrieval algorithm (copra) code [42]. The output was then directed into a Michelson interferometer equipped with an optical delay line to generate a pair of pulses. The probe pulse was a frequency-doubled output from a commercial nanosecond dye laser with the frequency bandwidth of $\approx 0.1 \text{ cm}^{-1}$. It was linearly polarized parallel to the excitation pulses and delayed by 200 ns relative to the excitation pulses. To determine the population of each rotational state, R2PI spectra of the 0–0 band of $A^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$ transition in NO were recorded using a time-of-flight mass spectrometer by scanning the probe-pulse wavelength. The rotational assignments of the observed lines are based on Refs. [43,44].

Two excitation schemes for the coherent population transfer adopted in the present study are shown in Figs. 6(a) and 6(b). The R2PI spectrum without the excitation pulse is shown in Fig. 6(c), where only three peaks appear. They are assigned to the transitions from the lowest $J = 1/2$ level, confirming the population concentration into the single initial state.

For the population transfer to $J = 3/2$, we initially tried to apply the HOPE approach, but the transfer efficiency was quite low. This is essentially because the efficiency depends sensitively on the relative optical phase between the two chirped pulses in case of small interpulse delay. As described in detail in the Supplemental Material [39], the population is altered by almost 40% with 1.4 fs shift in the interpulse delay. The present experimental setup did not include active phase stabilization and thus the target-state population suffered from averaging over the fluctuating phase. An alternative approach would be to use more strongly stretched pulses that contain multiple beat cycles, which would reduce the sensitivity of the temporal pulse shape to the relative phase. However, our apparatus did not have these capabilities. So, we switched to the transition-restricted WPI, where the excitation-pulse duration (FWHM) was stretched to 2.2 ps and the interpulse delay was set to around 6 ps. The spectrum thus obtained with an estimated double-pulse fluence of $\sim 80 \text{ mJ mm}^{-2}$ is shown in Fig. 6(d), where four peaks of the transitions from $J = 3/2$ become prominent while the transitions from $J = 1/2$ almost disappear. The excitation efficiency is estimated to be 90% based on the integrated intensity ratio of the $R_{21}(3/2)$ line against $R_{21}(1/2)$ and the corresponding rotational line strengths [45].

The HOPE approach has been applied to the population transfer into $J = 5/2$, $7/2$, and $9/2$. We note that the experimentally available double-pulse fluence was $\sim 180 \text{ mJ mm}^{-2}$ at maximum. The TDSE calculation estimated the optimum fluence for $J = 5/2$ to be $\sim 80 \text{ mJ mm}^{-2}$, which was well below the experimental limit. So, we adjusted the output from the fs laser system and recorded R2PI spectrum, as shown in Fig. 6(e). There appear four dominant transitions from $J = 5/2$, while those from $J = 1/2$ and $3/2$ are hardly observed. The optimized delay was 280 fs. The excitation efficiency was evaluated to be 85% from the line intensity ratio.

For $J = 7/2$ and $9/2$, the optimum fluence was estimated above $\sim 200 \text{ mJ mm}^{-2}$, beyond the experimental limit. Then, we recorded R2PI spectra with maximum laser fluence ($\sim 180 \text{ mJ mm}^{-2}$) with delays at 580 and 510 fs, which were optimized for $J = 7/2$ and $9/2$, respectively. The results are shown in Figs. 6(f) and 6(g). The excitation efficiency for $J = 7/2$ was evaluated to be 70%, much degraded from complete population transfer. Still, state-selective nature was maintained, as evidenced by no appearance of transitions from other than $J = 1/2$ or $7/2$. The transfer efficiency was quite low (17%) for $J = 9/2$, since the applied laser fluence was much below the optimum value ($\sim 300 \text{ mJ mm}^{-2}$). State selectivity was also largely deteriorated, as evidenced by the transitions from $J = 3/2$ appearing in the spectrum.

We note that the strong-field ionization by the chirped excitation pulses was below the detection limit at the laser fluence of $\sim 80 \text{ mJ mm}^{-2}$. When the fluence was raised to its maximum ($\sim 180 \text{ mJ mm}^{-2}$), weak ion signals induced by the excitation pulses were observed. However, we have verified that possible modification of population by strong-field ionization was negligible even at the limit condition, by confirming that no detectable change was observed in R2PI spectra recorded without and with the excitation pulses, of which interpulse delay was set so that no population transfer arose.

IV. DISCUSSION AND CONCLUSION

A. Floquet-state interpretation of HOPE

1. Reference case: Rabi oscillation in the Floquet picture

Before discussing HOPE, it would be beneficial to recall the two-level Rabi problem in a form that emphasizes the phase evolution of Floquet eigenstates. Here, we introduce a Floquet-state interpretation that will be generalized below. The Rabi problem can be formulated in terms of Floquet states [46,47]. We consider a two-level system consisting of two bare states coupled by a resonant field. In Floquet theory, a periodically driven two-level system described by a 2×2 time-dependent Hamiltonian $H(t)$ can be recast as a time-independent Floquet eigenvalue problem in an extended Hilbert space spanned by the material states and Fourier indices. After truncating the Fourier basis to M components, the Floquet Hamiltonian H_F is represented by a $2M \times 2M$ matrix.

The basis vectors are written as $|\alpha, n\rangle$, where $\alpha = 1, 2$ labels the bare material state and the integer n denotes the Floquet index, i.e., the Fourier index in the Floquet expansion.

In the resonant case, the two states $|1, n\rangle$ and $|2, n-1\rangle$ are degenerate in the absence of coupling. The full Floquet Hamiltonian is defined in the extended Hilbert space spanned by the basis states $|\alpha, m\rangle$ and is, in principle, infinite-dimensional with respect to the Floquet index m . Near resonance, however, the dynamics is dominated by the nearly degenerate pair $|1, n\rangle$ and $|2, n-1\rangle$. Projecting the Floquet Hamiltonian onto this resonant subspace, the effective Hamiltonian is written as

$$H_{\text{eff}} = \begin{pmatrix} n\hbar\omega & H_{12} \\ H_{12}^* & \Delta E + (n-1)\hbar\omega \end{pmatrix}, \quad (4)$$

where $\Delta E = E_2 - E_1$ is the bare energy splitting. At exact resonance, $\Delta E = \hbar\omega$, the two diagonal elements become degenerate. The eigenvalues are then

$$\epsilon_{\pm} = n\hbar\omega \pm |H_{12}| = n\hbar\omega \pm \frac{\hbar\Omega_R}{2}, \quad (5)$$

where $\Omega_R = 2|H_{12}|/\hbar$ is the Rabi frequency. The corresponding Floquet eigenstates are written as

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2}}(|1, n\rangle \pm |2, n-1\rangle). \quad (6)$$

If the initial state can be written as the basis vector $|1, n\rangle$, the time-evolved state can be represented as a superposition of the two Floquet eigenstates:

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}}(|\psi_{+}\rangle + e^{-i\Omega_R t} |\psi_{-}\rangle). \quad (7)$$

As a result, the population $P_1 - P_2$ oscillates between 1 and -1 . Here, $P_{\alpha} = \sum_m |\langle \alpha, m | \Psi \rangle|^2$ is the material-state population obtained by summing over the Floquet index. In its standard formulation, Floquet theory applies to Hamiltonians that are periodic in time [40,48]. Nevertheless, the Floquet picture is useful for interpreting strongly driven systems in terms of dressed states. For pulsed fields, the same idea may be used as an instantaneous Floquet-state picture, with the effect of the pulse envelope treated through the time dependence of the instantaneous Floquet states [49,50].

2. Generalization of Rabi oscillation to a multilevel system in a strong field

The Floquet-state view of Rabi oscillation can be generalized to a strongly coupled multilevel system. In such a system, the population-transfer dynamics is determined not only by the direct coupling between the field-free initial and final states but also by the Floquet eigenstates formed under the strong field. This distinction is central to HOPE because population transfer can occur even when the target state is not directly coupled to the initial state in the bare-state basis. These Floquet eigenstates contain the initial $|\alpha_i, n\rangle$, final $|\alpha_f, n-N\rangle$, and intermediate components such as $|\alpha_m, n_m\rangle$, thereby providing effective coupling pathways between states that are not directly coupled in the bare basis. In this sense, the mechanism is related to the ac Stark effect: Off-resonant allowed couplings to intermediate states can induce not only diagonal light-induced shifts but also effective off-diagonal couplings between otherwise uncoupled states. In the Floquet picture, both effects are incorporated into the quasienergies and eigenstates of the Floquet Hamiltonian.

The resonance condition $N\hbar\omega = E_f - E_i$ makes the two components $|\alpha_i, n\rangle$ and $|\alpha_f, n-N\rangle$ degenerate in the Floquet basis. The interaction lifts this degeneracy and splits the quasienergies of the two corresponding Floquet eigenstates, as represented in Eq. (6). A state expressed as a superposition of these two Floquet eigenstates then evolves through their time-dependent relative phase, as shown in Eq. (7). Projecting this state vector onto the bare-state basis gives Rabi-like population transfer.

Because the discussion so far does not assume a specific form of interaction, the concept of HOPE is, in principle, not limited to Raman interactions. Moreover, although this discussion is based on

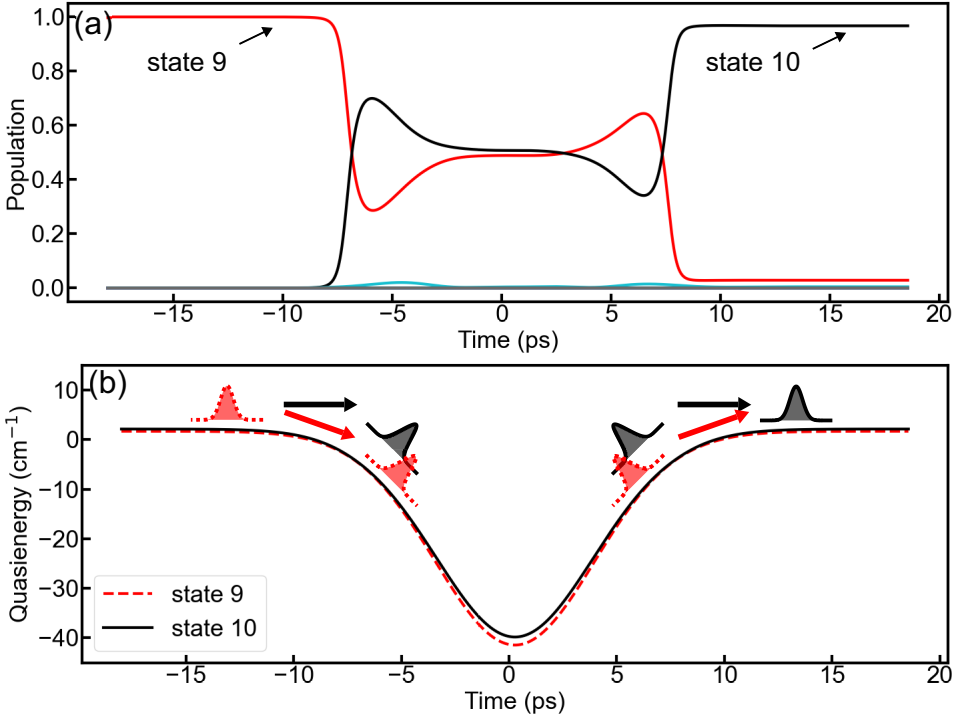


FIG. 7. (a) Adiabatic population dynamics between $J = 1/2$ and $9/2$ of NO in the $^2\Pi_{1/2}$ ground-state manifold. States 9 and 10 correlate with $|1/2, 0\rangle$ and $|7/2, -1\rangle$, respectively, in the absence of the optical interaction. Here, the initial population is set to be concentrated in state 9. The population is exclusively transferred into state 10, and other states essentially gain no appreciable population. (b) Quasienergy curves of states 9 and 10. The two states make two avoided crossings, and population dynamics across the crossings is schematically represented. Here, constructive interference between the two bifurcated populations results in the complete population transfer.

the Floquet picture for a time-periodic field, pulsed lasers provide a practical way to realize the high-intensity field needed for strong effective coupling. In this paper, we consider the experimental implementation based on the double-chirped-pulse method; therefore, we focus below on rotational Raman excitation in a pulsed field.

3. HOPE for NO rotational excitation by double-chirped-pulse method

To clarify the transfer mechanism under time-varying optical coupling, we analyzed the dynamics using an instantaneous Raman-Floquet basis constructed from the cycle-averaged Raman Hamiltonian. The details of the construction are given in the Supplemental Material [39]. Figure 7(a) shows the dynamics of adiabatic populations, where 25 basis states with $J = 1/2, 3/2, \dots, 9/2$ and $n = -2, -1, \dots, 2$ are included. Here, $n \equiv n_p - n_s$ denotes the Floquet index for the beating component, with n_p and n_s being the Floquet indices of the pump and Stokes components, respectively. The delay between the double-chirped pulses was set to 550 fs so that the energy corresponding to the beat frequency nearly matches $\Delta E = E_{7/2} - E_{1/2}$. In the absence of interaction, states 9 and 10 correlate with $|1/2, 0\rangle$ and $|7/2, -1\rangle$, respectively, and their unperturbed quasienergies are separated by only 0.4 cm^{-1} , as shown in Fig. 7(b). Before the interaction, state 9 is fully populated. At the beginning and the end of the interaction, states 9 and 10 form avoided crossings, and almost half of the population is transferred to state 10 at the first avoided crossing. The relative phase

between states 9 and 10 changes during the interaction, and the population after the second avoided crossing is concentrated in state 10 in the case of constructive interference. Thus, in the field-free limit, the final population fully resides in the rotational state corresponding to $|7/2, -1\rangle$. Ultimately, the quasienergy splitting, phase evolution, and recombination of the two adiabatic states result in the complete population transfer in this instantaneous adiabatic-state picture. Conventional pulsed Rabi oscillation, including the one-photon interaction case, can also be interpreted in the instantaneous Floquet picture as nonadiabatic branching and recombination of the wave packet, accompanied by relative-phase evolution between the Floquet components. Thus, the population-transfer dynamics discussed here can be regarded as a multilevel generalization of pulsed Rabi oscillation.

B. Practical aspects of HOPE

Here, we discuss the applicability of HOPE and the practical limitations that may arise in experimental implementations. The population-transfer efficiencies in our experiment were 85%, 70%, and 17% for $J = 5/2$, $7/2$, and $9/2$, respectively. These values demonstrate that HOPE can induce highly efficient population transfer, while also indicating that optimization of the excitation conditions becomes important for extending the transfer to higher rotational states. Another practical advantage is that the double-chirped field can be prepared simply by introducing a delayed replica of a single chirped pulse.

The experimentally available peak intensity and fluence of the excitation pulses are important practical constraints on the efficiency of HOPE. The maximum peak intensity to be applied is limited by the onset of nonresonant ionization. For the transfer to $J = 5/2$, the effective coupling strength is proportional to the laser intensity, since the initial and final states are two-photon coupled directly, and the complete population-transfer condition is determined by the time-integrated intensity, i.e., the fluence. Then, the peak intensity can be reduced to suppress undesired ionization by stretching the pulse duration, while keeping the fluence unchanged and maintaining the high population-transfer efficiency. Actually, undesired ionization was ignorable at the laser fluence applied for $J = 5/2$ ($\sim 80 \text{ mJ mm}^{-2}$), as mentioned above. The experimental excitation condition was set close to the optimal (giving the transfer efficiency $>99\%$) predicted by the ideal TDSE calculation (i.e., with the excitation pulses of a smooth Gaussian-like envelope). The almost complete population transfer was also verified with the retrieved pulses from SHG-FROG (see the Supplemental Material [39] for more details). Thus, the observed efficiency of 85% was limited mostly by experimental factors, such as shot-to-shot laser intensity fluctuations, the nonuniform intensity distribution of the excitation pulses in the probed region, and imperfect spatial overlap between the pump and probe pulses, rather than by the HOPE transfer mechanism itself.

For $J = 7/2$ and $9/2$, the present experimental setup is incapable of realizing the complete population transfer. If the pulse duration is kept as 9 ps (the maximum available for the setup), the optimum laser fluences are estimated to be ~ 200 and 300 mJ mm^{-2} , respectively, for $J = 7/2$ and $9/2$. However, ionization with excitation pulses became detectable at $\sim 180 \text{ mJ mm}^{-2}$ and increasing the fluence should not be effective with the same pulse duration. For the transfers to $J = 7/2$ and $9/2$, there is no direct two-photon Raman coupling between the initial and target states. In the TDSE calculations, the optimal fluence for these transfers increases with pulse duration, in contrast to the nearly constant optimal fluence for $J = 5/2$. This dependence appears to be consistent with that expected for higher-order Raman coupling. Importantly, the Floquet-index difference N that determines the resonance condition in HOPE is not necessarily identical to the order of the effective Raman coupling in a perturbative expansion. For a conventional K th-order Raman process involving repeated interactions with the same beat-frequency component, the resonance condition is $\Delta\omega \approx \Delta\omega_{m,n}/K$, whereas in HOPE the Floquet-index difference N determines the resonance condition $\Delta\omega \approx \Delta\omega_{m,n}/N$, as given by Eq. (1). In the strong-field regime relevant to HOPE, the off-diagonal Raman couplings become sufficiently strong to produce substantial mixing of multiple bare-state components in the Floquet eigenstates. The resulting population transfer is understood as a multilevel generalization of Rabi dynamics through the phase evolution and interference of these

Floquet states, rather than being based on sequential population transfer through the intermediate molecular eigenstates. We consider this realization of nonperturbative multilevel Rabi dynamics to be a distinct physical feature of HOPE, in contrast to a perturbative expansion picture for higher-order Raman coupling.

The temporal waveform of the pulse also affects the efficiency of HOPE. In the instantaneous adiabatic-state picture, the key processes in HOPE can be interpreted as avoided crossings formed by time-dependent effective Raman coupling, nonadiabatic transitions through these crossings, and the resulting interference. If the actual pulse deviates from the ideal waveform, the two nonadiabatic transitions can become asymmetric. As a result, population can remain in the initial state, thereby reducing the transfer efficiency. The TDSE calculations also show the appreciable population leakage into intermediate states in the case of excitation with nonideal pulses, even if the condition is optimized (see the Supplemental Material [39] for more details). Deformation of pulse waveform may originate from distortion of the temporal envelope or from nonideal spectral intensity and spectral phase. Pulse-shaping control may be useful for generating a constant-period beat waveform with a smooth Gaussian-like envelope that is suitable for the desired population-transfer dynamics.

In the present study, population control has been explored among rotational states exclusively within the $^2\Pi_{1/2}$ ground-state manifold of NO with $v = 0$. The excitation pulses are far off-resonant from any vibrational or electronic transitions of NO. So, we do not have to consider involvement of upper vibronic states. Rotational energy levels of the molecule are so sparse that Raman coupling dynamics among them can be interpreted in the instantaneous adiabatic-state picture. For heavier molecular systems, rotational energy levels may be so congested that state-selective population control is difficult. In this situation, the pulse duration should be stretched to narrow the instantaneous bandwidth.

C. Conclusion

In conclusion, we theoretically examined and experimentally verified two types of coherent population transfer based on the wave-packet interference and multiphoton Rabi oscillation driven by the induced Raman scattering. By appropriately optimizing the optical parameters, highly efficient state-selective population transfer was realized between rotational eigenstates of NO in its $X^2\Pi_{1/2}$ vibronic manifold using a pair of chirped pulses. The transfer efficiencies from the lowest initial $J = 1/2$ state to the three nearest-neighbor target states were 90%, 85%, and 70%, much improved from the previous pulse-shaping study ($\leq 60\%$ for $J = 5/2$) [36].

One important consequence of the multilevel Rabi dynamics of HOPE is that it can access target states that are not directly coupled to the initial state in the bare-state basis. It will be applied to prepare atomic/molecular ensembles residing in a quantum level with high excitation energy. In addition, utilization of ultrashort pulses allows us to execute coherent population transfer in systems where an ensemble of different quantum states resides in an initial condition. In particular, it will be highly valuable to realize the efficient population transfer of an ensemble in different rotational states in the vibrational ground state to highly excited vibrational levels. Even in the transfer from a single rotational level, multiple components have to be considered as an initial state if fine and/or hyperfine splittings are involved. When a narrow-band light source is used, a part of the multiple components is only subjected to population transfer [51]. In the case of HOPE, the final states will be superpositions of the split components, and the evolution of the resulting wave packets will be observed as hyperfine depolarization, similar to our previous report [52].

A future extension will allow HOPE to serve as a powerful coherent control technique for multilevel quantum systems. In particular, a creation of quantum wave packets composed of arbitrarily selected two eigenstates will be realized by appropriately adjusting the optical parameters, e.g., pulsed field strength. Its ability to drive state-selective coherent coupling beyond the constraints of optical selection rules could form the basis for advanced reaction control and high-speed selective gate operations in quantum computation.

ACKNOWLEDGMENT

This work was supported by the JSPS KAKENHI Grants No. JP18H03897, No. JP20K21169, No. JP22H00312, No. JP22K18327, and No. JP25K22240.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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- [1] C. P. Koch and M. Shapiro, Coherent control of ultracold photoassociation, *Chem. Rev.* **112**, 4928 (2012).
 - [2] H. Pan, S. Mondal, C.-H. Yang, and K. Liu, Imaging characterization of the rapid adiabatic passage in a source-rotatable, crossed-beam scattering experiment, *J. Chem. Phys.* **147**, 013928 (2017).
 - [3] H. Pan and K. Liu, Fermi-phase-induced interference in the reaction between Cl and vibrationally excited CH₃D, *Nat. Chem.* **14**, 545 (2022).
 - [4] W. E. Perreault, N. Mukherjee, and R. N. Zare, Quantum control of molecular collisions at 1 kelvin, *Science* **358**, 356 (2017).
 - [5] W. E. Perreault, N. Mukherjee, and R. N. Zare, Cold quantum-controlled rotationally inelastic scattering of HD with H₂ and D₂ reveals collisional partner reorientation, *Nat. Chem.* **10**, 561 (2018).
 - [6] R. Sussmann, R. Neuhauser, and H. J. Neusser, Stimulated Raman adiabatic passage with pulsed lasers: High resolution ion dip spectroscopy of polyatomic molecules, *J. Chem. Phys.* **100**, 4784 (1994).
 - [7] I. I. Rabi, On the process of space quantization, *Phys. Rev.* **49**, 324 (1936).
 - [8] S. Nandi, E. Olofsson, M. Bertolino, S. Carlström, F. Zapata, D. Busto, C. Callegari, M. Di Fraia, P. Eng-Johnsson, R. Feifel, *et al.*, Observation of Rabi dynamics with a short-wavelength free-electron laser, *Nature (London)* **608**, 488 (2022).
 - [9] A. de las Heras, C. Hernández-García, J. Serrano, A. Prodanov, D. Popmintchev, T. Popmintchev, and L. Plaja, Attosecond Rabi oscillations in high harmonic generation resonantly driven by extreme ultraviolet laser fields, *Phys. Rev. Res.* **7**, 023268 (2025).
 - [10] A. F. Linskens, I. Holleman, N. Dam, and J. Reuss, Two-photon Rabi oscillations, *Phys. Rev. A* **54**, 4854 (1996).
 - [11] M. Fushitani, C.-N. Liu, A. Matsuda, T. Endo, Y. Toida, M. Nagasono, T. Togashi, M. Yabashi, T. Ishikawa, Y. Hikosaka, T. Morishita, and A. Hishikawa, Femtosecond two-photon Rabi oscillations in excited He driven by ultrashort intense laser fields, *Nat. Photon.* **10**, 102 (2016).
 - [12] R. Vijay, C. Macklin, D. H. Slichter, S. J. Weber, K. W. Murch, R. Naik, A. N. Korotkov, and I. Siddiqi, Stabilizing Rabi oscillations in a superconducting qubit using quantum feedback, *Nature (London)* **490**, 77 (2012).
 - [13] K. Bergmann, H. Theuer, and B. W. Shore, Coherent population transfer among quantum states of atoms and molecules, *Rev. Mod. Phys.* **70**, 1003 (1998).
 - [14] N. V. Vitanov, T. Halfmann, B. W. Shore, and K. Bergmann, Laser-induced population transfer by adiabatic passage techniques, *Annu. Rev. Phys. Chem.* **52**, 763 (2001).
 - [15] B. W. Shore, Coherent manipulations of atoms using laser light, *Acta Phys. Slov.* **58**, 243 (2008).
 - [16] N. V. Vitanov, A. A. Rangelov, B. W. Shore, and K. Bergmann, Stimulated Raman adiabatic passage in physics, chemistry, and beyond, *Rev. Mod. Phys.* **89**, 015006 (2017).
 - [17] B. W. Shore, Picturing stimulated Raman adiabatic passage: A STIRAP tutorial, *Adv. Opt. Photon.* **9**, 563 (2017).
 - [18] N. Mukherjee and R. N. Zare, Stark-induced adiabatic Raman passage for preparing polarized molecules, *J. Chem. Phys.* **135**, 024201 (2011).
 - [19] N. Mukherjee, W. E. Perreault, and R. N. Zare, Stark-induced adiabatic passage processes to selectively prepare vibrationally excited single and superposition of quantum states, in *Frontiers and Advances in*

- Molecular Spectroscopy*, edited by J. Laane (Elsevier, Amsterdam, The Netherlands, 2018), Chap. 1, pp. 1–46.
- [20] N. Mukherjee, Quantum-controlled collisions of H₂ molecules, *J. Phys. Chem. A* **127**, 418 (2023).
 - [21] H. Chadwick, P. M. Hundt, M. E. van Reijzen, B. L. Yoder, and R. D. Beck, Quantum state specific reactant preparation in a molecular beam by rapid adiabatic passage, *J. Chem. Phys.* **140**, 034321 (2014).
 - [22] K. K. W. Ma and C. K. Law, Three-photon resonance and adiabatic passage in the large-detuning Rabi model, *Phys. Rev. A* **92**, 023842 (2015).
 - [23] K.-X. Yan, Y. Qiu, Y. Xiao, Y.-H. Chen, and Y. Xia, Generating three-photon Rabi oscillations without a large-detuning condition, *Phys. Rev. A* **110**, 043711 (2024).
 - [24] P. Li, W. Yang, X. Li, S. Xue, J. Li, and H. Du, Three-photon Rabi oscillations in N₂⁺ lasing at 391 nm, *Phys. Rev. A* **111**, 063501 (2025).
 - [25] L. Sirko, A. Buchleitner, and H. Walther, Rabi-nutations of four- and six-photon transitions between Rydberg states, *Opt. Commun.* **78**, 403 (1990).
 - [26] J. He, B. Pasquiou, R. G. Escudero, S. Zhou, M. Borkowski, and F. Schreck, Coherent three-photon excitation of the strontium clock transition, *Phys. Rev. Res.* **7**, L012050 (2025).
 - [27] R. E. Carley, E. Heesel, and H. H. Fielding, Femtosecond lasers in gas phase chemistry, *Chem. Soc. Rev.* **34**, 949 (2005).
 - [28] M. Gühr, Ultrafast molecular spectroscopy in the gas phase, in *Structural Dynamics with X-ray and Electron Scattering*, edited by K. Amini, A. Rouzée, M. J. J. Vrakking (Royal Society of Chemistry, Cambridge, UK, 2023), Chap. 1, pp. 1–53.
 - [29] J. Karczmarek, J. Wright, P. Corkum, and M. Ivanov, Optical centrifuge for molecules, *Phys. Rev. Lett.* **82**, 3420 (1999).
 - [30] D. M. Villeneuve, S. A. Aseyev, P. Dietrich, M. Spanner, M. Y. Ivanov, and P. B. Corkum, Forced molecular rotation in an optical centrifuge, *Phys. Rev. Lett.* **85**, 542 (2000).
 - [31] C. Wu, G. Zeng, Y. Gao, N. Xu, L.-Y. Peng, H. Jiang, and Q. Gong, Controlling molecular rotational population by wave-packet interference, *J. Chem. Phys.* **130**, 231102 (2009).
 - [32] K. Ohmori, Wave-packet and coherent control dynamics, *Annu. Rev. Phys. Chem.* **60**, 487 (2009).
 - [33] Y. Ohshima and H. Hasegawa, Coherent rotational excitation by intense nonresonant laser fields, *Int. Rev. Phys. Chem.* **29**, 619 (2010).
 - [34] S. Shi and H. Rabitz, Quantum mechanical optimal control of physical observables in microsystems, *J. Chem. Phys.* **92**, 364 (1990).
 - [35] D. Goswami, Optical pulse shaping approaches to coherent control, *Phys. Rep.* **374**, 385 (2003).
 - [36] A. Rouzée, O. Ghafur, K. Vidma, A. Gijsbertsen, O. M. Shir, T. Bäck, A. Meijer, W. J. van der Zande, D. Parker, and M. J. J. Vrakking, Evolutionary optimization of rotational population transfer, *Phys. Rev. A* **84**, 033415 (2011).
 - [37] T. Hellerer, A. M. Enejder, and A. Zumbusch, Spectral focusing: High spectral resolution spectroscopy with broad-bandwidth laser pulses, *Appl. Phys. Lett.* **85**, 25 (2004).
 - [38] K. Wang, A. Hardikar, A. A. Milner, and V. Milner, Optical centrifuge with zero rotational acceleration, *Phys. Rev. A* **112**, 053102 (2025).
 - [39] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/sy5j-g2cq> for details of the TDSE calculations, pulse characterization, and instantaneous Raman-Floquet analysis, which includes Refs. [53,54].
 - [40] J. H. Shirley, Solution of the Schrödinger equation with a Hamiltonian periodic in time, *Phys. Rev.* **138**, B979 (1965).
 - [41] H. Hasegawa and Y. Ohshima, Decoding the state distribution in a nonadiabatic rotational excitation by a nonresonant intense laser field, *Phys. Rev. A* **74**, 061401(R) (2006).
 - [42] N. C. Geib, M. Zilk, T. Pertsch, and F. Eilenberger, Common pulse retrieval algorithm: A fast and universal method to retrieve ultrashort pulses, *Optica* **6**, 495 (2019).
 - [43] R. Engleman, P. Rouse, H. Peek, and V. Baiamonte, Beta and gamma band systems of nitric oxide, Technical Report, Division of Technical Information Extension, U.S. Atomic Energy Commission, 1969.
 - [44] D. X. Wang, C. Haridass, and S. Reddy, The gamma (A²Σ⁺–X²Π_r) system of the nitric oxide isotopomers, *J. Mol. Spectrosc.* **175**, 73 (1996).

- [45] R. N. Zare, *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics* (John Wiley and Sons, Inc., New York, 1991).
- [46] C. Deng, F. Shen, S. Ashhab, and A. Lupascu, Dynamics of a two-level system under strong driving: Quantum-gate optimization based on Floquet theory, [Phys. Rev. A **94**, 032323 \(2016\)](#).
- [47] R. Merlin, Rabi oscillations, Floquet states, Fermi's golden rule, and all that: Insights from an exactly solvable two-level model, [Am. J. Phys. **89**, 26 \(2021\)](#).
- [48] H. Sambe, Steady states and quasienergies of a quantum-mechanical system in an oscillating field, [Phys. Rev. A **7**, 2203 \(1973\)](#).
- [49] K. Drese and M. Holthaus, Floquet theory for short laser pulses, [Eur. Phys. J. D **5**, 119 \(1999\)](#).
- [50] T. N. Ikeda, S. Tanaka, and Y. Kayanuma, Floquet-Landau-Zener interferometry: Usefulness of the Floquet theory in pulse-laser-driven systems, [Phys. Rev. Res. **4**, 033075 \(2022\)](#).
- [51] A. Kuhn, S. Steuerwald, and K. Bergmann, Coherent population transfer in NO with pulsed lasers: The consequences of hyperfine structure, Doppler broadening and electromagnetically induced absorption, [Eur. Phys. J. D **1**, 57 \(1998\)](#).
- [52] D. Ikeda, K. Mizuse, and Y. Ohshima, Direct imaging of the hyperfine depolarization in electronically excited NO molecules, [Phys. Rev. A **107**, 043116 \(2023\)](#).
- [53] S. A. McDowell and W. J. Meath, Average energy approximations for anisotropic triple-dipole dispersion energy coefficients using three-body interactions involving, [Can. J. Chem. **76**, 483 \(1998\)](#).
- [54] J. Danielak, U. Domin, R. Ke, M. Rytel, and M. Zachwieja, Reinvestigation of the emission γ band system ($A^2\Sigma^+-X^2\Pi$) of the NO molecule, [J. Mol. Spectrosc. **181**, 394 \(1997\)](#).