Quantum State Reconstruction of a Rotational Wave Packet Created by a Nonresonant Intense Femtosecond Laser Field

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We have experimentally determined the amplitudes and phases of a rotational wave packet in an adiabatically cooled benzene molecule, created by a nonresonant intense femtosecond laser field. In this wave-packet reconstruction, the initial wave packet is further interfered by a replica of the first laser pulse, and the resultant modulation in population is observed in a state-resolved manner. Though several states with different nuclear-spin modifications are populated in the initial condition, a single wave packet created from one of them (with $J = 0$) is specifically reconstructed. Phase shifts characteristic of stepwise Raman excitation beyond the perturbative regime are experimentally identified.

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The quantum-state reconstruction of a wave function (WF) has attracted a lot of attention for over more than a decade (see, for examples, [1–3]). Its importance is rapidly growing in conjunction with advances in ultrafast laser technologies. Here, highly controlled light pulses are exploited for manipulating a time-dependent WF, i.e., a quantum wave packet (WP), via optical transitions and an experimental retrieval of the resultant WP is crucial for further WP processing. So far, several studies have reported the experimental realization of quantum-state reconstruction from a series of measurements on observables of atomic or molecular systems [4–9].

Another quickly emerging field initiated by the advance in ultrafast laser technologies is the exploration of nonadiabatic molecular alignment [10]. When an intense nonresonant ultrafast laser pulse is irradiated onto gaseous molecules, the rotation of the molecules is coherently excited to create a rotational WP, owing to a nonadiabatic interaction between the laser field and the molecular anisotropic polarizability. Soon after the original theoretical consideration [11], the nonadiabatic molecular alignment was experimentally demonstrated [12]. Currently, many researchers are focusing on control of the molecular alignment by the manipulation of light fields, i.e., multipulse excitation [13–17] and pulse shaping [18–20].

Though the excitation mechanism in nonadiabatic molecular alignment has been well described, WP creation is sensitive to the light field because of the highly nonlinear nature of the excitation process, far beyond the perturbative regime in light-matter interactions. In addition, a precise determination of the light field at the position of the interaction is not an easy effort, particularly for a sophisticatedly structured excitation pulse. In this context, quantum-state reconstruction suitable for the nonadiabatic molecular alignment is of great significance, but has scarcely been studied; there is only a single report on a proposed tomographic reconstructing procedure for a rotational WP, or more properly a density matrix for a mixed state, created by an intense ultrafast laser pulse [21].

In the work presented here, a rotational wave packet created nonadiabatically by an intense nonresonant femtosecond pulse is reconstructed experimentally by a method different from that already proposed [21]. The approach adopted herein is based on a quantum-state-resolved spectroscopic observation [16,22,23], in which one utilizes rotational-distribution measurements after the excitation of a pair of femtosecond pulses with identical intensity and shape. We show that a finite time sequence of observations on the distribution allows us to retrieve the phases and absolute amplitudes of the WP created by a single pulse in the excitation pulse pair.

Here, we deal with a closed-shell symmetric-top molecule (benzene in this case), in which electronic orbital and spin angular momenta are quenched. An eigenstate of the molecule in a field-free condition is denoted as $|J, K, M\rangle$, where J is the rotational angular momentum, and K and M are its projections onto the molecular symmetry axis and the space fixed axis, respectively. Its eigenenergy is $E_{J,K} = hBJ(J+1) + h(C-B)K^2$ when we neglect a small contribution from the centrifugal distortion terms, and B and C are rotational constants (in Hz unit). The interaction with a linearly polarized nonresonant laser field is represented as $\hat{V}(t) = -\frac{1}{4}[E(t)]^2(\Delta\alpha\cos^2\theta + \alpha_\perp)$, where $E(t)$ is the envelope of the electric field of the laser pulse, $\Delta\alpha = \alpha_\parallel - \alpha_\perp$, with static polarizabilities parallel and perpendicular to the molecular symmetry axis, $\alpha_\parallel$, $\alpha_\perp$, respectively, and θ is the angle between the symmetry axis and the laser polarization. Matrix elements $\langle J, K, M|\hat{V}(t)|J', K', M'\rangle$ are diagonal in K and M. Furthermore, they are nonvanishing only if $\Delta J = 0, \pm 2$ for $K = 0$ and/or $M = 0$, or $\Delta J = 0, \pm 1, \pm 2$ for $K \neq 0$ and $M \neq 0$ [23].

The laser pulse converts an initial $|J_i, K_i, M_i\rangle$ state to the rotational WP, $|\Psi(t)\rangle$, which is expanded as

$$\begin{aligned}|\Psi(t)\rangle &= \hat{U}(t,0)|J_i, K_i, M_i\rangle \\ &= \sum_J A_J e^{i\delta_J} e^{-i\omega_{J,K_i}t}|J, K_i, M_i\rangle. \qquad (1)\end{aligned}$$

Here, $\hat{U}(t_2, t_1)$ is the time evolution operator from time t_1 to t_2, $\omega_{J,K} = E_{J,K}/\hbar$, and A_J and δ_J are the amplitude and phase of each $|J, K_i, M_i\rangle$ state in the rotational WP.

If another laser pulse, which is a replica of the first one, is irradiated onto the molecule at $t = \tau$, the WP represented in Eq. (1) is further modified as

$$|\Psi(t)\rangle = \hat{U}(t,\tau)|\Psi(\tau)\rangle = \sum_J B_{J,J_i}(\tau) e^{-i\omega_{J,K_i}t}|J, K_i, M_i\rangle, \qquad (2)$$

where $B_{J,J_i}(\tau)$ is the transition amplitude from $|J_i, K_i, M_i\rangle$ to $|J, K_i, M_i\rangle$ by the interaction with the double pulses. The population of the rotational eigenstate for J after the interaction corresponds to $|B_{J,J_i}(\tau)|^2$. Specifically, when we probe the population of the initial $|J_i, K_i, M_i\rangle$ state *after* the double-pulse excitation, we obtain

$$|B_{J_i,J_i}(\tau)|^2 = \sum_{J'} A_{J'}^4 + 2\sum_{J'>J''} A_{J'}^2 A_{J''}^2 \cos(\Delta\omega_{J'J''}\tau + \Delta_{J'J''}), \qquad (3)$$

where $\Delta\omega_{J'J''} = \omega_{J',K_i} - \omega_{J'',K_i}$ and $\Delta_{J'J''} = 2(\delta_{J'} - \delta_{J''})$. Thus, a series of measurements on $|B_{J_i,J_i}(\tau)|^2$ by varying τ allows us to determine the set of A_J and δ_J in the rotational WP created from the $|J_i, K_i, M_i\rangle$ state.

The experimental setup used in the present study is quite similar to that previously reported [23]. Briefly, the fundamental output from a femtosecond Ti:sapphire laser system is divided into double pulses of identical energies with a variable time delay τ. These pump pulses are collinearly focused onto jet-cooled benzene ensembles in a molecular beam to induce nonadiabatic rotational excitation. A linear chirp is applied to stretch the pulse duration (30 fs for transform-limited) to 70 fs by adjusting the compressor grating. Here, a high-pressure pulsed valve [24] with a stagnation pressure of 90 bar is incorporated for an efficient rotational cooling of molecules. The probe pulse with a 0.05 cm^{-1} bandwidth, from a nanosecond frequency-doubled dye laser, ionizes benzene molecules by (1 + 1) resonance enhanced multiphoton ionization (REMPI) via the S_1-S_1 6_0^1 band. The generated benzene cations are detected by a time-of-flight mass spectrometer (TOF-MS). The polarization direction of the pump and the probe pulses is set to be parallel to each other, and along with the ion-extraction field in the TOF-MS. Great care has been taken to probe only a molecular ensemble exposed by a uniform pump pulse field. To this end, the probe pulse, kept as weak as possible ($\leq$10 μJ/pulse), was tightly focused with an $f = 170$ mm lens, while the pump pulse was loosely focused by an $f = 300$ mm lens and its focal position was slightly shifted from the probed (i.e., ionization) region.

REMPI excitation spectra observed without pump pulses have shown that the initial state distribution is almost restricted to levels with $J_{|K|} = 0_0, 1_0, 1_1, 2_2$ and 3_3, i.e., the lowest ones with the nuclear-spin wave functions belonging to different symmetries [23,25]. When applying a single pulse onto the initial distribution, excitation up to $J \geq 6$ is clearly observed.

For reconstructing the rotational WP, we focus on the A_1 nuclear-spin species, in which the lowest level is $J_K = 0_0$. The initial state distribution in the A_1 manifold is concentrated mostly to the $J_K = 0_0$ state (>96% in the present condition with 0.5 K), and this state contains a single $M(= 0)$ sublevel only. Thus, we regard it as a good approximation that the initial molecular ensemble in this nuclear-spin manifold is in a pure state, i.e., $|J_i, K_i, M_i\rangle = |0, 0, 0\rangle$.

To experimentally probe $|B_{0,0}(\tau)|^2$, we recorded REMPI signals by fixing the probe pulse on the ${}^rR_0(0)$ transition, while scanning the delay τ. A typical example of the observed signal is shown in Fig. 1. This trace was least-squares fitted to Eq. (3) to determine the amplitudes and phases, with the beat frequencies, $\Delta\omega_{J'J''}$, fixed to those obtained from the precisely known rotational constants. Excitation to states with $J > 8$ are negligibly small, so five eigenstates ($J_K = 0_0, 2_0, \ldots, 8_0$) were included in the analysis. Because of the normalization condition on the population, the sum of A_J^2 should be unity. This constraint was taken into account in the fit. Since $|B_{0,0}(\tau)|^2$ depends on not the values of each phase, but the phase differences $2(\delta_{J'} - \delta_{J''})$, the choice of $\delta_0 = 0$ was adopted. The determined phase δ_J and population A_J^2 is indicated in Fig. 2(a). It is noted that the determined δ_J has an uncertainty of π because δ_J and $\delta_J + \pi$ give the same $\Delta_{JJ'}$.

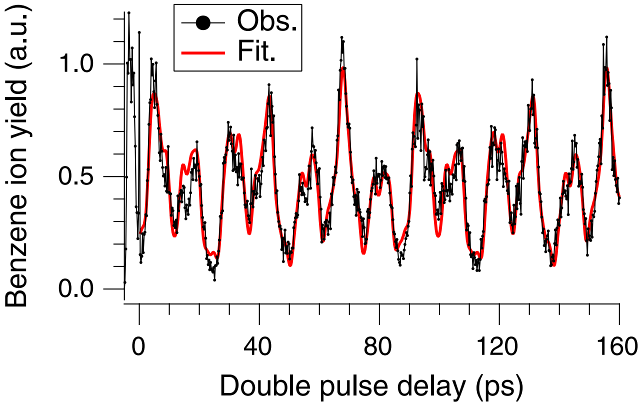

FIG. 1 (color online). Population of the $J_K = 0_0$ state $|B_{0,0}(\tau)|^2$ in benzene molecules after double-pulse excitation, plotted against the delay τ between the two pulses. The ${}^rR_0(0)$ transition is used for probing the population. The black dots represent the observed value, and the red (or gray) line is the results from a least-squares fitting. The population was normalized against the value observed without the pump pulses.

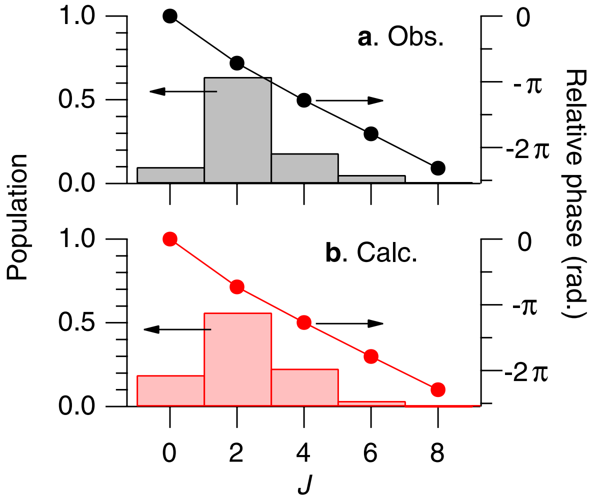

FIG. 2 (color online). Final population A_J^2 and phase δ_J. (a) Retrieved from the observed data and (b) calculated by solving TDSE. The initial state is $|0, 0, 0\rangle$.

Here, an appropriate choice can be made by a comparison with the calculation mentioned below.

As can be seen in Fig. 1, $|B_{0,0}(\tau)|^2$ almost (but not perfectly) revives at certain delay times (e.g., 68 ps, 156 ps). When the probe laser sampled a wider region with a nonuniform pump field, the extent of the revivals was greatly reduced because of the inhomogeneous dephasing inherent in a mixed state, created by the varying field, even though the initial state was a pure state. In this case, the sum of the determined A_J^2 without the constraint for the normalization in population became much less than unity. On the other hand, for the trace in Fig. 1, the sum of population reached to 0.97, validating the creation of a WP by an intense laser field with acceptable uniformity.

The phases and population calculated by solving the time-dependent Schrödinger equation (TDSE) are also displayed in Fig. 2(b). Here, the pump laser intensity was adjusted so as to best reproduce the observed δ_J and A_J. The thus-obtained value (10 TW/cm^2) reasonably agrees with that (8.4 TW/cm^2) evaluated from the experimental parameters (pulse energy, duration, and spot size). The calculation satisfactorily reproduced the experimental results. The rotational-state distribution after the single-pulse excitation was also calculated, and the spectrum was simulated based on the final distribution. Matchup between the observed and calculated was satisfactory.

The phase determined in the present rotational WP retrieval decreases monotonically as J becomes larger. This is a clear experimental signature for the stepwise excitation pathway during the interaction with the laser field, $J_K = 0_0 \rightarrow 2_0 \rightarrow 4_0 \rightarrow 6_0 \rightarrow \cdots$, obeying the rotational Raman selection rule of $\Delta J = \pm 2$ [23]. In the case of the weak-field limit, the phase difference between two states coupled with the lowest-order Raman process (proportional to the square of the field) is $-\pi/2$ (or $\pi/2$) for negative (or positive) $\Delta\alpha$ [26]. However, when the field is large enough to go beyond the perturbative regime, the phase shift substantially deviates from the limiting value. The phase differences show a characteristic dependence against the laser field intensity, as derived from the TDSE calculation [Fig. 3(a)]. Figure 3(b) shows the experimentally determined $\delta_{J+2} - \delta_J$ along with the corresponding calculated values for 10 TW/cm^2. The difference reaches almost 1.5 times the limiting value ($-\pi/2$) for $J = 0 \leftrightarrow 2$, but gradually approaches to $-\pi/2$ for higher J. Interestingly, Renard *et al.* [27] have shown analytically that all of the phase differences between adjacent states again becomes $-\pi/2$ in the case of a high field limit, where $\hat{V}(t)$ is much larger than the eigenenergies for field-free rotation, if matrix elements of $\hat{V}(t)$ are independent of J.

The phase, as well as amplitude, certainly controls the WP dynamics. For instance, if $\delta_{J+2} - \delta_J = -\pi/2$ as in the two limiting cases mentioned above, $|B_{0,0}(\tau)|^2$ becomes unity when $\tau = (n + 1/2)T_{\text{rev}}$, where T_{rev} is the revival time defined as $1/(2B)$ (=87.9 ps for benzene) with n being an integer (≥ 0). Here, the quantum state after the sequential interactions with two identical pulses goes back to the initial state, so the two pulses are a "zero effect pulse pair (ZEPP)" [28]. In an actual situation, $|B_{0,0}(\tau)|^2$ at $(n + 1/2)T_{\text{rev}}$ reaches only to 0.86, as seen in Fig. 1, while the

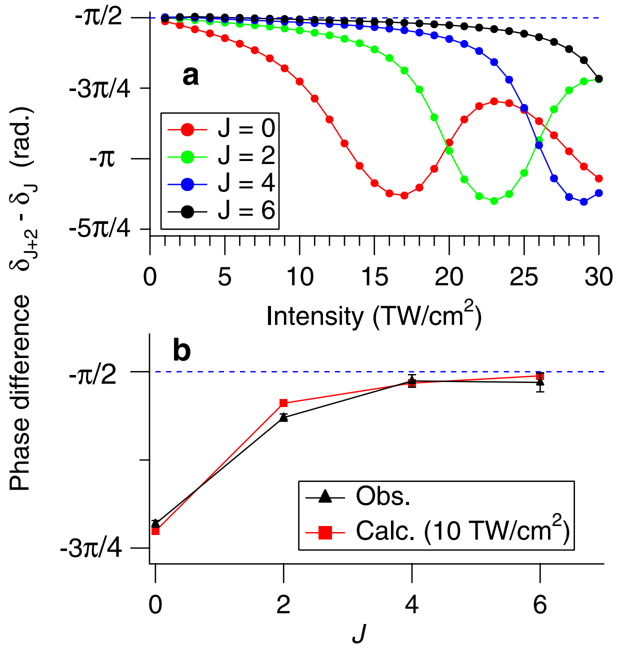

FIG. 3 (color online). (a) laser intensity dependence of $\delta_{J+2} - \delta_J$ calculated for a rotational WP of benzene created from the $|0, 0, 0\rangle$ initial state. The laser pulse duration is fixed to 70 fs. (b) Experimentally derived $\delta_{J+2} - \delta_J$ plotted against J, along with the corresponding calculated ones for 10 TW/cm^2. Error bars for the experimental values denote one standard of deviation in the least-squares fitting.

maxima (0.98) appear at 68 ps, 156 ps, etc., as mentioned previously. The substantially different delays from $(n + 1/2)T_{\mathbf{rev}}$ for the approximate ZEPPs are definitely due to the phase shifts in the nonperturbative regime, as shown in Fig. 3(b).

In the previous proposal for rotational WP reconstruction [21], a polar angular distribution of the molecular ensemble was expected to be used. Such data can be obtained via, for instance, photofragment ion imaging [29], but a very accurate record of images is necessary for the noise-sensitive Abel inversion to the 3D distribution. In the cases of polyatomic molecules, care must be paid for effects of dissociation dynamics, i.e., fragment recoil-velocity anisotropy in the molecular frame [30]. In addition, an initial ensemble in a single quantum state must be prepared, since all the molecules are subjected by photodissociation. On the other hand, the present WP reconstruction procedure relies on the modification of the initial WP by the second laser pulse, being free from possible dynamical effects in the probe process. It is not necessary to prepare a single-state initial ensemble, thanks to the quantum-state-resolved probe by REMPI to select an appropriate state out of a mixed ensemble. This is a great advantage, particularly for symmetric-top molecules with $K = 0$ (and linear molecules in the vibrational ground state) as well as asymmetric-top molecules, for which state selection via, e.g., hexapole filtering is practically difficult.

We have already reported on measurements of the rotational-state distribution after single-pulse excitation with an intense fs laser field [22,23]. In these studies, the amplitudes for each eigenstate in the rotational WP thus created were precisely evaluated, but we were unable to extract any phase information. The present work utilizing double-pulse excitation has provided a substantial advance, where phases as well as amplitudes are retrieved experimentally, leading to the full reconstruction of the WP. Maijer *et al.* reported similar measurements [16], but did not successfully probe the population in the initial state after the double-pulse excitation, nor did they mention the WP retrieval at all.

In summary, we have demonstrated a successful experimental reconstruction of a rotational wave packet, which was created nonadiabatically from the $J_K = 0_0$ state in a cold molecular ensemble of benzene by a nonresonant intense femtosecond laser field. The present retrieval procedure can be applied to various types of molecules, including asymmetric tops, as well as linear and symmetric tops. It is also extendable to holographic reconstruction, which is similar to those developed for resonant excitations in a perturbative regime [1–9], where an unknown "target" state will be interfered by a "reference" state, and thus the phases of the former state will be ambiguously determined.

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