# Reconstruction of a Rotational Wave Packet Created in the $X^2\Pi_{1/2}$ State of the NO Radical by a Nonresonant Intense Ultrashort Laser Pulse

*Hirokazu Hasegawa[1)] and Yasuhiro Ohshima[2)]*
*[1)]Department of Basic Science, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan*
*[2)]Institute for Molecular Science, National Institute of Natural Sciences and SOKENDAI (The Graduate University for Advanced Studies), 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan*
*chs36@mail.ecc.u-tokyo.ac.jp and ohshima@ims.ac.jp*

**Abstract:** We experimentally reconstructed a rotational wave packet created in NO($X^2\Pi_{1/2}$) by a nonresonant intense ultrashort laser field. The determined phase shifts show a clear signature of bifurcated pathways in the nonadiabatic rotational excitation.

**OCIS codes:** (020.0020) Atomic and molecular physics; (020.2649) Strong field laser physics; (320.7120) Ultrafast phenomena

## 1. Introduction

When an intense nonresonant ultrafast laser pulse is irradiated onto gaseous molecules, rotation of the molecules is coherently excited to create a rotational wave packet (WP) owing to the nonadiabatic interaction between the laser field and the molecular anisotropic polarizability. This process, now commonly termed "nonadiabatic molecular alignment," has attracted much attention over more than a decade since it has been implemented to control the direction of molecules in the laboratory flame in field-free condition [1,2]. The WP creation is quite sensitive to the light field because of the highly nonlinear nature of the excitation process, far beyond the perturbative regime in light-matter interaction. In addition, precise determination of the light field at the position of the interaction is not an easy effort. Therefore, an experimental retrieval of the created WP is crucial for further WP processing, but quantum state reconstruction suitable to the nonadiabatic molecular alignment has scarcely been studied [3].

Recently, we proposed and verified an experimental procedure for the reconstruction of a rotational WP created nonadiabatically by an intense nonresonant femtosecond (fs) pulse [4]. The method was based on the quantum-state resolved spectroscopic observation, in which one utilizes the rotational-distribution measurements after the excitation of a pair of femtosecond pulses with identical intensity and shape. Through the measurement on an adiabatically cooled sample of benzene molecules, we demonstrated 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. In the present study, we extend the study to an open-shell molecular system, i.e., a free radical, where an electronic orbital and/or spin angular momentum are unquenched. Adiabatically cooled nitric oxide (NO) in the $^2\Pi$ ground state has been examined, and the experimentally determined phases in the rotational WP are discussed in the relation to the WP creation process, which is characteristic to a molecule in a degenerate vibronic state [5].

## 2. Experimental

The experimental setup used in the present study is basically the same to that previously reported [4]. Briefly, the fundamental output from a fs Ti:Sapphire laser system is divided into double pulses of identical energies with a variable time delay, $\tau$. These pump pulses are collinearly focused onto jet-cooled NO ensembles in a molecular beam. The probe pulse with 0.4 $cm^{-1}$ band width, from a nanosecond frequency-doubled dye laser, ionizes NO molecules by (1 + 1) resonance enhanced multi-photon ionization (REMPI) via the $A^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$ (0, 0) band. The generated NO cations are detected by a time-of-flight mass spectrometer (TOF-MS).

## 3. Results and Discussion

We examined the (1 + 1) REMPI excitation spectrum and verified that the rotational temperature in the present molecular beam condition was so low (< 2K) that the initial-state distribution was almost fully concentrated to the lowest rotational state, i.e., $J = 1/2$ in the $\Omega = 1/2$ manifold. Then, we traced the change of the population in the $J = 1/2$ state against the delay, $\tau$, between the pair of the fs pump pulses, by fixing the probe laser frequency to those of the $R_{21}(1/2)$ transition. The result is shown in Fig. 1 (left). As clearly seen, the population shows the oscillatory change against $\tau$, with its period of 19.7 ps = $1/(Bc)$, where $B$ is the rotational constant of NO (1.696 $cm^{-1}$).

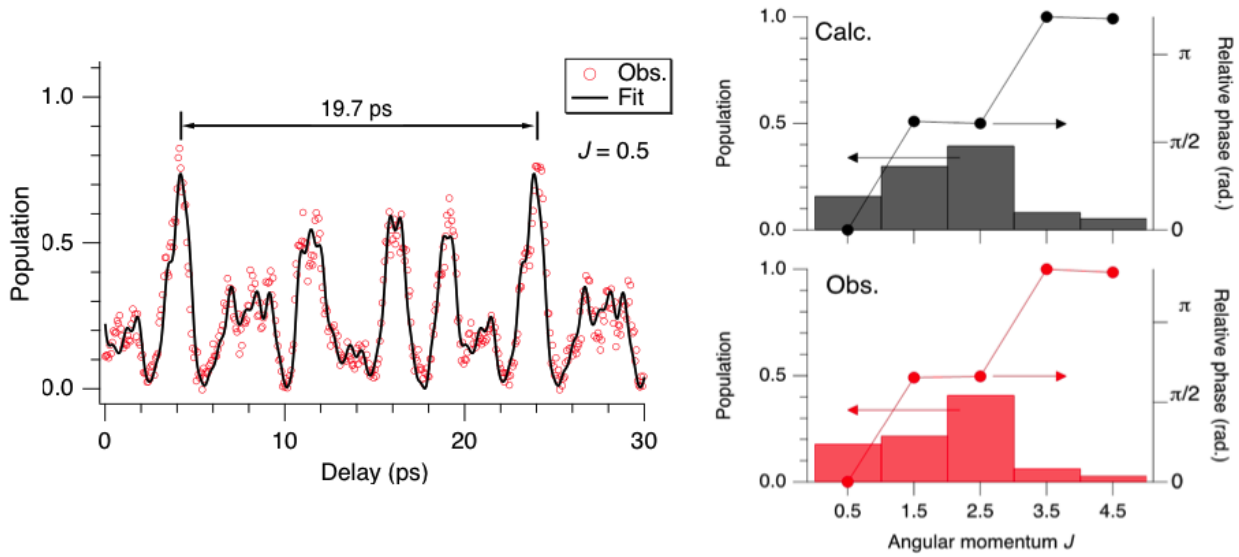


Fig. 1. (Left): Normalized population of the initially prepared $J$ = 1/2 state after the interaction with the pair of the fs pump pulses plotted against the delay between the pump pulses. (Right): Experimentally determined population (= the square of the amplitude) and the phase for each eigen state with $J$, compared with the calculated values.

We have shown that the population, $\left|B_{r_i,r_i}\right|^2$, of the initially prepared state, $|r_i\rangle$ ($=|J=1/2,\Omega=1/2,M=1/2,e/f\rangle$ in this case), is represented by the absolute amplitude, $A_{r_i,r}$, and the phase, $\delta_{r_i,r}$, for each eigen state, $|r\rangle$ ($=|J,\Omega=1/2,M=1/2,e/f\rangle$), constituting the rotational WP, as follows [2]:

$$\left|B_{r_i,r_i}(\tau)\right|^2=\sum_r\left(A_{r_i,r}\right)^4+2\sum_{r>r'}\left(A_{r_i,r}\right)^2\left(A_{r_i,r'}\right)^2\cos\left[\Delta\omega_{r,r'}\tau+2\left(\delta_{r_i,r}-\delta_{r_i,r'}\right)\right]. \quad (1)$$

where $\Delta\omega_{r,r'}=(E_r-E_{r'})/\hbar$ with $E_r$ being eigen energy of the $|r\rangle$ state. Thus, the experimental trace shown in Fig. 1 (left) was least-squares fitted to Eq. (1) to determine the amplitudes and phases, with the beat frequencies, $\Delta\omega_{r,r'}$, fixed to those obtained from the precisely known rotational constants. Excitation to states with $J$ > 9/2 is negligibly small, so five eigenstates were included in the analysis. The right panel of Fig. 1 shows the determined phase and population for each $J$ state.

The phases and population calculated by solving the time-dependent Schrödinger equation (TDSE) are also displayed in Fig. 1 (right). Here, the pump laser intensity was adjusted so as to best reproduce the observed phase and amplitude. The value thus-obtained (7.4 TW/cm$^2$) reasonably agrees with that (5.0 TW/ cm$^2$) evaluated from the experimental parameters (pulse energy, duration, and spot size).

As shown in Fig. 1 (right), the TDSE calculation satisfactorily reproduced the experimental results. The phase thus determined shows stepwise increases by an amount of ca. π/2 from $J$ = 1/2 to $J$ = 3/2 and 5/2 and another π/2 step from $J$ = 3/2 and 5/2 to $J$ = 7/2 and 9/2. This is a clear experimental signature for the two separated excitation pathway starting from the common initial state during the interaction with the laser field, $J$ = 1/2 → 3/2 → 7/2 ... and $J$ = 1/2 → 5/2 → 9/2 ... . This bifurcated pathway in the rotational WP creation was determined by the rotational Raman transition probability and distinctive to a molecule in a Π vibronic state [2,5].

[1] H. Stapelfeldt and T. Seideman, "Aligning molecules with strong laser pulses," Rev. Mod. Phys. **75**, 543-557 (2003).

[2] Y. Ohshima and H. Hasegawa, "Coherent rotational excitation by intense nonresonanct laser fields," Int. Rev. Phys. Chem. **29**, 619-663 (2010).

[3] A. S. Mouritzen and K. Mølmer, "Quantum state tomography of molecular rotation," J. Chem. Phys. **124**, 244311 (2006).

[4] H. Hasegawa and Y. Ohshima, "Quantum state reconstruction of a rotational wave packet created by a nonresonant intense femtosecond laser field," Phys. Rev. Lett. **101**, 053002 (2008).

[5] 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).