Design and Reconstruction of Molecular Quantum States of Motion

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Molecules are vital existence. In a gas-phase ensemble at room temperature, they are, in an average, flying away by a few hundred meters, making turns almost reaching to 10^{11} times, and shaking themselves more than 10^{13} times within the duration of only one second. The ultimate goal this research group has been aiming to is to capture the lively figures of molecules moving in such a dynamic manner and to have a perfect command over the molecular motions. Here lasers with ultimate resolution in time and energy domains are employed complementally and cooperatively for this purpose.

When a gaseous molecular sample is irradiated by an intense nonresonant ultrashort laser pulse, the rotation of the molecules is coherently excited to create a rotational quantum wave packet (WP). We developed a method to explore the nonadiabatic excitation in a quantum-state resolved manner and applied it to diatomic and symmetric-top molecules. It has been shown that the state distribution is a useful experimental source for verifying the excitation process. When a pair of excitation pulses is implemented, partial control of rotational-state distribution has been achieved. In a favorable case, the double-pulse excitation has enabled us to reconstruct experimentally a rotational WP thus created. The sense of rotation can also be controlled, yielding to a rotational WP exhibiting angular-momentum orientation.

Nonadiabatic interaction with an intense ultrashort laser field can also coherently excite vibration of molecule. We have succeeded in creating and observing WPs pertinent to intermolecular vibrations of several molecular clusters in their vibronic ground states.

In the course of the control over molecular motion with high-resolution lasers, we constructed an optical parametric amplifier (OPA), to realize rapid adiabatic passage (RAP), which drives coherent population transfer from an initial quantum state to a target state with 100% efficiency. The laser system is consisted with BiBO crystals, which are seeded by a phase-modulated cw beam in the 1,040–1,070 nm region. Two-stage pre-amplification by Yb-doped fibers are implemented for stable injection to the OPA. The frequency chirp in the OPA pulse was actively controlled. Down/up chirps with up to 500 MHz shift were demonstrated. The output pulse energy was ~40 mJ, which is sufficient for two-photon RAP.

Selected Publications

- 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 (4 pages) (R) (2006).
- H. Hasegawa and Y. Ohshima, "Quantum State Reconstruction of a Rotational Wave Packet Created by a Nonresonant Intense Femto-Second Laser Field," *Phys. Rev. Lett.* **101**, 053002 (4 pages) (2008).
- K. Kitano, H. Hasegawa and Y. Ohshima, "Ultrafast Angular-Momentum Orientation by Linearly Polarized Laser Fields," *Phys. Rev. Lett.* **103**, 223002 (4 pages) (2009).
- Y. Ohshima and H. Hasegawa, "Coherent Rotational Excitation by Intense Nonresonant Laser Fields," *Int. Rev. Phys. Chem.* **29**, 619–663 (2010).
- S. Miyake and Y. Ohshima, "Injection-Seeded Optical Parametric Amplifier for Generating Chirped Nanosecond Pulses," *Opt. Express* **21**, 5269–5274 (2013).

1. New Ion-Imaging Apparatus for Molecular Wave-Packet Dynamics Studies

To characterize the rotational wave-packet dynamics, ion imaging is one of the direct and powerful methods. In a conventional 2D ion imaging with a typical camera-based technique, only a 2D projection of the 3D particle distribution is observed. When the particle distribution is cylindrically symmetric, the original 3D distribution can be reconstructed from the 2D projection by utilizing a mathematical procedure (*e.g.*, inverse Abel transformation). However, we sometimes encounter non-Abel-invertable cases, such as unidirectional molecular rotation. Although 3D imaging techniques could be successfully applied for such a case, a 2D detector has many advantages over a 3D detector: Higher multi-hit capability, lower cost, and simpler setup.

In this study, we designed and built up a new 2D ion imaging apparatus. We installed a 2D imaging unit (MCP/screen/camera) and a repeller plate electrode in the middle of the flight tube of a typical imaging apparatus. A jet-cooled gaseous molecular sample was irradiated by the output of a Ti:Sapphire laser. The molecules were multiply ionized and then exploded within the laser duration (Coulomb explosion). The ion fragments were first accelerated perpendicularly to the laser propagation direction. At the time when the ions of interest arrived at the repeller, a fast high voltage pulse was applied to the repeller to push the ions perpendicularly to the imaging unit.

For dynamics studies, we carried out time-resolved pump–probe experiments on N_2 molecules by using circularly polarized light as a probe to explode molecules of all orientation angles. Pump pulse used was a linearly polarized light (800 nm, 120 fs, ~50 TW/cm^2), which induced rotational wave-packet dynamics. Figure 1 shows selected 2D polar plots for the Coulomb exploded fragment distribution of N^{3+}, recorded at various delay time between the linearly polarized pump and the circularly polarized probe pulses. This delay-dependent anisotropic distribution of the fragments directly correlates to the 2D slice of the molecular-axis probability distribution in the 3D laboratory frame, and the clear manifestation of spatio-temporal propagation of the rotational wave packet created by an impulsive strong laser field.

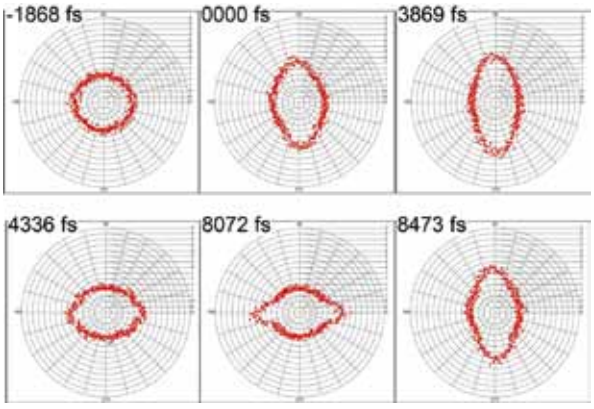

Figure 1. Delay-time dependent 2D distribution of Coulomb exploded N^{3+} fragments.

Owing to the multi-hit counting (*ca.* up to 150 events) for a single camera shot in the present imaging setup, we could record the snapshots with the time increment as small as 66.7 fs, within reasonable total data accusation time of 5 hours for 20 ps duration

2. Consideration of Coherent Population Transfer by Actively Phase-Controlled Nanosecond Laser Pulses

We have considered possible application of the newly developed ns OPA to advanced coherent population transfer and coherent control including chiral discrimination.

The constructed OPA is designed to produce the chirped signal and idler waves, of which energy difference is in the range of 0–400 cm^{-1}. Thus, by using the two beams as pump and Stokes pulses for stimulated Raman excitation, we will realize coherent population transfer in low-frequency Raman transitions. We numerically verified the robustness in the population transfer efficiency against the change of pulse intensity.

The amplification bandwidth of the constructed OPA is *ca.* 20 cm^{-1}. Multiple seeding beams can be amplified if their frequencies are covered in the OPA bandwidth, and multiple signal and idler waves with frequency chirp can be derived. This affords us to realize multiple chirped adiabatic Raman passage (CARP) within a single ns pulse operation. We numerically examined a ladder climbing coherent population transfer, $J = 0 \rightarrow 2 \rightarrow 4 \rightarrow 6 \rightarrow 8$, via CARP (Figure 2). As shown in the right panel, almost 90% of the initial population can be transferred to the final target state by setting the chirp rate and the seeding frequencies appropriately.

The seeding beam can be phase-modulated at up to 40 GHz. The relative optical phase between the carrier (ω_1) and the side band (ω_2) is precisely adjusted to that of the modulating microwave (MW) frequency (ω_3). Then, we can interfere constructively or destructively the stimulated Raman excitation pathway driven by ω_1 and ω_2 with the dipole transition pathway by ω_3. Among such quantum-control scenarios, the most interesting may be the realization of chiral discrimination. Here we numerically examined CARP excitation coupled with a resonant MW field and confirmed almost perfect enatio-selective population control.

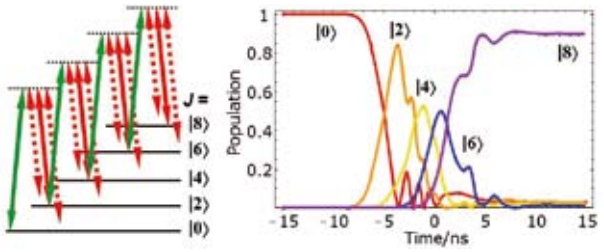

Figure 2. Rotational ladder climbing by multiple CARP process within a single-pulse OPA operation. (Light): Schematic energy levels and CARP transitions. (Right): Population change for five rotational levels involved.