Quantum-State Manupulation of Molecular Motions

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Molecules in gas phase undergo translational, rotational and vibrational motions in a random manner, and the total molecular system is a statistical ensemble that contains a number of molecules in many different states of motions. This research group aims to establish methods to manipulate the quantum-state distribution pertinent to molecular motions, by utilizing the coherent interaction with laser lights. Here lasers with ultimate resolution in time and energy domains are employed complementally and cooperatively for manipulation of molecular motions.

1. Nonadiabatic Rotational Excitation of Benzene by Nonresonant Intense Femtosecond Laser Fields$^{1)}$

When a gaseous molecular sample is irradiated by an intense nonresonant ultrafast laser pulse, the laser field exerts a torque that aligns the molecular axis along the laser polarization vector, due to the interaction with the molecular anisotropic polarizability. The process has now been termed commonly as “nonadiabatic molecular alignment,” and has been attracting much attention because of interesting physics involved and possible broader applications.$^{2)}$ Here the field–molecule interaction only remains in much shorter duration than the characteristic time for molecular rotation, and thus the nonadiabatic alignment is inherently accomplished by nonadiabatic rotational excitation (NAREX), where rotation of the molecules is coherently excited to create a rotational quantum wave packet (WP), a non-stationary superposition of rotational eigenstates.

We have recently developed a method for exploring the NAREX process in a quantum-state resolved manner by using resonance-enhanced multiphoton ionization (REMPI), and reported state distribution of NO molecules after the impulsive excitation with a fundamental output of a femtosecond titanium-sapphire laser.$^{3)}$ It has been shown that the state distribution is a useful experimental source for verifying the excitation process, since population for each rotational level is proportional to the square of the probability amplitude of the corresponding eigenstate in the rotational WP thus created.

The method has been further applied to the oblate symmetric-top molecule, benzene. Rotational excitation up to J = 10 was observed for the irradiation of a molecular ensemble, initially cooled to 0.5 K in an adiabatic expansion, by the femtosecond laser pulse with the intensity of 2.2 TW/cm^2 (Figure 1). The observed excitation was analyzed by the aid of quantum mechanical calculations. These calculations show the systematic change in the excitation pathways for different K, which is characteristic of NARAX in symmetric-top molecules.

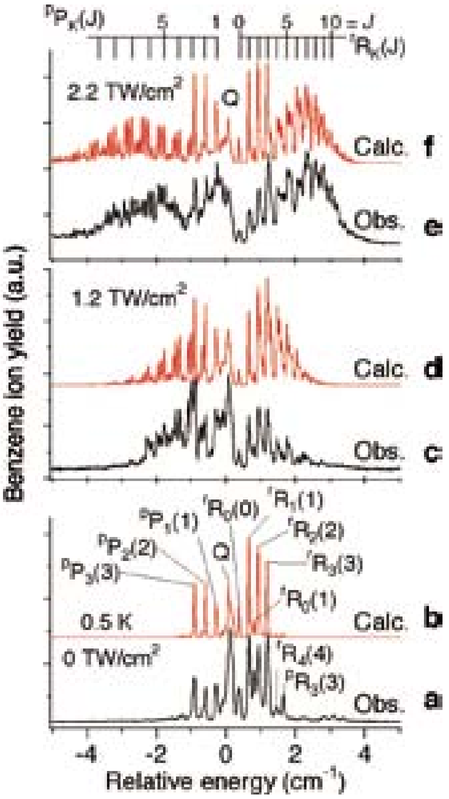

Figure 1. REMPI excitation spectra of the S_1–S_0 6_0^1 band of benzene. Observed (a) without pump pulses, (c) with the pump pulse of 1.25 mJ and (e) 2.40 mJ with 700 fs duration. Calculated with the laser intensities of (b) 0 TW/cm^2, (d) 1.2 TW/cm^2, and (f) 2.2 TW/cm^2.

2. Quantum State Reconstruction of a Rotational Wave Packet Created by a Nonresonant Intense Femtosecond Laser Field[4)]

We further succeeded in experimentally reconstructing a rotational WP created in the NAREX process by utilizing a nonresonant intense femtosecond laser field. Specifically, a rotational WP in an adiabatically cooled benzene molecule was determined. In this WP reconstruction, the initial WP was further interfered by a replica of the first laser pulse, and a REMPI probe was conducted to observe the resultant modulation in population. The time dependent population was fitted to determine the phases as well as the amplitudes of the WP, as shown in Figure 2. Though several states with different nuclear-spin modifications were populated in the initial condition, a single wave packet created from one of them (with $J = 0$) is specifically reconstructed owing to the state-selective probing. From the experimentally determined phases and amplitudes, the angular probability distribution can be evaluated, as shown in Figure 3.

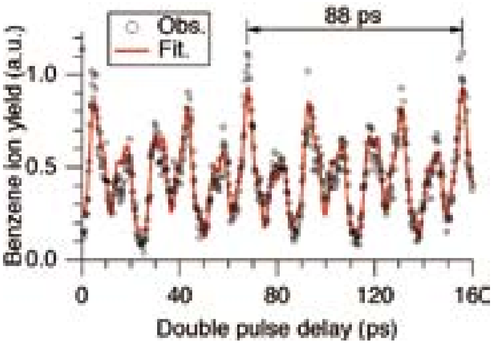

Figure 2. Population of the $J_{|K|} = 0_0$, state in benzene molecules after double-pulse excitation, plotted against the delay between the two pulses. Open circles represent the observed value, and the red line is the results from a least-squares fitting.

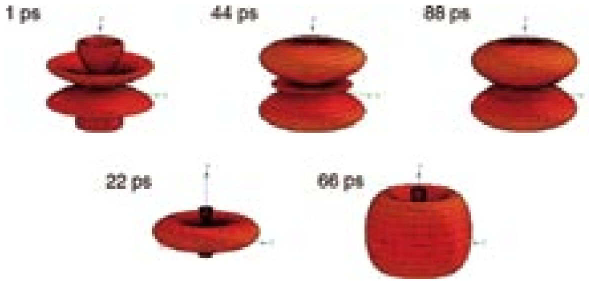

Figure 3. Angular probability distribution of the molecular symmetry axis of benzene at some delay times, evaluated from the experimentally determined amplitude and phase.

3. Realization of Nonadiabatic Vibrational Excitation by Nonresonant Intense Femtosecond Laser Fields

Nonadiabatic interaction with a nonresonant intense ultrafast laser field can also coherently excite the vibration of molecules. Realization of such a nonadiabatic vibrational excitation (NAVEX) and the resultant creation of a vibrational WP is definitely the next step to be proceeded. We have extended the research into this direction, and just recently succeeded in modifying the vibrational-state distribution by utilizing nonresonant intense femtosecond laser pulse(s).

4. Construction of Coherent ns Pulsed Light Sources for Adiabatic Population Transfer

Highly efficient population transfer between quantum states can be accomplished with adiabatic interactions with ns coherent laser pulses, such as stimulated Raman adiabatic passage.[5)] For realizing such an adiabatic quantum-state manipulation, we are constructing two independent laser systems, both of which will deliver pulsed outputs with almost Fourier-transform (FT) limited resolution. The first system, already in operation, is based on the pulsed amplification of the output from a cw ring titanium-sapphire laser.

The second laser system is based on the optical parametric oscillation (OPO) injection-seeded by an extra-cavity cw diode laser. We have succeeded in single-mode operation of the OPO system with the following characteristics: the laser bandwidth of 160 MHz (FWHM), the pulse duration of ~4 ns, and the output power of 7 mJ/pulse (at ~530 nm as the signal wave). Measurements of high-resolution excitation spectra of aromatic molecules are now underway by utilizing the single-mode OPO system.

References

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