

Quantum-State Manipulation 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 Molecules by Nonresonant Intense Femtosecond Laser Fields

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.¹⁾ 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.

This research group has developed a method for exploring the NAREX process in a quantum-state resolved manner by using resonance-enhanced multiphoton ionization (REMPI), and reported state distributions after the impulsive excitation with a fundamental output of a femtosecond (fs) Ti:Sapphire laser.^{2,3)} 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 state-resolved REMPI probe has also been coupled successfully with double-pulse fs excitation. The population for each rotational eigenstate changes oscillatory against the delay between the excitation pulses. When the population of the initial pure state is probed, the delay-time dependent signals provide the phases as well as amplitudes of the WP. Such an experimental reconstruction of WP has recently been demonstrated on the adiabatically cooled molecular sample of benzene by this research group.⁴⁾ The determined phases show a clear signature for impulsive rotational excitation in non-perturbative regime driven by the intense ultrashort pulse.

The double-pulse excitation study has been extended to probe population changes in various eigenstates with different rotational quantum numbers. For benzene molecules, states with J ranging from 0 to 4 with $K = 0-3$ have been examined. This systematic investigation experimentally verifies the K dependence of the excitation pathways in the NAREX process for symmetric-top molecules.

2. Ultrafast Angular-Momentum Orientation by Linearly Polarized Laser Fields

In a quantum-mechanical description, the anisotropy of molecular system is represented as a non-uniform distribution of projections, M , of angular momenta onto a space-fixed (Z) axis. In particular, the system is designated as being *oriented* when the populations for $+M$ and $-M$ are different, while it is *aligned* when the populations for $\pm M$ are the same, but those for different $|M|$ differ from one another. In previous studies, the application of circularly polarized radiations had been exclusively considered for the realization of orientation, because it is regarded as being the only way to induce the required helical interaction that breaks the right/left-handed symmetry around the Z axis. The molecular-axis orientation has already been reported in several studies with intense nonresonant radiation, but all of them implemented linearly polarized light, and thus were related to the angular-momen-

tum alignment. Quite recently, this research group theoretically shows and experimentally verifies that a pair of linearly-polarized intense ultrafast pulses creates molecular ensembles with oriented rotational angular momentum in ultrafast time scale, when the delay and the mutual polarization between them are appropriately arranged (as shown in Figure 1). Asymmetric distribution for $+M$ and $-M$ sublevels relies on quantum interference between the rotational WPs created in the stimulated Raman excitation by the first and the second pulses. The present approach provides spatiotemporally propagating ensembles, of which classical perspective are molecules rotating in clockwise or counter-clockwise direction.

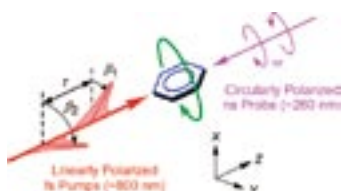


Figure 1. Experimental scheme to create and observe the angular-momentum orientation in molecular rotation.

3. Nonadiabatic Vibrational Excitation by Nonresonant Intense Ultrafast Laser Fields

Nonadiabatic interaction with a nonresonant intense ultrafast laser field can also coherently excite the vibration of molecules, because the molecular polarizability depends on vibrational coordinates. By adopting the similar method to the NAREX studies, nonadiabatic vibrational excitation (NAVEX) of intermolecular vibrations has been successfully realized for benzene clusters by this research group. Here, benzene clusters generated in a supersonic expansion were irradiated with laser pulses (~ 800 nm, 40–200 fs duration, up to 40 TW/cm² in intensity) from the fs Ti:Sapphire laser. Observed changes in intensities of vibronic bands of the benzene dimer indicated the population transfer pertinent to intermolecular vibrational excitation induced by impulsive Raman process. Double-pulse experiments have also been performed, to show that the populations in the ground and excited intermolecular vibrational states oscillatory changed against the delay between the two pulses (see Figure 2). The beat frequencies for the population changes match well with those of the intermolecular modes obtained by the previous ns stimulated Raman spectroscopic studies.⁵⁾ This fact confirms that quantum WPs pertinent to intermolecular vibrations in the ground state manifold were created via impulsive stimulated Raman process by a single fs laser pulse. The similar experiment has been performed to record the time-domain spectrum of benzene

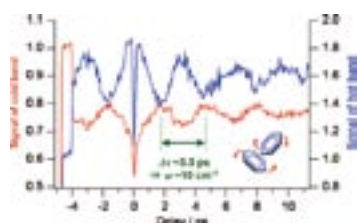


Figure 2. Double-pulse NAVEX spectra of benzene dimer, recorded by probing cold (red) and hot (blue) band transitions.

trimer, which provides the first experimental information on its intermolecular vibrations.

4. New Experimental Setup for NAREX and NAVEX Studies

A new vacuum chamber and a high-reputation rate dye laser system have been installed for REMPI-probed studies on NAREX/NAVEX processes. The chamber is differentially pumped in two stages and equipped with a high-pressure pulsed valve, which can be operated up to 80 atm at 1 kHz. The laser system runs also at 1 kHz by pumping with a third harmonic of a Nd:YLF laser with the pulse duration of <10 ns, and affords the doubled output of ~ 50 μ J/pulse at 220–260 nm. High reputation in data acquisition will greatly improve the quality of REMPI spectra to be observed. The performance of the new setup is now examined in the investigation of the intermolecular vibrational excitation of NO–Ar.

5. Development of Coherent ns Pulsed Light Sources and Its Application to Adiabatic Population Transfer

Adiabatic interactions with coherent pulsed radiation can accomplish highly efficient population transfer between quantum states. For realizing such an adiabatic quantum-state manipulation, we are constructing laser systems which derive single-longitudinal mode (SLM) ns pulses. Among various coherent population transfer methods, we are planning to mainly adopt chirped adiabatic Raman passage (CARP),⁶⁾ where one or both of the laser frequency to drive stimulated Raman transitions is swept so as to cross over the two-photon resonance. This method affords multiple advantages, e.g., robustness in transfer probability against variation in laser parameters and broader applicability without necessity for radiation in one-photon resonance to molecular transitions. The laser system for CARP experiments under construction is based on the optical parametric oscillation (OPO), which is injection-seeded by an extracavity cw diode laser to achieve the SLM operation. The seeding laser frequency is phase modulated at appropriate RF frequency to attain the frequency chirp to drive the CARP process. The OPO operates near the degenerate condition, so that its signal and idler waves can be used for pump and Stokes fields for stimulated Raman transitions. This design greatly reduces the complication in the setup and will provide much simpler and reliable operation for CARP experiments.

References

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