

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. At the present stage, the following three subjects have been extensively explored. The first one is an exploit of impulsive interaction with ultrafast intense laser fields to achieve a nonadiabatic excitation of molecular rotation. The second subject is pertinent to creation and observation of vibrational wavepackets by fs pump-probe experiments. An experimental method newly developed in this laboratory has been applied to probing wavepackets associated with internal rotation of jet-cooled polyatomic systems. The third subject aims to realization of complete population transfer *via* an adiabatic interaction with high-resolution coherent light pulses. For this purpose, we are constructing ns laser systems, all of which are sufficiently coherent to drive the adiabatic interaction.

1. Quantum Control of Wavepacket and State Distribution via Nonadiabatic Rotational Excitation

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. Because the interaction is nonadiabatic, *i.e.*, only remains in much shorter duration than the molecular rotational period, the torque is impulsive so that rotation of the molecules are excited. In a quantum mechanical point of view, this nonadiabatic rotational excitation (NAREX) creates a rotational wavepacket, a coherent 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, and reported state distribution of NO molecules, whose initial population was confined to the lowest state ($J = 0.5$), after the impulsive excitation with a fundamental output of a titanium-sapphire laser with ~ 120 fs duration.¹⁾ Population for each J after NAREX is proportional to the square of the probability amplitude of the corresponding eigenstate in the rotational wavepacket thus created. Therefore the state distribution is a useful experimental source for verifying the excitation process, and a model calculation has been performed to confirm it.

The present experimental method has been further applied to probe the state distribution after double-pulse excitation. As shown in Figure 1 (left), the population for each J changes oscillatory against the delay between the excitation pulses. Their beat patterns have been shown to provide definite information on excitation pathways in NAREX. Further theoretical consideration has proved that detailed examination in double-pulse experiments, in particular, on the population of the lowest rotational state will give rise to the full reconstruction of the rotational wavepacket even when arbitrary excitation pulses are employed. The experimental realization is now under way.

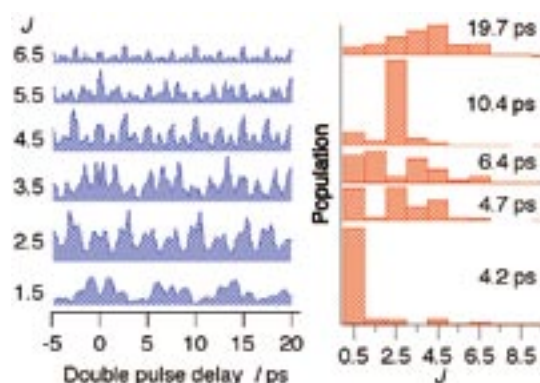


Figure 1. Population for each J state after the double-pulse NAREX against the pulse delay (left) and the corresponding state distributions at several delays (right).

Another important upshot from the double-pulse NAREX study is a partial attainment of control over rotational-state distribution with nonresonant ultrafast laser pulses. This is well demonstrated in Figure 1 (right): for instance, more than 80% of population comes back to the initial state when the delay is set to 4.2 ps, and almost 80% can be concentrated to a single eigenstate ($J = 2.5$, in this case) at delay of 10.4 ps. Implementation of elaborated shaping of excitation pulses is planned for further improvement in rotational-state control.

2. Wavepacket Dynamics of Methyl Internal Rotation Probed by fs Time-Resolved Fluorescence Depletion Spectroscopy

Real-time studies on low-frequency molecular vibrations with large amplitudes are of great significance, in particular, for potential application to control of isomerization reaction by coherent excitation of these motions. We have recently been exploring internal-rotation dynamics of methyl groups by utilizing ultrafast nonlinear spectroscopy, *i.e.*, fs time-resolved fluorescence depletion (fTRFD). While TRFD in ps regime has been applied previously for investigating slower intramolecular dynamics,²⁾ its implementation to fs regime for vibrational wavepacket studies is for the first time. We have performed fTRFD measurements in the S_1 – S_0 origin regions of several toluene derivatives in jet-cooled conditions. In particular, excitation-wavelength dependence has been examined in details for *m*-tolunitrile, as shown in Figure 2. Here the quantum interferences for the A_1 and E symmetry levels in both the S_0 and S_1 states are clearly observed. Beat components for each levels change their magnitudes for different excitation wavelengths. These dependences have been analyzed with model calculations numerically solving the time-dependent Liouville equations for methyl internal rotation.

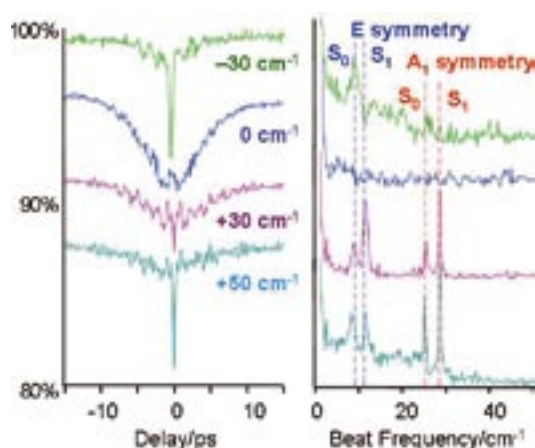


Figure 2. fTRFD spectra for different excitation wavelengths, indicated as offset wavenumbers from the origin band (left) and the corresponding power spectra (right).

Comparison of the observed fTRFD spectra with the calculated results shows that ca. 10% of population is transferred to the S_1 manifold in the present condition.

3. 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.³⁾ 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 third harmonics of the pulsed laser system has been applied for recording high-resolution excitation spectrum of the S_1 – S_0 6_0^1 band of jet-cooled benzene (Figure 3). Spectral Linewidth (0.013 cm^{-1}) of single ro-vibronic transitions is three times of FT limit. The second laser system is based on the optical parametric oscillation (OPO) injection-seeded by an extracavity cw diode laser. Quite recently, we have succeeded in single-mode operation of the OPO system, in which only a few mW of the cw light is necessary for stable injection seeding. The optical layout is now optimized for further increment of the output power up to the level sufficient for driving adiabatic population transfer.

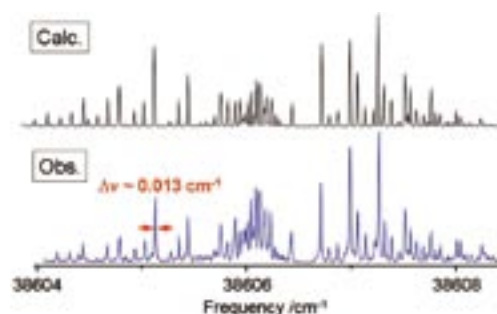


Figure 3. High-resolution excitation spectrum of benzene S_1 – S_0 6_0^1 band. Rotational temperature is set to 2 K for simulation.

References

- 1) H. Hasegawa and Y. Ohshima, *Phys. Rev. A* **74**, 061401 (4 pages) (2006).
- 2) M. J. Côté, J. F. Kauffman, P. G. Smith and J. D. McDonald, *J. Chem. Phys.* **90**, 2865–2873 (1989); G. V. Hartland, L. L. Connell and P. M. Felker, *J. Chem. Phys.* **94**, 7649–7666 (1991).
- 3) N. V. Vitanov, T. Halfmann, B. W. Shore and J. K. Bergmann, *Annu. Rev. Phys. Chem.* **52**, 763–809 (2001).

Award

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