

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 gaseous molecules are irradiated by an intense nonresonant ultrafast laser pulse, rotation of molecules is coherently excited via the interaction with the molecular anisotropic polarizability, to create a rotational quantum wave packet (WP). We have developed a method for exploring such a nonadiabatic rotational excitation (NAREX) process in a quantum-state resolved manner, and reported rotational-state distributions after the impulsive excitation with a fundamental output of a femtosecond (fs) Ti:Sapphire laser.^{1,2)} Such a state-resolved investigation has afforded details concerning the excitation process during exposure to laser fields, and in a favorable case, full characterization of a rotational WP itself.³⁾ In addition, frequency-domain studies can directly assess ultrafast control of the rotational-state distribution via the WP manipulation.⁴⁾

2. Ultrafast Angular-Momentum Orientation by Linearly Polarized Laser Fields⁵⁾

The anisotropy of molecular system is represented as a non-uniform distribution of projections, M , of angular momentum onto a space-fixed (Z) axis. In particular, the system is designated as being *oriented* when the populations for $+M$ and

$-M$ are different. In previous studies for the realization of orientation, circularly polarized radiation had been exclusively adopted, because it is regarded as the only way to induce the required helical interaction that breaks the right/left-handed symmetry around the Z axis. Recently, we show 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 the pulses are appropriately arranged. The experimental result that demonstrates such an angular momentum orientation is shown in Figure 1.

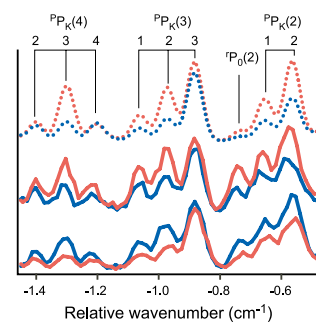


Figure 1. Excitation spectra of the $S_1 \leftarrow S_0 6_0^1$ band of C_6H_6 after fs double-pulse excitation. Blue and red lines correspond to right- and left-handed polarized probe pulses, respectively. The middle and lower panels are experimental ones for the mutual polarization angle of $-\pi/4$ and $\pi/4$, while the upper is simulated one for $-\pi/4$.

3. Coherent Correlation between Nonadiabatic Rotational Excitation and Angle-Dependent Ionization of NO in Intense Laser Fields⁶⁾

When the intensity of the nonresonant ultrafast pulse is increased, the irradiated molecules are ionized as well as being rotationally excited. The coherent correlation between NAREX and the strong-field ionization in NO has been studied in the state-resolved manner. When the molecule is partly ionized in intense laser fields, a hole in the rotational WP of the remain-

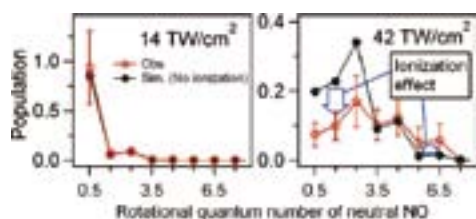


Figure 2. Rotational-state distribution of NO recorded after the excitation by a fs pulse at low (left) and high (right) intensity.

ing neutral NO is created by the ionization, whose rate depends on the alignment angle of the molecular axis with respect to the laser polarization direction. Rotational-state distributions of NO are observed and the characteristic feature that the population at higher J levels is increased by the ionization is identified, as shown in Figure 2. Numerical calculation for solving time-dependent Schrödinger equations including the effect of the ionization is carried out. The results suggest that the molecules aligned perpendicular to the laser polarization direction are dominantly ionized at the peak intensity of $I_0 = 42 \text{ TW/cm}^2$, where the multiphoton ionization is preferred rather than the tunneling ionization.

4. Nonadiabatic Vibrational Excitation of Molecular Clusters by Nonresonant Intense Femtosecond Laser Fields

Nonadiabatic interactions with a nonresonant ultrafast laser field can coherently excite molecular vibration. The quantum-state resolved approach with ns probe pulses will also contribute to the study of nonadiabatic excitation of molecular vibration. The best candidates are van der Waals (vdW) clusters, since the librations of constituent molecules in

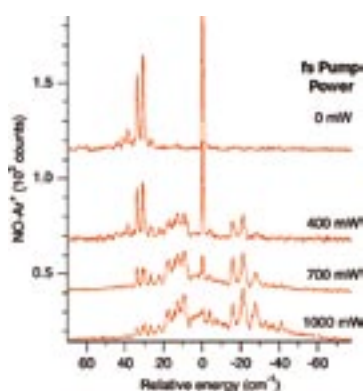


Figure 3. Excitation spectra of the A←X (0,0) band of NO–Ar after fs pulse excitation.

Award

KITANO, Kenta; Best Presentation Awards at the Annual Meeting of Japan Society for Molecular Science, 2009.

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vdW clusters have wide amplitudes and such intermolecular motions are inherently associated with large modulation of polarizability, yielding to strong Raman activities. We have indeed observed nonadiabatic vibrational excitation for the NO–Ar cluster. After the excitation with an intense fs pulse, several hot bands came to appear, as shown in Figure 3.

5. High-Resolution Laser Spectroscopy of Benzene Clusters with He Atoms

Electronic spectra of benzene–(He)_{1,2} clusters have been recorded via two-color resonant two-photon ionization with a single-mode ns-pulsed light source, consisting a dye amplifier injection-seeded by the CW output from a Ti:Sapphire laser. Owing to the narrow band width (~250 MHz) of the laser system and the efficient rotational cooling down to 0.3 K by implementing a high-pressure pulsed valve, rotational fine structures have been fully resolved in the observed spectra, as shown in Figure 4. Several vibronic bands associated to excitation of intermolecular vibrations have also been observed with rotational resolution. Their positions are reasonably matched with the prediction based on a high-level *ab initio* calculation.

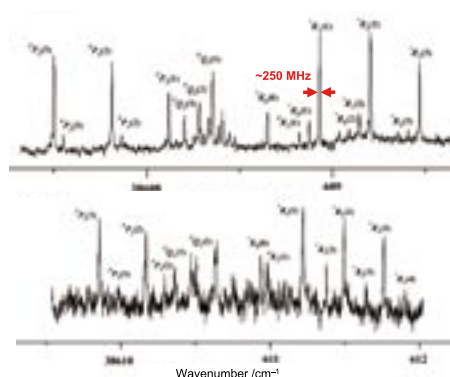


Figure 4. High-resolution excitation spectra of the $S_1 \leftarrow S_0 6_0^1$ band of C_6H_6 –He (top) and C_6H_6 –(He)₂ (bottom).

References

- 1) H. Hasegawa and Y. Ohshima, *Phys. Rev. A* **74**, 061401 (2006).
- 2) H. Hasegawa and Y. Ohshima, *Chem. Phys. Lett.* **454**, 148 (2008).
- 3) H. Hasegawa and Y. Ohshima, *Phys. Rev. Lett.* **101**, 053002 (2008).
- 4) Y. Ohshima and H. Hasegawa, *Int. Rev. Phys. Chem.* **29**, 619 (2010).
- 5) K. Kitano, H. Hasegawa and Y. Ohshima, *Phys. Rev. Lett.* **103**, 223002 (2009).
- 6) R. Itakura, H. Hasegawa, Y. Kurosaki, A. Yokoyama and Y. Ohshima, *J. Phys. Chem. A* **114**, 11202 (2010).