Design and Reconstruction of Molecular Quantum States of Motion

Department of Photo-Molecular Science
Division of Photo-Molecular Science I

OHSHIMA, Yasuhiro	Professor
MIZUSE, Kenta	Assistant Professor
HAYASHI, Masato	Post-Doctoral Fellow
MIYAKE, Shinichiro	Graduate Student
INAGAKI, Itsuko	Secretary

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.

1. Unveiling the Nonadiabatic Rotational Excitation Process in a Symmetric-Top Molecule Induced by Two Intense Laser Pulses[1)]

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 has 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.[2,3)]

We made an extended study for unveiling the NAREX process in symmetric-top molecules. Benzene molecules have been taken as a sample. The initial state distribution was restricted mostly to the five lowest rotational levels in different nuclear-spin manifolds by an extensive adiabatic cooling with the rotational temperature well below 1 K, and distributions after the interaction with a fs double-pulse pair (3–5 TW/cm^2 each with 160 fs duration) with time delays were probed by employing resonant enhanced two-photon ionization (R2PI) *via* the $S_1 \leftarrow S_0$ 6_0^1 vibronic transition with nanosecond (ns) dye laser pulses. Populations of 10 rotational levels with J ranging from 0 to 4 and K from 0 to 3 were examined to show an oscillatory dependence on the time delay between the two pulses. Fourier analysis of the beat signals provides the coupling strengths between the constituent levels of the rotational WPs created by NAREX. These data agrees well with the results from quantum mechanical calculations, evidencing stepwise excitation pathways in the wave packet creation with $\Delta J = 2$ for $K = 0$ stack while $\Delta J = 1$ and 2 in $K > 0$ stacks.

2. Controlling the Sense of Molecular Rotation: Classical vs Quantum Analysis[4)]

The anisotropy of molecular system is represented as a non-uniform distribution of projections, M, of angular momentum, J, onto a space-fixed (Z) axis. The system is designated as being *oriented* when the populations for $+M$ and $-M$ are different. In the classical vector model, the + or – orientation corresponds to clockwise or counter-clockwise rotation, respectively. We have shown that a pair of linearly-polarized intense ultrafast pulses creates molecular ensembles with oriented rotational angular momentum, when the delay and the mutual polarization between the laser fields are appropriately arranged.[5)]

We have further undertaken a comparative study of the classical and quantum aspects of the underlying mechanism of the effect. Good quantitative agreement is found between the classical description of the process and the rigorous quantum mechanical analysis at the relevant experimental conditions. Both approaches predict the same optimal values for the delay between pulses and the angle between them, and deliver the same magnitude of the induced oriented angular momentum of the molecular ensemble. As expected, quantum and classical analysis substantially deviate when the delay between pulses is comparable with the period of quantum rotational revivals. However, time-averaged characteristics of the excited molecular ensemble are equally good described by these two approaches. This is illustrated by calculating the anisotropic time-averaged angular distribution, which reflects persistent confinement of the molecular axes to the rotation plane defined by two polarization vectors of the pulses.

3. Reconstruction of the Rotational Wave Packet Created by NAREX and Ultrafast State-Distribution Control

The fs-pump and ns-probe approach has been also adopted for a detailed study on characterization and control of the rotational WP in NO. For double fs-pulse excitation, the population of each rotational state showed oscillatory change against the time delay between the two pulses. As has been shown previously,6) the delay dependence pertinent to the initially populated state allowed us to determine the amplitude and phase of each eigenstate that constitutes the rotational WP. The experimental results, in particular, the systematic phase shifts against J, represented a clear signature of bifurcated excitation pathways in the WP creation, which is characteristic to linear molecules in a doubly degenerate vibronic state. We have also shown that the final distribution can be concentrated into a narrow range of states if the time delay between the two pulses is properly arranged. For instance, almost 80% can be repopulated in the initial $J = 1/2$ state. Highly focused population has been achieved also for $J = 3/2$ and 5/2. The experimental finding has demonstrated the capability of state-distribution control in an ultrafast time scale (within several tens of picoseconds).

4. Coherent Intermolecular-Mode Excitation of NO–Ar by Nonresonant Intense Femtosecond Laser Fields

Nonadiabatic interactions with a nonresonant ultrafast laser field can coherently excite also molecular vibration. Here, vibrational distribution after nonadiabatic vibrational excitation (NAVEX) is probed in a quantum-state resolved manner. The method has been applied to NO–Ar. R2PI spectrum of NO–Ar associated to the monomer A–X (0,0) transition exhibited a number of hot bands when the fs pump pulse was applied. These hot band transitions are assigned to those from vibrationally excited states pertinent to intermolecular modes, of which excitation energies range in 4–30 cm^{-1}. Thus we have successfully probed the intermolecular vibrational energy levels up to 1/3 of the total binding energy of NO–Ar, which is estimated to be *ca.* 90 cm^{-1}. When the cluster was excited with a pair of fs pulses, the intensities of monitored vibronic bands changed oscillatory against the delay between the two pulses. These results indicate the creation of a quantum WP pertinent to intermolecular vibrations in the electronic ground state. Real-time WP propagation was calculated by numerically solving the time-dependent Schrödinger equation on the intermolecular potential energy surface.

5. High-Resolution Laser Spectroscopy of Benzene Clusters with He Atoms and H_2 Molecules

Molecular clusters containing benzene are prototypical systems for elucidating the intermolecular interaction pertinent to aromatic rings. We are now focusing on clusters of benzene attached by small numbers of atoms and molecules. Specifically, high-resolution electronic spectra of benzene–$(He)_n$ and –$(H_2)_n$ (n = 1, 2) have been examined via two-color R2PI in the vicinity of the monomer S_1–S_0 6_0^1 band. We employed a tripled output from a ns pulsed dye amplifier, which was injection-seeded by the CW output from a Ti:Sapphire laser, as an excitation source. 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 structures have been fully resolved. The observed spectra shows unambiguously that He and H_2 are located above the center of the benzene molecular plane (for the both sides in the case of n = 2), and the H_2 molecular axes are perpendicular to the plane. The rotational constants thus determined set the distances of He and H_2 above the plane to be: 3.602 (+0.063) Å and 3.477 (+0.131) Å, respectively, where values in parentheses represent the change by the excitation from S_0 to S_1. Several vibronic bands associated to excitation of intermolecular vibrations have also been observed for all the clusters examined. The vibrational frequencies of benzene(S_1)–He are derived as: 17 and 13 cm^{-1} for the intermolecular stretch and bend modes, respectively. The values in the complex with H_2 are: 48 cm^{-1} for the stretch, while 34 and 39 cm^{-1} for the two bend modes. The vibronic bands of benzene–He exhibit tunneling splitting due to a large-amplitude migration of He above and below the benzene molecular plane. This finding is matched with the prediction based on a high-level *ab initio* calculation.

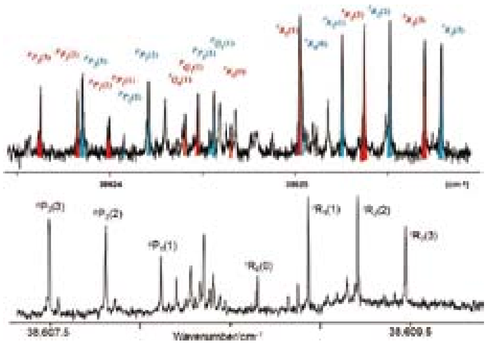

Figure 1. High-resolution excitation spectra of C_6H_6–He: (bottom) the $S_1 \leftarrow S_0$ 6_0^1 band, (top) the intermolecular-stretch excited band. Each rotational line is split into two (indicated in red and blue) due to quantum tunneling.

References

1) D. Baek, H. Hasegawa and Y. Ohshima, *J. Chem. Phys.* **134**, 224302 (10 pages) (2011).

2) H. Hasegawa and Y. Ohshima, *Phys. Rev. A* **74**, 061401 (4 pages) (2006).

3) H. Hasegawa and Y. Ohshima, *Chem. Phys. Lett.* **454**, 148–152 (2008).

4) Y. Khodorkovsky, K. Kitano, H. Hasegawa, Y. Ohshima and I. Sh. Averbukh, *Phys. Rev. A* **83**, 023423 (10 pages) (2011).

5) K. Kitano, H. Hasegawa and Y. Ohshima, *Phys. Rev. Lett.* **103**, 223002 (4 pages) (2009).

6) H. Hasegawa and Y. Ohshima, *Phys. Rev. Lett.* **101**, 053002 (4 pages) (2008).