Design and Reconstruction of Molecular Quantum States of Motion

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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. Nonadiabatic Excitation of Molecular Rotation Induced by Intense Ultrashort Laser Fields

When a gaseous molecular sample is irradiated by an intense nonresonant ultrashort laser pulse, the rotation of the molecules is coherently excited to create a rotational quantum wave packet (WP). We developed a method to explore the nonadiabatic excitation in a quantum-state resolved manner and applied it to diatomic and symmetric-top molecules.1) It has been shown that the state distribution is a useful experimental source for verifying the excitation process.2,3) When a pair of excitation pulses is implemented, partial control of rotational-state distribution has been achieved.1,4) In a favorable case, the double-pulse excitation has enabled us to reconstruct experimentally a rotational WP thus created.5) The sense of rotation can also be controlled, yielding to a rotational WP exhibiting angular-momentum orientation.6,7)

2. Coherent Excitation of Intermolecular Vibrations by Nonresonant Intense Ultrashort Laser Fields

Nonadiabatic interaction with an intense ultrashort laser field can also coherently excite vibration of molecule. We have succeeded in creating and observing WPs pertinent to intermolecular vibrations of several molecular clusters in their vibronic ground states.

3. Construction of an Ion-Imaging Apparatus for Wave Packet Imaging

We have constructed an ion-imaging apparatus for tracking the time-dependent molecular alignment by monitoring the 2D spatial distribution of Coulomb-exploded fragment ions. In the apparatus, ion clouds are repelled perpendicularly to hit a 2D detector, of which detection plate is set parallel along the initial flight direction of the ions. This unique arrangement allows us to record ion images for non-cylindrically symmetric fragment distribution. By using this experimental setup, we have monitored spatiotemporal propagation of the molecular alignment of jet-cooled N_2.

4. High-Resolution Laser Spectroscopy of Benzene Clusters with Atoms and Small Molecules8,9)

As prototypical systems for elucidating the intermolecular interaction pertinent to aromatic rings, we studied clusters of benzene with small numbers of atoms and molecules (such as He and H_2), by exploring via two-color resonant two-photon ionization in the vicinity of the monomer S_1–S_0 6_0^1 band. Extensive adiabatic cooling with the rotational temperature of < 0.5 K was conducted by the high-pressure pulsed expansion. Sub-Doppler resolution yielding the line width of 250 MHz was realized in a collimated molecular beam by employing Fourier-transform-limited ultraviolet pulses for the excitation.

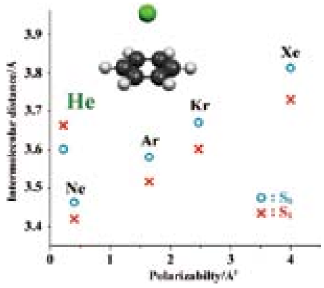

Figure 1. The effective intermolecular distances in the benzene–rare gas complexes.

The observed transition frequencies of benzene–$(He)_n$ with n = 1 and 2 were fitted to derive the molecular constants with accuracy improved by a factor of 50 than those reported previously.10) The determined rotational constants for n = 1 set the distance of the He atom from the benzene ring, which is even larger than those of the analogous systems, *i.e.*, benzene–Ne and –Ar, as shown in Figure 1. This apparent anomaly is discussed with the recent theoretical results based on high-level quantum mechanical calculation coupled with the numerical solution of the 3D eigenvalue problem.11) The electronic excitation induces the increase in the distance for benzene–He, as opposed to the contraction of other benzene–rare gas systems. The distance and the change for n = 2 are almost the same as those for n = 1. We also recorded the excitation spectrum of n = 1 with the mono ^{13}C-substituted benzene. The asymmetric substitution lifts the degeneracy of the S_1 6^1 state in the benzene molecule, and two vibronic bands located nearby to each other were observed.

For C_6H_6–$(H_2)_n$, two distinguished isomers, correlating to *para* and *ortho* H_2, are identified for n = 1 and 2. This finding is the manifestation of the internal rotation of the H_2 unit(s) located above (and below) the benzene molecular plane within the clusters. For the observation of the weaker binding *para* species, a gas sample of pure *para* H_2 was used. Rotationally resolved spectra allowed us to fix the cluster geometry unambiguously. Three vibronic bands involving vdW-mode excitation were observed for the *ortho* species with n = 1, yielding to probable sets of vibrational frequencies of all the three vdW modes. One of them correlates to the splitting between the m = 0 and ±1 sublevels in the j = 1 state of a freely rotating H_2 molecule, and the potential barrier for the hindered internal rotation has been evaluated from the values, as shown in Figure 2. Rotationally resolved spectrum of benzene–(*ortho* $H_2)_3$ is consistent with a (2 + 1) binding motif, where two H_2 molecules on one side of the benzene plane seem to scramble their positions and roles. All the clusters examined with rotational resolution exhibited homogeneous line broadening, which corresponds to the upper-state lifetimes in the sub-nanosecond regime, most probably due to vibrational predissociation in the S_1 6^1 manifold.

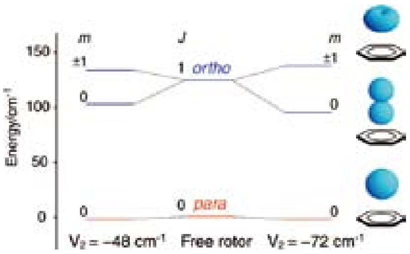

Figure 2. Schematic energy diagram for the internal rotation of H_2 inside benzene–H_2. Two probable values for the potential parameter, V_2, from the experimental results are adopted. On right, probability angular distributions of the H_2 molecular axis are schematically shown for the lowest three states.

5. Seeded Optical Parametric Amplifier for Generating Chirped Nanosecond Pulses12)

To realize rapid adiabatic passage (RAP), which drives coherent population transfer from an initial quantum state to a target state with 100% efficiency, we constructed an optical parametric amplifier (OPA) with BiBO crystals, which was seeded by a phase-modulated cw beam in the 1,040–1,070 nm region. Two-stage pre-amplification by Yb-doped fibers were implemented for stable injection to the OPA. The frequency chirp in the OPA pulse was actively controlled, as shown in Figure 3. Down/up chirps with up to 500 MHz shift were demonstrated. The output pulse energy was ~40 mJ, which is sufficient for two-photon RAP.

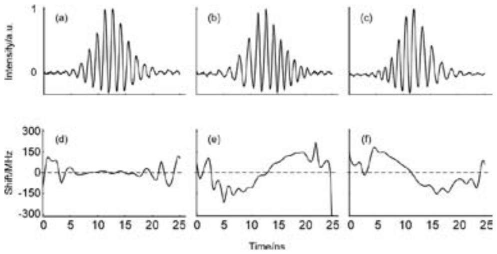

Figure 3. Observed heterodyne signals of the OPA pulses (a): without the phase modulation to the seeding beam, (b) and (c): with the phase modulation, and the time-dependent frequency shifts: (d), (e) and (f), corresponding to (a), (b) and (c), respectively.

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