

III-E Quantum-State Manipulation of Molecular Motions

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. Three complement methods are now being explored for manipulation of molecular motions. The first method exploits an impulsive interaction with ultrafast intense laser light to transform the initial distribution into an arbitral non-equilibrium one. We have succeeded in applying the method to nonadiabatic rotational population transfer in various molecular systems. The second one employs creation and detection of molecular wavepackets by fs pump-probe experiments. Experimental methods newly developed in this laboratory have been applied to probing vibrational wavepackets associated with internal rotation of jet-cooled polyatomic systems. The third one utilizes an adiabatic interaction to achieve the complete population transfer, by which all the molecules are launched into states with high excitation of vibrations or rotation. We have constructed ns laser systems with sufficiently high frequency resolution to drive the adiabatic coherent interaction. Along the development of the instruments, appropriate candidates for the quantum-state adiabatic manipulation are searched. Laser spectroscopic studies are carried out to explore energy-level structure of the intermolecular vibrations in molecular clusters containing benzene.

III-E-1 Nonadiabatic Population Transfer by Intense Femtosecond Laser Light

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A new vacuum chamber was constructed for the study of nonadiabatic population transfer processes induced by intense fs laser light, and has been utilized to explore the rotational excitation of NO. A fundamental output (~ 800 nm, ~ 120 fs duration, and < 1 mJ/pulse) of a titanium-sapphire laser was introduced to transiently align NO molecules, which were initially jet-cooled to < 2 K where states with $J = 0.5$ were only populated. Rotational distribution after the impulsive excitation was monitored by two-photon resonance enhanced ionization by ns laser pulses through the A-X(0,0) transition. States with up to $J = 8.5$ were populated through the nonadiabatic transfer process, and characteristic population alternation in J was identified. A model calculation has been performed to quantitatively explain the observations. The excitation is achieved through a ladder climbing mechanism by Raman process with $\Delta J = \pm 1$ and ± 2 . Because the transition probabilities with $\Delta J = \pm 2$ are much larger than those with $\Delta J = \pm 1$ and the initial distribution is restricted only to $J = 0.5$, populations in $J = 2.5, 4.5, 6.5, \dots$ become superior.

For further detailed insight into the nonadiabatic rotational excitation, experiments utilizing double excitation pulses with an appropriate delay in time have been performed. Population of each rotational state changes oscillatory against the delay, with frequency components matching with rotational-energy differences. It has been shown the rotational states are grouped into two, in which states strongly couples *via* $\Delta J = \pm 2$ matrix elements to form the coherent superposition. The two groups are weakly coupled to each other *via* $\Delta J = \pm 1$ matrix elements. Such an excitation process is typical to molecules in degenerate states.

In addition to the simple diatomic molecule NO, much larger molecular systems, *i.e.*, benzene and styrene, have been examined for the nonadiabatic rotational excitation by intense short laser pulses. These successful applications demonstrate the potential of the present

method in manipulation of quantum-state distribution of various types of molecules.

III-E-2 Wavepacket Observation of Methyl Internal Rotation in Substituted Toluenes

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Femtosecond (fs) time-domain experiments have been performed in the S_1 - S_0 origin regions of jet-cooled *o*-fluorotoluene and *m*-cresol to explore the wavepacket dynamics associated with internal rotation of the methyl group. The COIN (Coherence Observation by Interference Noise) method, a variant of fs interferometry,¹ has been applied to observe quantum beats, of which frequencies correspond to differences between vibronic transitions. Time-resolved fluorescence depletion (TRFD)² has been implemented in fs domain for the first time, where change in excited-state population induced by the pump-dump process was monitored as fluorescence depletion. In *o*-fluorotoluene, quantum interferences in S_1 were exclusively observed in the TRFD spectrum. Comparison with the COIN and TRFD data allows us to reconstruct the vibronic band structure without ambiguity. On the other hand, TRFD spectrum of *m*-cresol was dominated by quantum beats in S_0 , because the separations between internal-rotation levels are smaller in S_0 than in S_1 . The modulation amplitude of the beats reached to 5% of the total fluorescence, indicating substantial coherent population transfer to excited internal-rotation states in S_0 *via* Rabi oscillation induced by the pump pulse.

References

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III-E-3 Development of High-Resolution Coherent Pulsed Lasers

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We are constructing a pulsed laser system with Fourier-transform (FT) limited resolution for quantum-state manipulation by coherent light-matter interaction, such as stimulated Raman adiabatic passage. In the system, the output from a cw ring titanium-sapphire laser seeds a pulsed dye amplifier pumped by a single-mode Nd:YAG laser. The laser system delivers the output power of 30 mJ/pulse at around 780 nm, with spectral bandwidth of 200 MHz ($< 0.007 \text{ cm}^{-1}$). This fundamental output is tripled by nonlinear crystals to have UV radiation at 260 nm, which is suitable to excite S_1 - S_0 transitions of the benzene molecule and its van der Waals clusters.

In addition to the pulsed amplifier system, an all solid-state pulsed laser system based on the optical parametric oscillation (OPO) pumped by the Nd:YAG laser is now in under construction. The OPO system is injection-seeded by an extra-cavity cw diode laser. For stable external seeding operation, the ring-type cavity is adopted for the OPO. The frequency locking mechanism for the cavity is now designed and constructed. This OPO system will deliver the almost FT-limited ns pulse with $> 10 \text{ mJ/pulse}$ at 520 nm.

III-E-4 Laser Spectroscopy of the van der Waals Vibrations of Benzene-Water

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Benzene-water is a prototypical system containing the π hydrogen bond. We have recently examined in detail the vibronic spectra of various isotopomers of the benzene-water 1:1 cluster pertaining to the S_1 - S_0 6_0^1 transition of the benzene moiety, recorded by utilizing resonance two-photon ionization (R2PI) time-of-flight mass spectrometry. UV-UV hole-burning measurement has been performed to observe weak vibronic bands, which are buried in the R2PI excitation spectrum by background signals due to fragmentation of higher clusters. For the H_2O isotopomer, bands from the $m = 0$ and ± 1 internal-rotation states were separately observed by probing split components in the 6_0^1 origin. A dozen of bands with intermolecular mode excitation clearly appeared in the region up to 160 cm^{-1} . Observed level structure was compared with the 6D dynamical calculation by Felker and co-workers¹ based on the model potential by Karlström *et al.*² Levels pertaining to the vdW stretching and bending modes show reasonable agreements between observation and calculation, while states probably associated to the 3D internal rotation of water unit exhibit extremely large discrepancies. This result indicates the necessity for the substantial refinement in the model potential, especially for its anisotropic part (*i.e.*, angular dependence on the 3D internal-rotation coordinates).

References

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