

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 one employs creation and detection of molecular wavepackets by fs pump-probe experiments. New experimental methods for probing vibrational and/or rotational wavepackets are developed and applied to jet-cooled polyatomic systems. The second method exploits an impulsive interaction with ultrafast intense laser light to transform the initial distribution into an arbitral non-equilibrium one. We are now constructing a vacuum chamber system for this purpose. 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 are now constructing ns laser system with sufficiently high frequency resolution to drive the adiabatic coherent interaction. Along the development of the instrument, 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 Femtosecond Random-Phase Interferometry of Jet-Cooled Polyatomic Molecules

MIYAZAKI, Mitsuhiro¹; HARUNA, Atsuyuki²;
OHSHIMA, Yasuhiro
(¹IMS and Kyoto Univ.; ²Kyoto Univ.)

Interferometric measurements with fs laser pulses have been extensively utilized to characterize coherent motion and decay of wavefunctions. The method, however, demands precise control of optical lengths, and it is a difficult task in particular for shorter laser wavelength. Recently, an alternative way for fs interferometry has been demonstrated,^{1),2)} in which the relative optical phase between the two laser pulses is randomly modulated while the corresponding fluctuation in fluorescence is monitored. The method termed COIN (Coherence Observation by Interference Noise) is robust to turbulence in optical lengths and thus has vast applicability. Here we have applied COIN to several polyatomic molecules to investigate wavepacket dynamics and ultrafast nonradiative processes.

In the present setup, the third harmonic with ~200 fs duration of a 1 kHz Ti:Sapphire regenerative amplifier or an output of an optical parametric oscillator was sent to a Mickelson interferometer, in which optical length of one arm was modulated by hot air stream from a blower. Two laser pulses with delay up to several hundred ps were colinearly introduced onto molecules, which were adiabatically cooled in a CW supersonic expansion. The resultant fluorescence was observed in a single shot basis, and more than 1000 laser pulses were subjected to the statistics giving the variance of fluorescence intensity at certain delay.

Rotational wavepacket dynamics has been studied by the COIN observation on the S_1-S_0 6_0^1 band of benzene. After the initial decay of coherence, weak (~5%) rotational revivals are observed in the range of 10–30 ps. The signals depend strongly on rotational temperature, and their feature is well reproduced by a model calculation with the known spectroscopic parameters. Such a sharp dependence on the rotational distribution is in pronounced contrast to the results from a related method, *i.e.*, rotational coherence spectroscopy,³⁾ where gross shape of signals is not so sensitive to the temperature. The present study demonstrates the utility of COIN for monitoring the rotational distribution with high temporal resolution.

Electronic relaxation after the naphthalene S_2 excitation has also been examined by COIN. The initial coherence decays within the laser pulse duration due to the ultrafast ($\ll 100$ fs) internal conversion from S_2 into S_1 . This observation is in accord with the results from fs photoelectron spectroscopy,⁴⁾ indicating potentiality of COIN to studies on ultrafast relaxation dynamics after photoexcitation.

References

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III-E-2 Wavepacket Observation of Methyl Internal Rotation in *o*-Fluorotoluene

MIYAZAKI, Mitsuhiro¹; HARUNA, Atsuyuki²;
HASEGAWA, Hirokazu; OHSHIMA, Yasuhiro
(¹IMS and Kyoto Univ.; ²Kyoto Univ.)

The S_1-S_0 origin region of *o*-fluorotoluene has been examined to observe wavepacket dynamics associated with internal rotation of the methyl group. In addition to COIN observation, time-resolved fluorescence depletion (TRFD) is implemented in fs time domain for the first time. The experimental arrangement for TRFD is essentially the same with COIN: total fluorescence intensity is recorded in this case as a function of delay between two fs laser pulses. Here optical cycle interference is smeared out by the random modulation in optical length, so population change induced by pump-dump process is only monitored as fluorescence depletion. The laser beam is focused at the molecular jet and fluorescence from the central part of the irradiated region is only collected to observe depletion as large as possible.

The observed TRFD and COIN spectra are shown in Figure 1, and the corresponding power spectra after

Fourier transformation are indicated in Figure 2. In the case of methyl internal rotation, the ground and the lowest excited states are coupled with *ortho* and *para* nuclear spin wavefunctions, respectively, and thus both states are populated even in adiabatically cooled jet conditions. Accordingly, TRFD spectrum is a sum of independent beats between the vibronic levels in S_1 that are optically connected with the two internal-rotation states in S_0 . On the other hand, COIN spectrum exhibits all the interferences between the transitions from the two states, because it is given as the variance, *i.e.*, the average of the square of fluorescence fluctuation. The present study demonstrates the significance of the two complement experiments in extracting the energy-level structure of the internal rotation from the time-domain observation.

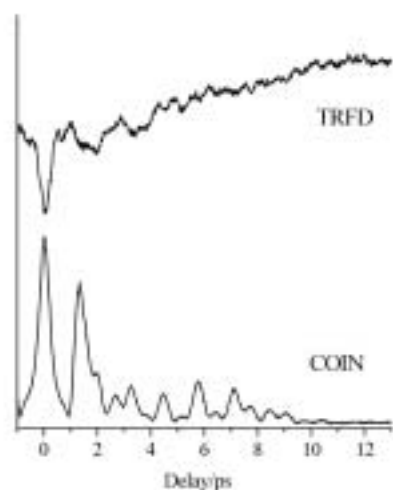


Figure 1. TRFD and COIN spectra observed by the excitation of the S_1 – S_0 origin region of *o*-fluorotoluene.

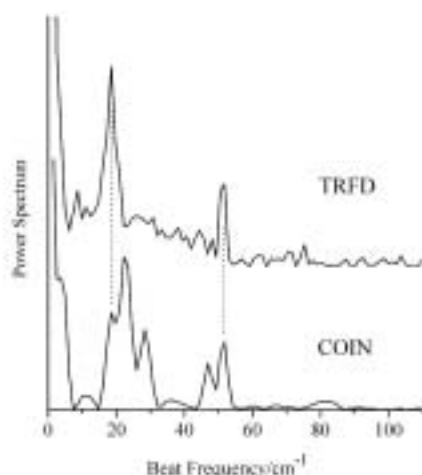


Figure 2. Power spectra obtained from the Fourier transformation of the time-domain TRFD and COIN spectra in Figure 1.

III-E-3 Construction of an Experimental Apparatus for Nonadiabatic Quantum-State Manipulation of Molecular Motions

HASEGAWA, Hirokazu; OHSHIMA, Yasuhiro

A vacuum chamber system and a data acquisition system have been designed and constructed to achieve quantum-state manipulation of molecular motions, in particular nonadiabatic molecular alignment induced by laser fields in gas phase. Molecules aligned by the interaction of intense fs laser pulses with induced electric dipole are probed through ionization. Ionization is attained by field ionization using delayed-intense fs pulses or resonance enhanced multiphoton ionization using ns laser pulses. In the former approach, dynamics of transiently aligned molecules are probed in time domain, while the change in rotational-state distribution induced by impulsive interaction with intense fs light is monitored in the latter method.

The vacuum system, composed of three differentially pumped chambers, is designed so as to be coupled with continuous or pulsed supersonic molecular beam (Figure 1). Ions produced by the interaction of laser fields with jet-cooled molecules are detected by a time-of-flight mass spectrometer. The electrode for ion extraction is designated with a small pinhole (< 1 mm), in order to ensure the detection of ions that are produced only in the region, where pump and probe laser pulses are overlapped. The integrated environment software for a data acquisition and laser control has been developed on the computer.

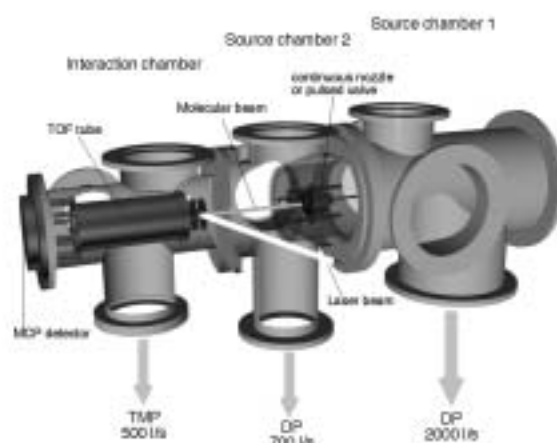


Figure 1. Vacuum chamber system for quantum-state manipulation of molecular motions.

III-E-4 Development of High-Resolution Coherent Pulsed Laser

OHSHIMA, Yasuhiro

We are constructing an all solid-state single-mode pulsed laser with Fourier-transform limited resolution (≤ 0.01 cm^{-1}), for quantum-state manipulation by coherent light–matter interaction, such as stimulated Raman adiabatic passage. In the system, the output from a cw extra-cavity diode laser or a Ti:Sapphire laser injection-seeds the optical parametric amplification by BBO nonlinear crystals excited by a single-mode Nd:YAG laser. At present, we routinely achieve the output power of 20 mJ/pulse, which reaches to 20% conversion efficiency, without injection seeding. Precise adjustment of optical layout is now under way for narrow band operation by the external seeding.

III-E-5 Laser Spectroscopy of the van der Waals Vibrations of Benzene–Water

MIYAKE, Shin-ichiro¹; MIYAZAKI, Mitsuhiro²;
OHSHIMA, Yasuhiro

(¹Kyoto Univ.; ²IMS and Kyoto Univ.)

Benzene-water has attracted much attention as a prototypical system containing the π hydrogen bond. Still, more experimental information should be accumulated for quantitative description of the intermolecular interaction in the complex. We have recently examined in detail the vibronic spectrum 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. A dozen of bands associated to van der Waals (vdW) mode excitation are clearly seen in the region up to 160 cm^{-1} from the 6_0^1 transition. The vdW structure cannot be assigned as a simple combination of a few normal modes, implying a substantial anharmonic coupling between the intermolecular vibrations. In particular, the appearance of an extremely low-frequency ($\sim 8\text{ cm}^{-1}$) band, similar to the case in the S_0 state, is considered to be the signature of the 3D hindered internal rotation of water in the cluster. Detailed analysis on the vdW structure is now under way with the aid of the results on isotopic variants.