II-D Ultrafast Dynamics of Surface Adsorbed Species

Understanding of reaction dynamics at surfaces using ultra-short laser techniques is an important issue to clarify the mechanism of the reactions. Real-time observation of temporal change of surface species induced by UV, visible, and (Near-) infrared pump pulses is carried out using mid-IR pump-probe vibrational spectroscopy and Sum-frequency generation (SFG) spectroscopy which is one of the non-linear spectroscopies using ultra-short laser has high sensitivity for detection of molecular vibrations of adsorbed species on surface in the first layer. The aim of this study is the identification of molecular structures of the intermediates generated by electronic, vibrational, or thermal excitation and understanding of the reaction kinetics including potential energies, activation barriers, and entropies. Typical systems of our recent studies are formate (DCOO) adsorbed on Ni(111) surface, olefins on OH group of zeolite. In addition to the ultrafast observation of surface events, controls of excited states of molecules and chemical reaction are tried using optimized pulse shaping technique. In the study, we succeeded in controlling the two-photon excitation efficiency and selective excitation of excited states of an α-perylene crystal.

II-D-1 Dynamic Processes of Olefins Adsorbed on Hydroxyl Groups of DM20 Zeolite Excited by Picosecond Infrared Pulses

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We have investigated olefins adsorbed on Brønsted acidic hydroxyl groups (OD) of DM20 zeolite by transient infrared absorption spectra after excitation of the OD stretching mode using picosecond infrared lasers. The olefins studied were ethylene, deuterated ethylene, propylene, and isobutene, and only isobutene was adsorbed on OD at its methyl group while the other olefins were adsorbed at their double bonds. For all the olefins except isobutene, simple vibrational relaxation of the $v = 1$ state was observed and the lifetimes were 2–4 ps. These lifetimes are an order faster than that of isolated OD. For isobutene, a long lifetime component lasting more than 500 ps was observed in addition to vibrational relaxation of 2 ps. The transient absorption spectra for isobutene-adsorbed zeolite at various time delays and frequencies indicated the existence of a short-lived species and a slow desorption process compared with vibrational relaxation.

II-D-2 Dynamical Response of Formate/Ni(111) System to Picosecond Near Infrared Pulses

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Time-resolved sum-frequency generation (TR-SFG) spectroscopy was carried out on a deuterated formate (DCOO) adsorbed on Ni(111) surface to investigate the surface reaction dynamics induced by irradiation of picosecond near-infrared laser pulses. The irradiation of pump pulse (800 nm) caused rapid intensity decreases of both CD and OCO stretching modes of bridged formate on Ni(111). Different temporal behaviors of intensity recovery between these two vibrational modes were observed, *i.e.*, the intensity of CD stretching mode recovered significantly faster than that of OCO symmetric stretching mode. From the results of transient measurements, we concluded that the observed intensity change was mainly due to a transient structural change of formate and we discussed about the mechanisms of the change.

II-D-3 Optical Control of Excited States of α-Perylene Crystal Using Optimized Pulse Shaping Method

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Optical control of excited states of α-perylene crystal was realized by a femtosecond optimized pulse shaping method using Genetic Algorithm (GA). We succeeded in controlling the emission spectral feature of an α-perylene crystal; the intensity of E-emission was increased by a factor of 1.4 without the change of Y-emission intensity. Furthermore, we found a near-infrared pulse shape whose multi-photon excitation efficiency is larger than that of a single femtosecond pulse by a factor of two. On the auto-correlation traces of these shaped pulses, the several satellite peaks appeared beside the main peak. The origin and mechanism of the attained change were discussed.

II-D-4 Optical Control of Two-Photon Excitation Efficiency of α-Perylene Crystal by Pulse Shaping

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Optimized pulse shaping experiments were carried out on the control of two-photon excitation efficiency of an α-perylene crystal in the temperature region from 30

K to 290 K. It was found that a pulse train with a pulse interval of 90 fs and an alternately reversing phase relation increased the excitation efficiency by a factor of 2 for the whole temperature region. The pulse shape characteristic for effective efficiency increase was educed by double pulse experiments in which the dependence of the emission intensity on the pulse interval and relative phase between pulses were measured. The mechanism of the efficiency increase is briefly discussed using a sliding-window Fourier transform of the pulse shape.