II-F 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 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, CO on Ni(111) surface, and D₂O on OD groups in alumina.

II-F-1 Time-Resolved Study of Formate on Ni(111) by Picosecond SFG Spectroscopy

KUSAFUKA, Koji¹; ONDA, Ken¹; NOGUCHI, Hidenori¹; KUBOTA, Jun¹; DOMEN, Kazunari¹; HIROSE, Chiaki¹; WADA, Akihide²
(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

Time-resolved vibrational measurements were carried out on formate (HCOO) adsorbed on Ni(111) surface by combining the sum-frequency generation (SFG) method and picosecond laser system (time-resolution of 6 ps). Rapid intensity decrease (within the time-resolution) followed by intensity recovery (time-constant of several 10 s ps) of CH stretching signal was observed when picosecond 800 nm pulse was irradiated on the sample surface. From the results of temperature and pump fluence dependences of temporal behaviour of signal intensity, we concluded that the observed intensity change was induced by non-thermal process. Mechanism of the temporal intensity change was discussed.

II-F-2 SFG Spectroscopy of CO/Ni(111): UV Pumping and Transient Hot Band Transition of Adsorbed CO

BANDARA, Athula¹; KANO, Satoru S.²; ONDA, Ken¹; KATANO, Satoshi²; KUBOTA, Jun¹; DOMEN, Kazunari¹; HIROSE, Chiaki¹; WADA, Akihide³
(¹Tokyo Inst. Tech.; ²Hosei Univ.; ³IMS and Tokyo Inst. Tech.)

A UV excitation by a picosecond pulse at 266 nm induced an unusual shoulder to the ν_CO = 1 ← 0 resonance peak of CO/Ni(111) monitored by sum-frequency generation (SFG) of visible and IR pulses. The observed line shape was reproduced by the use of a dipole-dipole interaction model with the coherent potential approximation (CPA) where the hot band transition with a population ratio of 0.3 to 0.7 (ν = 1 to ν = 0) was assumed. Neither the transition to the two-phonon bound state nor the coupling with the low-frequency phonon modes explained the observed changes. The shoulder appeared only during the UV excitation, which indicat-