

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 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, CO on OH group of zeolite, and C₆H₆ on Cu(111) surface.

II-F-1 Time-Resolved SFG Study of Formate on Ni(111) Surface under Irradiation of Picosecond Laser 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 under instantaneous surface temperature jump induced by the irradiation by picosecond laser pulses. The irradiation of pump pulse (800 nm) caused the rapid intensity decrease 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.*, CD stretching mode recovered faster than OCO. This is the first result to show that the dynamics of adsorbates on metals strongly depends on the observed vibrational mode. From the results of temperature and pump fluence dependence, we concluded that the observed intensity change was not due to the decomposition or desorption, but was induced by a non-thermal process.

II-F-2 Vibrational Relaxation of Adsorbate and Adsorbent in the CO-adsorbed DM-20 Zeolite System

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We made the first observation of transient vibrational spectra of both adsorbate and adsorbent at molecule-adsorbed surface using a two-color infrared picosecond laser system. The transient measurements were carried out on the CO-adsorbed surface hydroxyl group (OD) of DM-20 zeolite by pumping the CO stretching mode (2175 cm⁻¹) or OD stretching mode (2470 cm⁻¹) and probing over the CO and OD stretching region (2000–

2700 cm⁻¹). The T₁ lifetime for OD was 5.8 ps and that for CO was 540 ps. By comparison with other CO-adsorbed systems, vibrational relaxation mechanisms of CO on various surfaces are discussed. We also found evidence of energy flows from the vibrational mode of the adsorbent (OD stretching) to that of the adsorbate (CO stretching) *via* van der Waals interaction.

II-F-3 Second Harmonic Observation of Cu(111) Surface: *In Situ* Measurements during Molecular Adsorption

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Second harmonic generation (SHG) spectroscopy using a tunable femtosecond laser has been demonstrated as an effective and a practical *in situ* monitor of surface electronic states during adsorption processes. We have successfully shown this technique to be suitable for the study of surface electronic states, not only those induced by adsorbed molecules but also those associated with clean surfaces. By observing the change in the SH signals from a Cu(111) surface during exposure to benzene or CO molecules, we discovered new resonances of the clean Cu surface that could not be ascribed to the well-known surface state (SS)–image state (IS) transition. One of these was from a surface site that is less likely to adsorb benzene, where the SH signal intensity was kept constant until the Cu surface was covered by the sub-monolayer.