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 Ni(111) surface, and D_2O on OD groups in alumina.

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

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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 10s 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

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[*Bull. Chem. Soc. Jpn.* **75**, 1125 (2002)]

A UV excitation by a picosecond pulse at 266 nm induced an unusual shoulder to the $\nu_{CO} = 1 \leftarrow 0$ 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 ($v = 1$ to $v = 0$) 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 indicated that the electronically driven excitation, presumably by the hot electrons generated by the irradiation, dominated the process. As possible mechanisms, the involvement of intermediate negative ion resonance state and/or the non-adiabatic coupling of electronic states with C–O stretching mode were considered.

II-F-3 Surface Hydroxyl Group and Adsorbed Water on γ-Al_2O_3 Studied by Picosecond Infrared Pump-Probe Experiment

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Picosecond infrared-infrared pump-probe experiments in the OD stretching region were carried out on dehydrated and multilayer water-adsorbed γ-Al_2O_3. For the dehydrated γ-Al_2O_3, transient bands assigned to the bleaching and hot bands of the OD stretching mode of isolated surface hydroxyl groups were observed, and the population lifetime (T_1) of the vibrational excited state ($v = 1$) of the mode was 200 ± 10 ps at 293 K. The characteristic temperature dependence of T_1 is indicative of a seven-phonon process. For the water-adsorbed γ-Al_2O_3, the transient bleaching and transient hot bands with a lifetime of 10–12 ps were observed by excitation of the absorption peak at 2630 cm^{-1}. In addition to these bands, weak transient bands were observed in the low frequency region. These results are considered evidence of the existence of isolated water molecules on the γ-Al_2O_3 surface. Pure dephasing is also discussed based on the bandwidth of the observed transient bands.