Molecular Structures on Solid Surface Studied by Broad-band Sum Frequency Generation (SFG) Spectroscopy

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INTRODUCTION

The sum frequency generation (SFG) spectroscopy is attracting more attention in the field of surface science because of its extremely high surface selectivity and sensitivity.[1,2] This method has been applied successfully in the studies of the water structures on the chemically modified quartz and electrolyte solution interfaces. [3,4]

In the present study, the molecular structures of organic thin layers formed on solid substrate were investigated by a newly constructed broad-band SFG system.

EXPERIMENTAL

In the present broad-band SFG system, a vibrationally resolved SFG spectrum is obtained from a broad-band *fs* IR pulse and a narrow-band visible pulse.[5,6] Comparing to the usual *ps* or *ns* SFG system, an SFG spectrum with a high S/N ratio can be obtained in a shorter acquisition time by the present system.

A number of organic thin layers of self-assembled monolayer (SAM), Langmuir-Blodgett (LB) films and polymer films were formed on a metal thin film or a quartz substrate. The *in situ* SFG measurements were carried out with internal reflection geometry. The potential of the metal films were controlled by a potentiostat.

RESULTS

Figure 1 shows SFG spectra of octadecyl-trichlorosilane (OTS) monolayer on quartz surface observed in (a) air and (b) phosphate buffer solution (pH=7), respectively, with polarization combination of SFG, Visible and IR as *ssp*. The SFG spectrum of OTS in air was similar to that of OTS with lower coverage reported previously.[4] Intensity of the SFG spectrum of OTS monolayer observed in aqueous solution was much stronger than that observed in air, which can be attributed to the change of local factors. Two strong peaks due to C-H symmetric stretch and Fermi resonance of the terminal CH_3 group were observed clearly while the SFG bands due to CH_2 groups were very weak. This result indicated that the present broad-band SFG system works well and a highly organized OTS monolayer with low defect density was constructed in the solution.

Figure 1c shows a *ppp*-polarized SFG spectrum of octadecanethiol (ODT) SAM formed on a gold thin film with a thickness of 200 nm on a quartz prism. Three downward peaks, which can be attributed to the C-H stretching of terminal CH_3 group of the ODT SAM, were observed. This result is different from the previous SFG spectra obtained by using *ps* laser system.[7] The thickness and potential dependence of the SFG spectra of the ODT monolayer will be discussed in detail.

Reference

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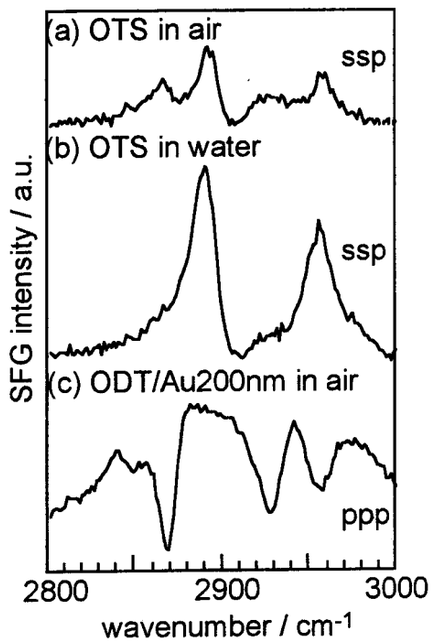

Figure 1. SFG Spectra of (a) OTS in air; (b) OTS in phosphate buffer solution and (c) ODT/gold in air.