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Vibrational SFG Spectroscopy of Organic Monolayers Fabricated on Silica-deposited CaF_2 Substrates

(Center for Quantum Life Sciences and Graduate School of Science, Hiroshima University[1], Institute for Nanoscience Design, Osaka University[2], Graduate School of Engineering Science, Osaka University[3])
○Adchara Padermshoke[1], Shouta Konishi[1], Toshiki Maeda[1], Masato Ara[2], Hirokazu Tada[3], Taka-aki Ishibashi[1]

Introduction. Infrared (IR)-visible/UV sum-frequency generation (SFG) spectroscopy is a method for measuring vibrational spectra of interface molecules. Because only surface or interface species give a resonant contribution to SFG signal, the technique is highly surface-specific and has been developed into a very powerful surface analytical tool. Biomolecular interfaces play a vital role in biological processes. An insight into the chemical composition and molecular structure of functional interfaces in nature and also in artificial devices is therefore of great importance. As a model system for biomolecular sensors, we are investigating organic monolayers silanized on solid substrates by SFG technique. The silanized monolayers are robust, chemically stable, and can serve to surface-immobilize various types of biological molecules. Since biomolecular interfaces exist physiologically in aqueous media, it is crucial to conduct the SFG study under such condition in order to gather the molecular information closely reflects that in nature. However, unlike in air, the probing geometry in which the SFG probe reaches the monolayers from the non-substrate side (geometry 1) (see Figure 1) is not applicable in aqueous solution because water does absorb most of the IR probe light. As a consequence, the probing is only possible via another geometry in which light impinges on the monolayers through the substrate (geometry 2). Unfortunately, conventional substrates generally used for silanization, i.e., fused silica (SiO_2) plates, are opaque throughout the IR region where the fingerprints of many organic molecules are embedded. A very thin SiO_2 layer, however, is transparent over that region. Therefore, we have developed a new substrate composed of a calcium fluoride (CaF_2) window and a thin SiO_2 layer, which allows silanization and is transparent over a broad range of the IR probe.

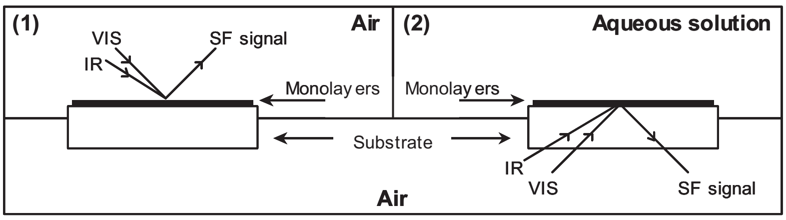

Fig. 1 SFG measurement geometries in air (geometry 1) and in aqueous solution (geometry 2).

Silica-deposited CaF_2 Substrate Development. We have made composite substrates that comprise a SiO_2 (500 nm) layer overlying a CaF_2 (1 mm) plate using an electron-beam deposition process and found that the strength of the SiO_2 layer is not reproducible. However, the presence of a very thin silicon (Si) (3 nm) layer at the SiO_2 and CaF_2 interface significantly improves the strength of the SiO_2 layer. Thus, the composite substrates being used in our study are composed of $SiO_2/Si/CaF_2$ (500 nm/3 nm/1 mm). We have ensured that the substrate transparency in the UV/visible, near-IR, and IR spectral regions is sufficient for SFG measurements (see Figure 2).

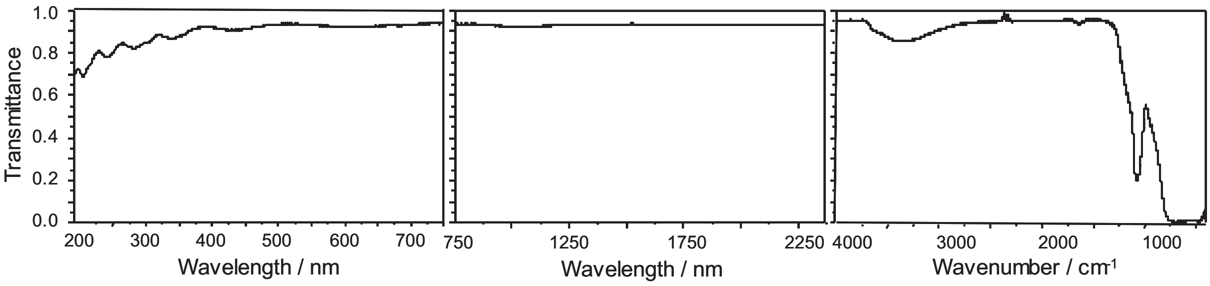

Fig. 2 Transmission spectra of a $SiO_2/Si/CaF_2$ (500 nm/3 nm/1mm) composite substrate in the UV/visible, near-IR and IR spectral regions (left to right).

Monolayer Fabrication. In this study, SFG measurements of phenyltriethoxysilane (PTES) ($C_6H_5Si(OC_2H_5)_3$), have been carried out. The SFG spectra of PTES on SiO_2 substrates and those of PTES on the $SiO_2/Si/CaF_2$ ones were compared in order to validate the efficiency of the newly developed substrates. A 2% (v/v) solution of PTES was prepared in a mixture of acetone and water (45:10 v/v) and adjusted to pH 4.5-5.5 with acetic acid. Silanization of PTES on the SiO_2 and $SiO_2/Si/CaF_2$ substrates was performed by immersing the ozone-pretreated substrates in the silane solution at 37 ^oC for 120 hr with stirring. The substrates were subsequently removed from the solutions, rinsed with acetone, and heated in air at 95 ^oC for 20 min.

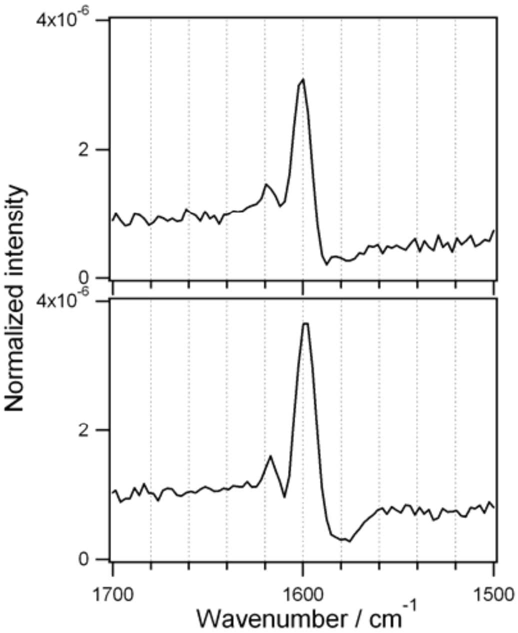

Fig. 3 Normalized SFG spectra of PTES on the SiO_2 (top) and $SiO_2/Si/CaF_2$ substrates (bottom) in ppp polarization.

Results and Discussion. SFG spectra of the PTES monolayer fabricated on the SiO_2 substrate and those of the monolayer fabricated on the composite one were recorded with ppp (SFG,visible,IR) and ssp polarization combination. Figure 3 shows the normalized SFG spectra of PTES on the two types of substrates in ppp polarization collected with the probing geometry 1. The spectrum obtained from the composite substrate well reproduces that obtained from the SiO_2 one. A band attributed to the phenyl ring vibration of PTES is clearly seen at 1600 cm^{-1} in both spectra. We are going to measure SFG spectra of PTES on the composite substrates with the probing geometry 2 in air and then in aqueous environment. Detailed analyses of the observed SFG spectra will be presented. The efficiency and usefulness of the $SiO_2/Si/CaF_2$ substrates will be verified, and possible improvement of the substrates and/or monolayer fabrication will be discussed.