Highlight Review

Multiplex Sum-frequency Spectroscopy with Electronic Resonance Enhancement

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Abstract

Multiplex detection of broad bandwidth light brings remarkable improvements in the experimental design of sum-frequency spectroscopy. Highly sensitive, interface-specific observations of molecular vibrations are demonstrated with examples of *n*-alkyl chains covalently anchored on Si(111) and an organic compound chemisorbed on $TiO_2(110)$.

◆ Introduction

An interface between two different phases controls the exchange of materials, charges, photons, and spins. There is a strong need to determine the chemical composition and molecular structure of functional interfaces in nature and also in artificial devices.[1] Sum-frequency (SF) spectroscopy has been used for this purpose. Sum-frequency light is generated specifically at an interface irradiated with infrared (IR) and visible (vis) lights. This second-order optical process is forbidden in centrosymmetric media (vapors, liquids, and most solids). The intensity of the SF light as a function of the IR wavenumber provides a vibrational spectrum of polyatomic species at the interface, where the centrosymmetry breaks down. The efficiency of the SF generation is enhanced by the resonance with vibrational transitions.

The IR and vis light pulses should be intense so that detectable SF light is generated with a limited number (monolayer or less) of molecules. When Shen and co-workers[2] invented this method in 1987, they employed nanosecond IR and vis pulses. Picosecond light sources were soon utilized to improve the SF light intensity. Self-assembled monolayers,[3] polymer films,[4] model catalysts,[5] biological materials,[6] air–liquid,[7] liquid–liquid,[8] and liquid–solid[9] interfaces have been characterized with picosecond spectrometers. Further improvements are demanded to extend the range of applications including time-resolved measurements,[10] and two-dimensional imaging.[11] This Highlight Review summarizes recent, discontinuous developments in SF experiments using femtosecond light pulses.

◆ Multiplex Detection of Broad Bandwidth SF Light

In the conventional design with picosecond pulses, narrow bandwidth IR and narrow bandwidth vis lights are focused on an interface. A narrow bandwidth SF light is generated, the intensity of which is monitored by a single-channel detector. The IR wavenumber is scanned to produce a spectrum containing several vibrational bands (the lower panel of Figure 1).

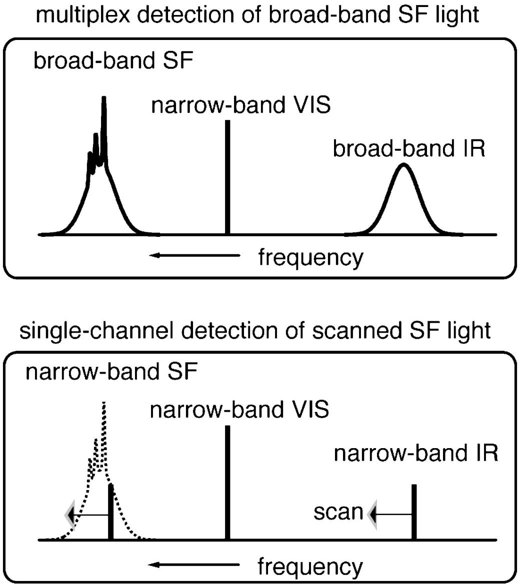

Figure 1. Multiplex and single-channel detection of SF spectrum.

The bandwidth of a femtosecond light pulse broadens owing to the principle of uncertainty. When the bandwidth of the IR light (typically 200 cm^{-1} for 100-fs timewidth) covers the wavenumber range of interest, the full spectrum is projected on each broad bandwidth SF pulse (the upper panel of Figure 1). The pro-

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jected spectrum is dispersed as a function of frequency and detected by a multichannel detector. The full spectrum is accumulated without scanning the IR wavenumber and the first advantage is the acquisition time thus shortened. The authors refer to this method as 'multiplex SF spectroscopy' after multiplex Raman spectroscopy,[12] while 'broad-band SF spectroscopy' is sometimes used by other researchers.

The multiplex detection of SF spectrum has a second advantage of improved signal-to-noise ratio. The intensity of light pulses emitted from a laser source fluctuates more than 5%. The pulse-to-pulse fluctuation makes noise in the spectrum obtained in the single-channel method with scanning the IR wavenumber. A number of pulses should be accumulated to remove the noise. The fluctuation cannot affect the SF spectrum determined in the multiplex method, because each SF pulse contains the full spectrum. The two advantages enable the quick acquisition. The typical acquisition time is 1 min with an octadecanethiol monolayer on gold.[13] By comparing with a spectrum obtained in the single-channel method,[14] the effective sensitivity, i.e., the reciprocal time to acquire a spectrum of a given signal-to-noise ratio, is improved by one order of magnitude.

Figure 2 illustrates a multiplex spectrometer developed by the authors.[15] A Ti:sapphire laser source provides near-infrared light pulses (wavelength: 800 nm, timewidth: 110 fs, bandwidth 250 cm^{-1}, pulse energy: 2.8 mJ, repetition frequency: 1 kHz). The broad bandwidth IR pulse (center wavenumber: 3000–1300 cm^{-1}, bandwidth: 280 cm^{-1}, pulse energy: 3–1 µJ) is prepared from the outputs of an optical parametric amplifier (OPA-1) via difference frequency generation. A major portion of the 800-nm pulse is converted to the second harmonic light (wavelength: 400 nm, pulse energy: 500 µJ). The bandwidth is compressed to 8 cm^{-1} and the timewidth is expanded to 5 ps at this stage using phase-conjugated mixing of two 800-nm pulses.[16] The second harmonic output serves as a vis pulse, or else pumps the other optical parametric amplifier (OPA-2). The OPA output (wavelength: 470–800 nm, bandwidth: 10 cm^{-1}, pulse energy: 50 µJ) is suitable for a vis pulse tunable in wavelength. Most molecular monolayers are damaged with femtosecond vis pulses more intense than 5 µJ. The SF pulse generated in the reflected direction is dispersed with a grating polychromater and detected by a multichannel detector (CCD).

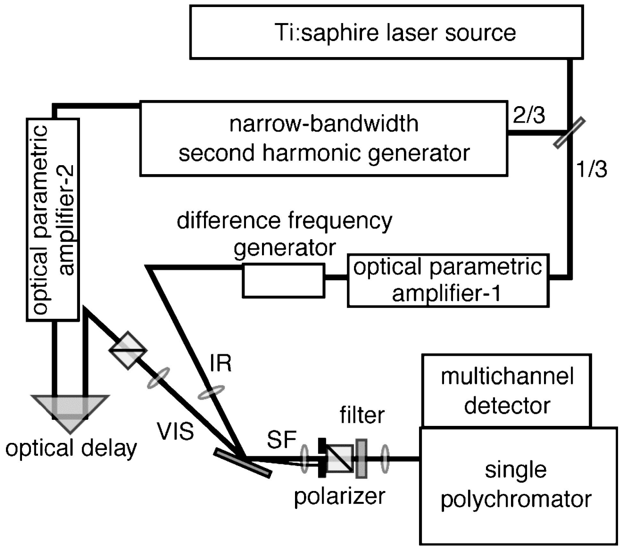

Figure 2. A multiplex sum-frequency spectrometer.[15]

Other schemes of multiplex detection have been proposed before the authors'. The key issue is how to prepare a narrow bandwidth vis pulse synchronized with a broad bandwidth IR pulse. van der Ham et al.[17] combined a tabletop laser source with a free-electron laser facility. Richter et al.[18] first demonstrated a laboratory-scale spectrometer. The bandwidth of the near-infrared (800 nm) pulse from their tabletop laser source was compressed in a grating monochromator to serve a fixed-wavelength vis pulse. The tunable vis pulse provided in the scheme of Figure 2 affords a remarkable advantage of resonance enhancement, as described in the last section.

Figure 3 presents an example of multiplex SF spectra.[19] *n*-alkyl (C_nH_{2n+1}) chains were covalently anchored on a hydrogen-terminated Si(111) surface in a hydrosilylation reaction,[20]

$$\mathrm{RHC{=}CH_2 + H{-}Si{\equiv} \rightarrow RCH_2CH_2{-}Si{\equiv}}.$$

Alkyl monolayers thereby prepared are thermally[21] and chemically[22] stable. Applications to molecule-based electric devices, modified electrodes, and tips of scanning probes[23] are examined with appropriate functional groups in R. SF spectroscopy is an adequate method to observe vibrations of the monolayers on a Si wafer.

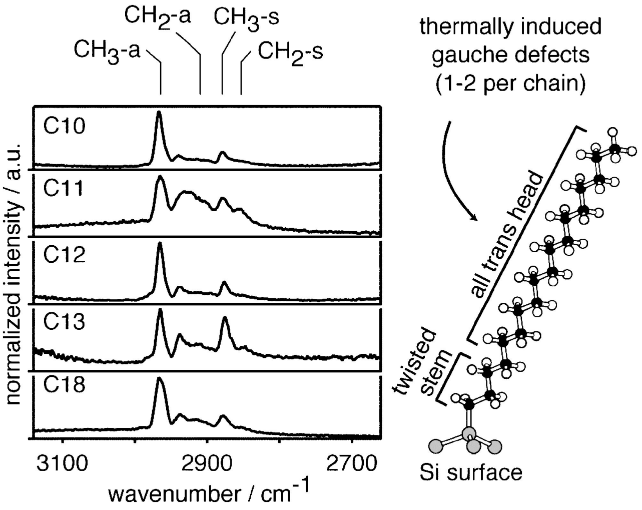

Figure 3. Vibrational bands of *n*-alkyl monolayers covalently anchored on a Si(111) surface. SF, vis (633 nm, 2 µJ pulse^{-1}), and IR (3 µJ pulse^{-1}) lights were p-polarized.[19] The conformation of the anchored chain is illustrated after theoretical predictions.[24,25]

n-Alkyl monolayers of different carbon numbers (10, 11, 12, 13, and 18) were observed with the spectrometer of Figure 2. A full spectrum containing five C–H stretching bands was obtained without scanning the IR wavenumber. The terminal CH_3 exhibited three bands; asymmetric stretch at 2965 cm^{-1}, symmetric stretch at 2877 cm^{-1}, and a Fermi resonance at 2938 cm^{-1}. The relative intensity of the symmetric and asymmetric bands was sensitive to the length of the chains, strong (weak) asymmetric bands with odd (even) numbers of carbon atoms. This indicates that the CH_3 terminals of all-*trans* alkyl chains are oriented in two distinct directions depending on the parity of the carbon number.

On the other hand, two weak bands at 2850 and 2914 cm^{-1} are the symmetric and asymmetric stretch of CH_2. The presence of the CH_2-related bands suggests a discernible number of CH_2 segments in gauche conformation. CH_2 segments in an all-*trans* chain are locally centrosymmetric. The two bands related to the centrosymmetric CH_2 are forbidden in a first approximation. The finite population of the gauche segments agreed with theoretical predictions[24,25] and made contrast to alkylthiol monolayers crystallized in the all-*trans* conformation on gold substrates. The signal-to-noise ratio improved by the multiplex detection was important to recognize the weak CH_2-related bands.

♦ Enhancement by Resonance to Electronic Transitions

The multiplex detection of a broad bandwidth spectrum is advantageous in observing C–H stretching modes as described in the preceding section. This is also the case for O–H, N–H, C≡N modes at 2000 cm^{-1} or higher wavenumbers. However, observing fingerprint vibrations at 1500 cm^{-1} or lower is sometimes problematic because of the limited intensity of low-wavenumber IR light. More efficient generation of SF light is required and achieved with the aid of the resonance to an electronic transition.

Figure 4 illustrates the optical transitions to generate SF light. Ground-state molecules are coherently excited to a vibrationally excited state by IR light, and then further excited to a virtual state by vis light. The SF light is generated in the transition from the virtual state to the ground state. This conventional scheme of SF generation is singly resonant to the vibrational excitation (upper panel). When the virtual state is resonant to a real electronically excited state of the molecule, the transition probability is remarkably enhanced. That scheme of SF generation is doubly resonant to the vibrational excitation and the electronic excitation (lower panel).

The vis wavelength should be tunable to be resonant to the electronic transition of various compounds. Raschke et al.[26] and Mani et al.[27] developed a vis-tunable spectrometer of the single-channel detection. The spectrometer of Figure 2 provides the multiplex detection of doubly resonant SF light. Figure 5 presents the doubly resonant, multiplex SF spectrum of an organic compound adsorbed on an atomically flat surface of TiO_2.[28]

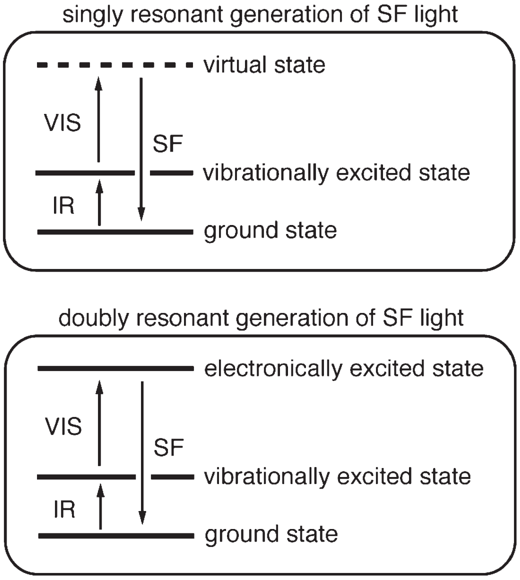

Figure 4. Optical transitions resonant and nonresonant to a real, electronically excited state.

Nanometer-sized TiO_2 particles modified with organic dyes are used in efficient photochemical solar cells.[29] The dye–TiO_2 interface is thought to control the electron transfer between the excited state of the dye and the conduction band of TiO_2. However, it is unknown how the atomistic structure of the adsorbed dye affects the dynamics of the electron transfer. One experimental difficulty comes from heterogeneous adsorption sites on TiO_2 particles. Although vibrational bands of dye-sensitized TiO_2 particles are obtained by infrared absorption and Raman scattering, the observed spectra are always interpreted as a mixture of different adsorption structures.

Here, an atomically flat, single-crystalline surface of rutile $TiO_2(110)$ is used as a model substrate. All-*trans* retinoic acid (a) is chosen for a test compound. The carboxylate moiety is the main anchoring ligand for binding organic sensitizers to TiO_2 particles.[29] It is established that small carboxylic acids (RCOOH with R=H, CH_3, CF_3, $C(CH_3)_3$, C≡CH, and C_6H_5) are dissociated on this TiO_2 surface. The corresponding carboxylate anion is chemically adsorbed on two Ti cations exposed at the surface.[30] Retinoic acid is expected to be dissociated to retinoate and adsorbed in a similar form (b). Adsorbed retinoates were resolved as protrusions in a scanning tunneling microscope

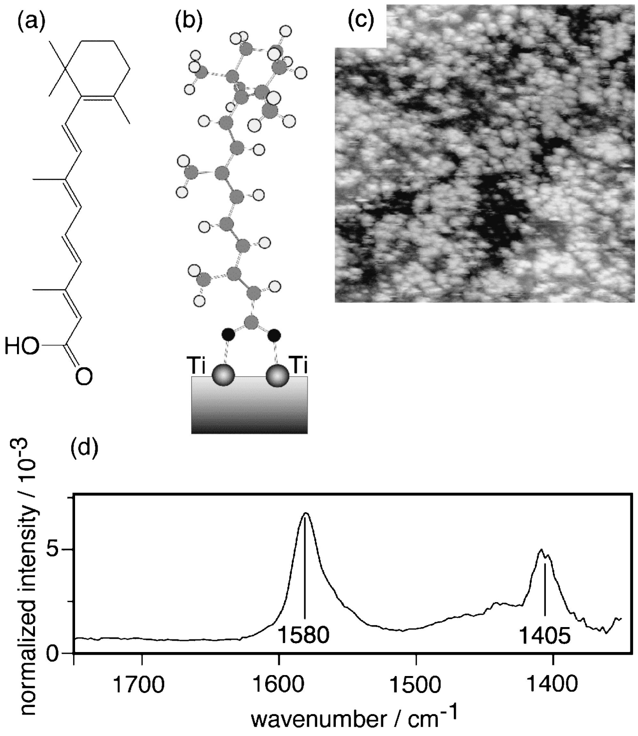

Figure 5. Retinoate chemisorbed on an atomically flat surface of rutile $TiO_2(110)$.[28] A free retinoic acid (a) and a retinoate bridge-adsorbed on two Ti cations (b) are illustrated. A scanning tunneling microscope topography ($80 \times 80\,\mathrm{nm}^2$) of the retinoate-covered surface is shown in (c). The doubly resonant, multiplex SF spectrum of the adsorbed retinoate is in (d). SF, vis (0.2 μJ pulse^{-1}), and IR (2 μJ pulse^{-1}) lights were p-polarized.

image (c). The uniform height and width of the protrusions suggested retinoates exist in one form of adsorption, which is assigned to the bridge structure on the basis of the fingerprint bands in the doubly resonant, multiplex SF spectrum (d).

The spectrum consists of two distinct peaks at 1580 and 1405 $\mathrm{cm^{-1}}$ with weak bands at 1500–1430 $\mathrm{cm^{-1}}$. The former of the two is assigned to the in-phase stretching of the conjugated C=C double bonds. The latter comes from the symmetric stretch mode of COO^- anchored on the TiO_2 surface. The absence of the C=O stretch evidences the bridge fashion of adsorption rather than a monodentate coordination.

The optical process to generate the spectrum is resonant to the electronic transition of retinoate. The vis wavelength was tuned at 480 nm to give SF light of 446 nm on the long-wavelength tail of the electronic absorption band of retinoate. When the vis wavelength was shifted to 535 nm, to be more off-resonant, the SF intensity decreased by 6 times. It is difficult to quantitatively determine the resonance enhancement. The in-phase C=C stretch band of Figure 5 was 20 times more intense than the C–H band of Figure 3. This number is not more than a guide to experiments, because the two bands coming from different vibrational modes cannot be directly compared. The Raman scattering cross section is enhanced by four or five orders of magnitude when resonant to an electronic transition. A comparable enhancement may be expected for the electronic resonance in the SF generation. Indeed, the intense bands of Figure 5 were far below the detection threshold with vis wavelengths completely off-resonant.

♦ Summary and Future Directions

The multiplex detection of broad bandwidth SF spectra has been achieved with a tabletop, femtosecond laser source. When the bandwidth of 100-fs SF light pulses covers a wavenumber range of interest, the full vibrational spectrum is projected on each pulse and recorded by a multichannel detector. This multiplex advantage of detection without scanning the IR wavenumber leads to an effective sensitivity improved by one order of magnitude. The efficiency of SF generation is further enhanced by tuning the vis wavelength to be resonant with an electronic transition.

The highly sensitive, interface-specific observation of molecular vibrations thereby achieved affords a wide range of applications including two-dimensional imaging of organic polymers and biochemical materials. Photoinduced dynamics at interfaces can also be traced with a multiplex spectrometer extended for pump-and-probe measurements.[31] Another practical advantage is the stability of Ti:sapphire laser sources operated at 1-kHz repetition frequency. The authors are ambitious to develop an easy-to-operate spectrometer that works without continuous adjustments by laser professionals. Routine operation is an essential requirement for application-oriented research.

On the other hand, a molecular level interpretation of experimentally observed SF spectra remains to be developed. Although the theoretical framework of SF spectroscopy has been established,[32] parameters involved in the framework should be related to the microscopic structure of the interface. Efforts have been made to simulate a SF spectrum.[33,34] Intense collaboration of theoretical and experimental researchers is still demanded.

♦ Acknowledgements

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