Sum-Frequency Generation Spectra of Thin Organic Films on Silver Enhanced Due to Surface Plasmon Excitation

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We have studied vibrational spectra of thin films of copper phthalocyanine and fullerene of different thicknesses on silver obtained by a visible-infrared sum-frequency generation (SFG). The free electron laser FELIX was used as a source of broadband infrared and the pulsed Nd:YLF laser system as a source of visible radiation. Excitation of a surface plasmon on silver has allowed to enhance the efficiency of the SFG process. The SFG signal has appeared to be almost independent of the film thickness demonstrating the exclusive contribution of the interfacial layer to the SFG signal.

1. Introduction

Interface sensitive techniques like electron-energy-loss spectroscopy [1], reflection-absorption infrared spectroscopy [2], surface-enhanced Raman spectroscopy (SERS) [3] and surface electromagnetic wave spectroscopy [4] have been developed to study the interaction of overlayers on surfaces. Recently, such nonlinear methods as second harmonic generation (SHG) and sum-frequency generation (SFG) have been applied in researches of surface species [5]. In the dipole approximation for centrosymmetric media both SHG and SFG can take place only at the surface where the symmetry is broken. Due to this surface specifity, SFG is a valuable tool for interface vibrational spectra studies. Since SFG is a second-order nonlinear process, its yield is rather low. To increase the SFG signal we have proposed to enhance the electric field at the surface by a visible surface plasmon-polariton (SP) [6] excitation. The SP is a TM (transverse magnetic) mode and has a maximum of an electromagnetic field exactly at the interface exceeding the field in the bulk up to two orders. Silver is the most suitable metal for the enhancement of the electromagnetic field in the interfacial layers due to the smallest electromagnetic losses in visible spectral region. In our first experiments on the thin film SFG spectroscopy we have obtained the vibrational spectra of the centrosymmetric

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copper phthalocyanine [7] and fullerene [8] films on silver exhibiting both infrared and Raman active bands. This result showed the lack of the inversion symmetry either in the interfacial layer or on the whole film. To resolve this alternative and to understand the role of the film thickness in this effect we have compared in the present paper SFG spectra of copper phthalocyanine and fullerene films of different thickness.

2. Experiment

A scheme of the SFG experiment is shown in Fig. 1. TM (p-polarized) radiation of a pulsed frequency-doubled Nd:YLF laser system at 523.5 nm with a pulse duration of 7 ps falls onto the sample with the plane of incidence perpendicular to the grating grooves. The angle of incidence of the visible laser beam was chosen to have a minimum of the reflectivity from the grating, which corresponds to the maximal efficiency of the bulk radiation conversion into the SP. At the sample surface the intensity of the visible beam was 4×10^3 to 4×10^4 W/cm^2, and the spot size was 10 mm^2. It was spatially overlapped at the surface with the infrared beam of the free electron laser FELIX incident onto the sample at the angle near 60°. The IR radiation intensity was 5×10^6 W/cm^2 at the sample, the spot size was 18 mm^2 and the pulse duration varied from 0.5 to 5 ps depending on the spectral width of the pulse. These beam parameters were chosen to avoid sample damage. Both lasers were temporally synchronized with a picosecond accuracy.

Using the optical scheme with counter-propagating IR and visible laser beams and the grating SP excitation we could enhance the SFG output by a factor of 10^3 to 10^4 due to the excitation of two SPs at the visible laser and SFG frequencies simultaneously [9, 10]. The angle of the sum-frequency wave propagation direction relative to the surface normal depends strongly on the infrared frequency and can be calculated from the law of the momentum conservation [7 to 11]. The sum-frequency radiation was focused by a lens L with a focal length 20 cm onto a chip of a slow-scan CCD camera, which consists of 512×512 elements. For the spectral measurements the short pulses of FELIX with a bandwidth of the order of 5% of the laser wavelength were used. The SFG signal from the sample was transformed to a line image at the CCD array, different frequencies being dispersed along the horizontal direction.
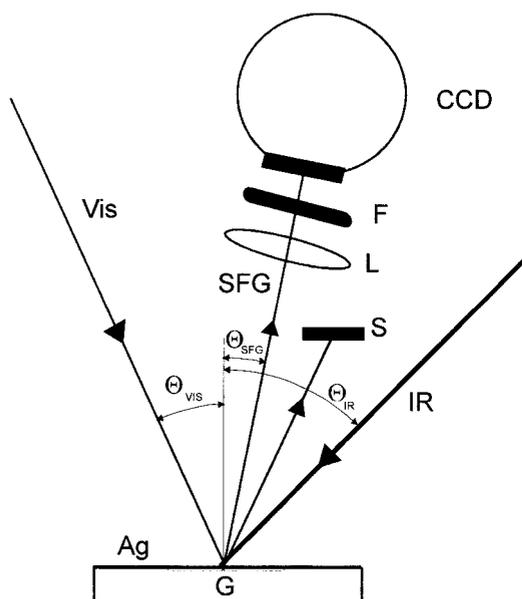

Fig. 1. Optical scheme of the SFG experiment. The angles Θ_{VIS}, Θ_{IR} and Θ_{SFG} correspond to the visible and infrared radiation incidence and the SFG radiation emission, respectively. The specularly reflected visible beam is stopped by a black screen S

In this way we were able to record a spectrum over a $\approx$40 to $70\,\mathrm{cm}^{-1}$ wide range in a single measurement. To cover a larger spectral range, the central wavelength of the FELIX pulse was scanned, spectrally overlapping the consecutive measurements. For a spectral calibration we measured the positions of the SFG signal on the CCD using the narrow band FELIX radiation (0.5% of the central frequency) at several frequencies. The resolution of the spectra, determined by element dimensions ($25\,\mu\mathrm{m}^2$) and the geometry of the set-up, was better than $1\,\mathrm{cm}^{-1}$. To suppress visible stray light from the sample in the direction of SFG, narrow-band filters F located in front of the detecting system were used.

The gratings used to excite the SP on the silver surface had a period near 300 nm and a depth in the range of 15 to 20 nm. They were made on glass plates by a holographic technique [12] with subsequent ionic etching [13]. The gratings were then covered by the opaque silver films and finally by the films of copper phthalocyanine or of fullerene of the thickness about a few nm. The films were deposited by thermal evaporation in a vacuum chamber under a residual gas pressure of 10^{-5} Torr or better. The film thickness was controlled by using a quartz microbalance technique to monitor the deposited mass.

For a more complete characterization of the films we have measured reflection–absorption and Raman spectra of some of the samples. The reflection–absorption spectra were recorded at the grazing angle using Fourier transform spectrometers "Michelson 110" (BOMEM) with a MCT detector and FTS-40A (BIORAD). The Raman spectra were measured by a Spex triple spectrograph and a CCD OMA (EG & G PARC) detector at a laser wavelength $\lambda = 514.5$ nm. To increase the Raman signal output we have used the surface plasmon excited at the laser wavelength by the grating like it was done in the SFG experiments.

3. Results and Discussion

The SFG signal can be considered as a sum of a nonresonant I_{NR} and a resonant I_R part. The nonresonant part is primarily due to silver and weakly depends on the frequency, so its shape should approximately follow the spectral FELIX pulse distribution. The resonant part of the SFG signal constitutes the fingerprint of the film as it depends on the vibrational bands of the surface species. The procedure of getting the SFG spectra from the experimental data had been described in detail in [7, 8]. The SFG spectra of the copper phthalocyanine films of different thicknesses are presented in Fig. 2a. Squares and circles are the experimental points for 5 and 8 nm thick films, the line shows the best fit of the SFG spectrum of the 10 nm film [7] by a set of Gauss contours. These spectra include all main features of the reflection–absorption spectra shown in Fig. 2b. It was found that the band intensities of the SFG spectra do not depend on the film thickness. It means that only the interface rather than the bulk of the film contributes to the SFG signal. Our conclusion contradicts with [14] where the second harmonic generation signal increased with copper phthalocyanine film thickness demonstrating the breaking of central symmetry in the bulk of the film. It could mean the difference of the structure of our films and the films studied in [14].

We could not use thinner copper phthalocyanine films in the experiment described above because they were not continuous. The fullerene films appear to be continuous even below 2 nm. The SFG spectra of the 2, 5 and 10 nm thick fullerene films in the
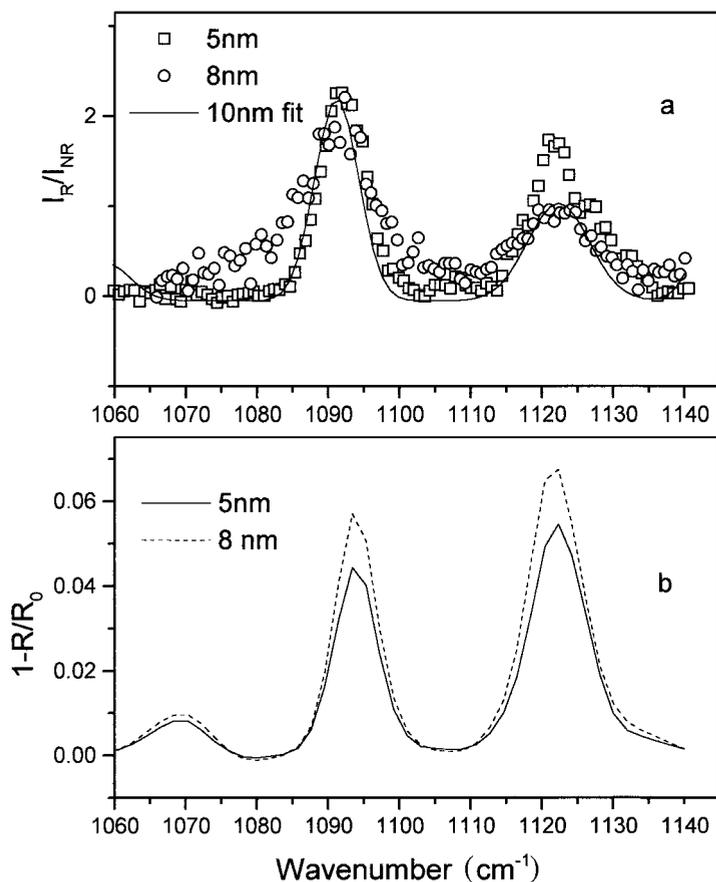
Fig. 2. The spectra of copper phthalocyanine films on silver. a) SFG spectra for the 5 and 8 nm thick films (squares and circles, respectively) compared with the 10 nm thick film (line). b) Reflection–absorption spectra of the 5 and 8 nm thick films. The film reflectivity R was normalized on the bare silver mirror reflectivity R_0

20 μm spectral region are presented in Fig. 3a. Reflection–absorption and Raman spectra of the the 5 nm thick film are shown in Fig. 3b. Three bands are present. There are IR ($528\,cm^{-1}$) and Raman ($496\,cm^{-1}$) active bands and also one extra band near $510\,cm^{-1}$. The first two bands seem to be independent of the film thickness. The band near $510\,cm^{-1}$ appears to be even stronger for the thinner film. It could be explained by the stronger sensitivity of this band to the deposition conditions. In [15] this band was observed by SERS and assigned to the fullerene triply degenerate vibration F_{1u} at $528\,cm^{-1}$ that splits due to the molecule symmetry reduction at the fullerene–silver interface. Our results confirm this conclusion. Note that the electron spectroscopy of an ultrathin fullerene film on Au(110) [16] and the SFG spectroscopy of fullerene on Ag(111) in the 1300 to $1500\,cm^{-1}$ spectral region [17] had shown that the first monolayer of fullerene is chemisorbed at the metal surface. Thus, the vibrational band near $510\,cm^{-1}$ in the fullerene film SFG spectrum appears due to the chemical interaction between fullerene and silver.
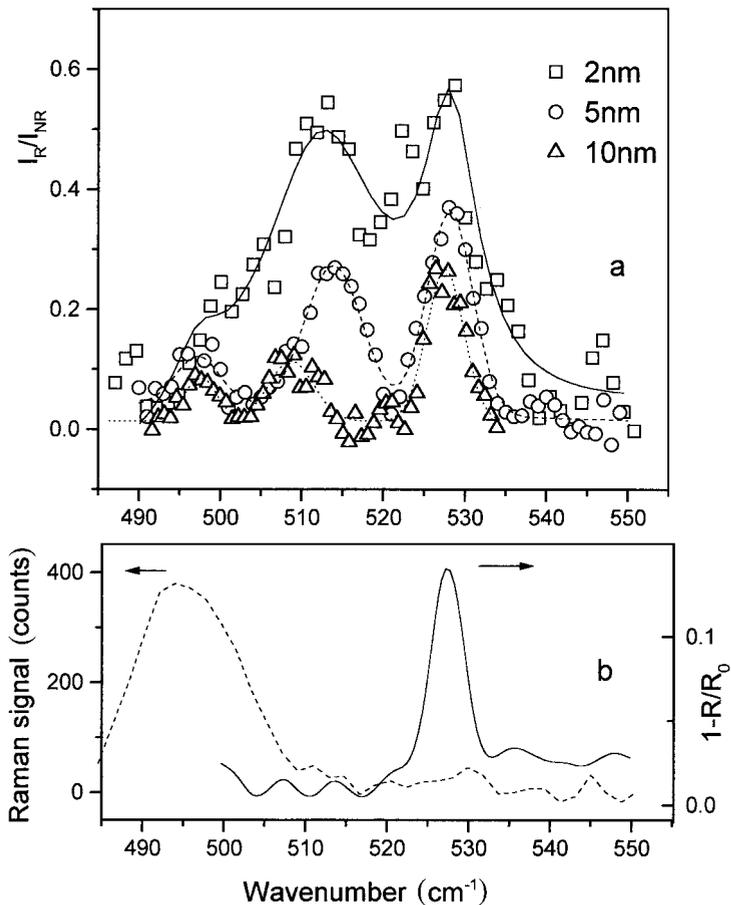
Fig. 3. The spectra of fullerene films on silver. a) SFG spectra for the 2, 5 and 10 nm thick films (points) and their fits by mixed Gauss-Lorentz contours (lines). b) Reflection–absorption (full line) and Raman (dashed line) spectra of the 5 nm thick film on silver. The film reflectivity R was normalized on the bare silver mirror reflectivity R_0

Finally, we can conclude that the large enhancement of the SP assisted SFG technique allowed us to measure the vibrational spectra of thin organic films on silver and to define the structure of their interfacial layer.

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