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Sum-frequency generation as a vibrational and electronic probe of the electrochemical interface and thin films

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Abstract

Standard vibrational sum-frequency generation (SFG) spectroscopy is performed to probe the electrochemical cyanoacetylene/Au(1 1 1) interface, enlightening a 20 cm^{-1}/V Stark shift of the free CN vibration mode of this cyanopolyynes-class molecule. SFG data suggest an orientation for the adsorbed molecules with the CN moiety pointing out in a direction perpendicular to the metal surface. A newly developed two-colour SFG (2C-SFG) set-up based on the CLIO free electron laser synchronized with a tuneable visible laser source is used to probe simultaneously the vibrational and electronic fingerprint of a thiophenol/Ag(1 1 1) interface. Structural information on the adsorbed self-assembled monolayer is put in evidence as a function of the immersion time of the silver substrate in the thiophenol solution (24 h or 5 days). With a longer immersion time, the molecular packing is of better quality and more compact, with the carbon rings less tilted with respect to the surface normal. This new experimental set-up combines the advantages to have a higher spectral and temporal resolution with higher power energies at far infrared wavelengths than these presently available from tabletop infrared optical parametric oscillators.

Keywords: Cyanopolyynes; Thiophenol; Interfaces; Gold; Silver; Nonlinear optics

1. Introduction

The electrochemical interface requires specific in situ optical tools in order to identify the chemical nature and organization of adsorbed species. Since the success of SFG spectroscopy as a vibrational probe for such systems [1], numerous works have been performed, among which we may mention the characterization of the CN/metal interface in aqueous solutions [2], the hydrogen deposition on Pt [3], the catalytic reduction process of ethanol and methanol at the Pt surface electrode with CO poisoning [4,5] in relation to the development of alcohol-based fuel cells, the effect of organic additives on electroplating on gold [6] and alloys [7].

Infrared–visible SFG (IV-SFG) is a vibrational spectroscopy whose intrinsic surface-specific selectivity lead to the identification of adsorbed species [8], whatever the nature (metals, insulators, semiconductors) or the phase (solid, liquid, gaseous) of the probed interface. SFG signal is generated by mixing at the same point of a sample two laser beams, one tuneable in mid- or near-infrared spectral range to probe vibration modes while the other one is in general at fixed visible wavelength. For picosecond setups, the visible beam is usually that of a doubled YAG laser at 532 nm. The temporal and spatial synchronization of the two beams on the probed point allows the generation of SFG photons through the excitation of the nonlinear second-order susceptibility of the system. From 2002, IV-SFG spectroscopy was extended to the so-called two-colour SFG (2C-SFG) thanks to the replacement of the fixed wavelength visible source by a tuneable device covering the visible spectral range from blue to red. Both vibrational

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and electronic fingerprints of the interface become accessible as shown in works ranging from the enhancement of doubly resonant SFG processes (DRSFG) [9] in molecular systems to the enlightening of interband electronic properties effects of metallic electrodes [10] on the molecular vibrational activity. However, most of the SFG works are limited to available tabletop infrared sources based on optical parametric devices (e.g., optical parametric oscillators OPO) with a limited power in the 2800–3200 cm^{-1} or 2400–1100 cm^{-1} spectral ranges. This allows probing a variety of vibration modes, for instance the stretching of the OH, CH, C–O, C–C, C–N, NO_2 moieties. The technical limits of such tabletop infrared sources are progressively extended to the far infrared and a few limited works overcoming these restrictions appeared more recently [11,12]. However, the gain of the far infrared optical devices is still limited and their output power low compared to the near-infrared range. As the vibrational features in the far infrared (e.g., carbon skeleton deformation, bending, rocking or scissoring vibration modes, heavy atom bond stretching) have in general a low SFG cross-section, this often leads to poor signal-to-noise ratio experiments. A possible alternative to such present technical limitations is the use of powerful infrared sources with high temporal and spectral resolution as these encountered in free electron lasers (FEL) [13]. Some works have already been performed in the past years using such infrared sources [14].

In this work, we illustrate the versatility of IV-SFG spectroscopy by two sets of experimental results. On one hand, we characterize by SFG a controlled electrochemical interface made of adsorbed cyanopolyynes species on a gold single crystal electrode using a standard infrared tabletop OPO source. We evidence its structural organization related to the static electric field in the double layer. On the other hand, we present 2C-SFG measurements in the middle infrared using a FEL as an alternative source. A self-assembled monolayer (SAM) made of aromatic cores adsorbed on silver via a sulphur bond is used to illustrate the advantages of the combined use of an infrared FEL and a visible tuneable OPO for nonlinear optics, and in particular for further SFG experiments to be performed in the electrochemical environment. This latter shows that electronic structure investigation, far-infrared modes and their coupling in a SFG experiment are now accessible.

2. Experimental setups

2.1. Lasers and SFG detection setups

Two distinct SFG setups have been used. On one hand, for the electrochemical measurements, we use a classical IV-SFG set-up based on a 15 ps Nd:YAG laser source which has already been described in details elsewhere [15,16]. SFG measurements were performed in the 2075–2275 cm^{-1} infrared spectral range to probe the CN stretching vibration mode. On the other hand, to perform 2C-SFG experiments on thin films adsorbed on a metal substrate at ambient air, we used the original SFG set-up depicted in Fig. 1 with the CLIO FEL as the infrared source. This setup represents an evolution of the previous YAG experiment. Its main tabletop laser source is a diode-pumped Nd:YLF (HighQ Lasers), continuously delivering 5–7 ps pulses at 1.047 μm with a 62.5 MHz repetition rate and an average power of 2 W. A few hundreds of pulses are then selected by an acousto-optic modulator (AOM) to generate the final temporal structure of the source: 10 μs long trains of pulses, with a repetition rate of 25 Hz. The length of the trains is tuneable between 2 and 10 μs. The CLIO FEL [13] has the same temporal structure at the microsecond range, but delivers shorter picosecond pulses (around 1 ps FWHM). The two main advantages of CLIO lie in its wide tuneability, at present between 5 and 150 μm, with an effective far-infrared limit around 50 μm for SFG experiments, coupled to a high spectral resolution around 0.1–0.5% of the frequency for optimal settings. Typical energies of the FEL output can reach values up to more than 10 μJ per pulse, but for actual experiments it is usually reduced around 2 μJ per pulse in order to preserve the spectral resolution and avoid any damage to the sample. Finally, the YLF laser is synchronized with the FEL through a common high-frequency electronic clock. As illustrated in Fig. 1, the YLF trains of pulses are then amplified in two double-pass flash-pumped Nd:YLF amplifiers. This step is necessary to reach the energy range required by the OPO generation processes and needs the use of an optical insulator (OI) to prevent any damage during the amplification process. Part of beam is used to pump separately two nonlinear crystals ($LiNBO_3$ or $AgGaS_2$) of the infrared OPO as in an identical configuration as for the YAG setup [16]. For the visible OPO, the remaining beam is successively frequency-doubled (523.5 nm) then tripled (349 nm), respectively in BBO and LBO crystals. The third harmonics UV output of the LBO has a typical energy value of 7 μJ per pulse. It is then used to pump the BBO crystal of the visible OPO. The pump is divided inside the crystal into an idler and a signal oscillating in a synchronous laser cavity, in which one of the mirrors is partly transparent and allows the use of the signal as the OPO output. The wavelength tuneability is achieved through a calibrated rotation of the BBO crystal. Typical output power of the visible OPO is 4 μJ per pulse, tuneable between 420 and 700 nm with around 6 cm^{-1} resolution. For SFG experiments, the infrared source may be either the infrared OPO or the CLIO FEL. The infrared beam is then temporally synchronized at the picosecond scale through the addition of an optical delay on the tuneable visible beam and spatially overlapped on the probed interface with this latter as described in the lower part of Fig. 1. For the thiophenol/Ag(1 1 1) interface, we probed the 960–1040 cm^{-1} spectral range, specific of phenyl ring deformation modes.

Whatever the experimental setup, the infrared and visible beams are mixed at the probed interface with 65° and