

Assessing the Viability of Heterodyne VSFG Spectroscopic Studies of Electrode Interfaces

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Introduction

Vibrational Sum Frequency Generation (VSFG) spectroscopy selectively probes vibrational transitions of species at interfaces, avoiding the interference of bulk solvent/substrate signals. In recent years we have developed a homodyne VSFG experiment using ULTRA-B that has provided valuable new insights into the mechanisms of small molecule electrocatalysts when they are present at an electrode surface.¹⁻⁴

During a homodyne VSFG experiment, when the frequency of the pulsed mid IR laser (fs) matches the vibrational mode of a molecule at the interface the vibrationally polarised molecules can interact with the pulsed 800 nm laser light (ps) resulting in the generation of light at the sum of the frequency of the IR and the Vis photons.^{5,6} SFG generation is forbidden in bulk centrosymmetric environments, giving rise to the interfacial selectivity. Unfortunately resonant VSFG is a weak effect which is often swamped by non-resonance (NR) response. To suppress the NR response with the homodyne VSFG experiment we typically introduce a short time delay (0.5 -1.0 ps) between the 800 nm and mid IR laser pulses, in a manner previously outlined elsewhere.⁷ However vibrational modes with very short lifetimes can be hard to detect at such time delays and the VSFG signal detected can also become a function of the time delay due to coherent beating effects,⁸ complicating analysis. A further complication of homodyne VSFG experiments is that the strength of the VSFG signal decreases quadratically with the surface coverage of the molecules.⁹

Here we describe our attempts to construct a heterodyne (HD) VSFG spectrometer at the UK Central Laser Facility (ULTRA). Detailed descriptions of HD-VSFG spectroscopy are provided elsewhere,¹⁰ briefly the interference of the generated SFG optical field (E_{SFG}) with the electric field of a reference beam, the local oscillator (E_{LO}), is detected (Figure 1). The LO beam is typically generated by the sum frequency mixing of a small portion of the mid IR and 800 nm beams in a non-linear (e.g. KNbO_3 , ZnO) medium and temporally delayed with-respect to the IR and Vis pulses at the surface under interrogation by a time delay (t) typically of several picoseconds. When $E_{\text{LO}} \gg E_{\text{SFG}}$ the intensity of the cross term of the heterodyne signal (obtained after subtraction of the independently measured LO intensity) can be considered to have an approximately linear dependence on the surface coverage. A further advantage is that HD-SFG yields both the phase and the amplitude of the signal enabling accurate subtraction of the NR response of the system. This also provides access to details about the geometry of the molecules at the interface, information that is currently lost in our homodyne ULTRA SFG experiment.

Experimental approach

Widespread application of HD-VSFG spectroscopy has not occurred, and to the best of our knowledge, there are no published

in-situ electrochemical HD-VSFG studies. This is primarily a result of the technical challenges of implementation. In the experiment described here broadband mid IR radiation is used, a spectral interferogram (SI) with a characteristic fringe pattern resulting from interference of the LO and VSFG beam is measured following dispersion onto the array detector. The intensity of the light detected during the HD-SFG experiment is given by equation 1.

$$I_{\text{HD-VSFG}} = |\bar{E}_{\text{LO}}|^2 + |\bar{E}_{\text{VSFG}}|^2 + \bar{E}_{\text{VSFG}}\bar{E}_{\text{LO}} \exp(i\omega t) + \bar{E}_{\text{VSFG}}\bar{E}_{\text{LO}} \exp(-i\omega t) \quad \text{Eq. 1.}$$

An inverse Fourier transform of the SI into the time domain is carried out and by gating the signal at $t > 0$, a region corresponding to the $\bar{E}_{\text{VSFG}}\bar{E}_{\text{LO}}\exp(i\omega t)$ term of equation 1, and by transforming back into the frequency domain, the real and imaginary parts of $\chi_{\text{eff}}^{(2)}(\omega)$ can be found. The imaginary part of $\chi_{\text{eff}}^{(2)}(\omega)$ directly reports on the vibrational transitions, with the sign of the observed spectral feature indicative of the dipole derivative vector. However to remove $\chi_{\text{NR}}^{(2)}$ contributions measurement of a reference sample is typically required. Therefore it is vital that LO and VSFG beams with excellent relevant phase stability are generated and that the reference sample is placed in the exact position of the electrode interface under study.

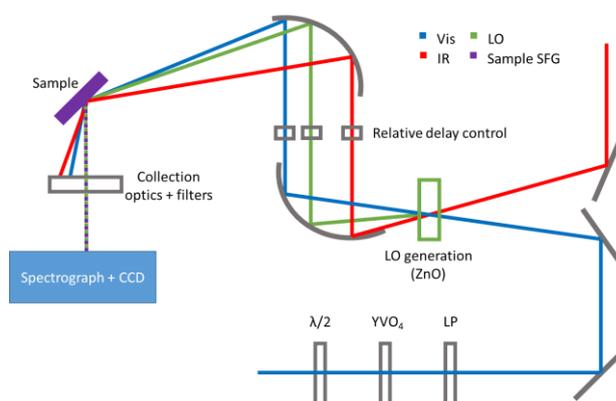


Figure 1 –HD-VSFG setup developed at CLF, based on design by Petersen. Fused silica (2 mm) is used to introduce a delay between the LO and the Vis & IR beams, producing the required interferogram. Various thicknesses of CaF_2 are introduced in the Vis and IR beampaths after LO generation to compensate for the relative delay between IR and Vis introduced by transmission through the LO generation substrate (ZnO/CaF_2 , 2mm).

An experiment design based upon the modified approach of Petersen *et al.*¹¹ was constructed using ULTRA-B, Figure 1. LO generation occurred in a thin ZnO sample with a fixed delay between the LO and mid IR and 800 nm beams being introduced

by the use of fused silica (4 ps). Fine tuning of this delay, along with compensation of the relative delays of the IR and Vis beams introduced by transmission through the LO generation medium, and the window and electrolyte of the sample cell, was achieved by insertion of various thickness of calcium fluoride in the paths of these two beams. To test the experiment we initially have carried out experiments on $[\text{Mo}(\text{bpy})(\text{CO})_4]$ (1 mM) in CH_3CN in the presence of a $\text{TBA}^+\text{PF}_6^-$ (0.1 M) electrolyte at a gold electrode under potentiostatic control. Full experimental details of the electrochemical apparatus and the cell for electrochemical VSFG experiments can be found in our previous report.¹ Experiments were carried out in the metal carbonyl stretching region with the mid IR light centred around 1900 cm^{-1} (ca. 500 cm^{-1} usable bandwidth) generated from a home-built OPA, details described elsewhere.¹ The 800 nm output of the femtosecond laser was passed through an air-spaced etalon (SLS optics) to provide a spectrally narrow (ca 10 cm^{-1}) time-asymmetric pulse. The HD-VSFG light was dispersed (Andor HoloSpec), detected using a CCD (Andor iDus 420).

Results

We have previously shown that the reduction of $[\text{Mo}(\text{bpy})(\text{CO})_4]$ to initially form $[\text{Mo}(\text{bpy})(\text{CO})_4]^+$, which is then in turn reduced to form $[\text{Mo}(\text{bpy})(\text{CO})_3]^{2-}$, can be followed by homodyne VSFG spectroscopy.¹ The homodyne VSFG spectra of $[\text{Mo}(\text{bpy})(\text{CO})_4]$ were recorded here using the experiment in Figure 1 with the LO blocked and this data is shown in Figure 2. The z-axis is plotted as a ratio of the spectrum at the stated potential to the spectrum at open circuit to allow direct comparison to the HD-VSFG spectra. Clear changes in the $\nu(\text{CO})$ modes with applied potential can be seen in figure 2 with a band at $\sim 1940\text{ cm}^{-1}$ at -0.7 V (vs. a Ag pseudo reference electrode) showing a Stark tuning of $\sim 20\text{ cm}^{-1}$. Assignment to a specific mode of the Mo carbonyl complex is complicated by the presence of CO bound directly to the Au electrode used and degradation products as a result of the repeated number of experiments carried out during this equipment development study. Nonetheless the potential dependence of the resonant SFG modes demonstrates that we are able to monitor the electrochemistry of the interface using homodyne VSFG.

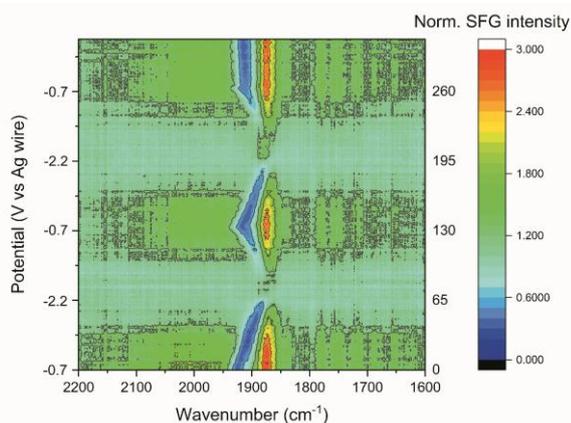


Figure 2. Homodyne VSFG spectra (2 s per spectrum) recorded as the potential of the Au working electrode is modulated between -0.7 and -2.2 V in the presence of $[\text{Mo}(\text{bpy})(\text{CO})_4]$ at 10 mV s^{-1} . The figure shows potential dependent SFG modes indicating that the electrode surface is being interrogated.

The HD-VSFG spectra recorded during an electrochemical experiment of $[\text{Mo}(\text{bpy})(\text{CO})_4]$ in CH_3CN at a Au electrode are shown in Figure 3. A good agreement between figures 2 and 3 indicates that the HD-SFG experiment has been able to successfully probe the Au electrode surface. In particular the Stark tuning of the $\nu(\text{CO})$ modes can still be detected. It is however notable that despite similar data accumulation times (2 s per spectrum Hom, 0.4 s per spectrum Het) the signal to noise ratio in the HD-SFG experiment is significantly worse. The time

delay between the LO and VSFG beams was optimized in order to maximize the number of fringes observed, while attempting to maintain the optimum resolution between fringes, which was limited by the spectrograph/camera employed. Unfortunately the precision with which the fringe pattern could be defined, combined with the lack of phase stability between the LO and VSFG over the prolonged time period of the experiment ($\sim 700\text{ s}$), led to decreased signal to noise in the HD-SFG experiment, and future studies will attempt to further optimize the experimental set-up

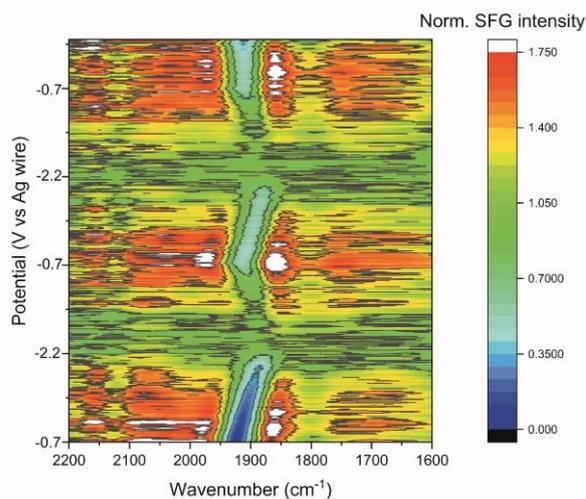


Figure 3. Heterodyne VSFG spectra (0.4 s per spectrum – longer acquisition times would saturate the camera) recorded under the same electrochemical conditions as used in Figure 2.

Conclusions

HD-VSFG spectroscopy has the potential to be a powerful experiment for interrogating electrode interfaces. Here we present our initial attempts to build a HD-VSFG experiment at the UK Central Laser Facility using the ULTRA-B apparatus. In a proof-of-principle study on $[\text{Mo}(\text{bpy})(\text{CO})_4]$ in CH_3CN at a Au electrode we demonstrate that we are able to detect a species at the electrode interface, however the signal to noise is significantly below that achieved in the homodyne VSFG experiment on the same cell. Future studies will focus on further developing the experiment with the aim of reporting the first in-situ studies of electrocatalysis using HD-VSFG.

Acknowledgements

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