

Contact: paul.donaldson@stfc.ac.uk

G Karras, C Kirkbride, PM Donaldson

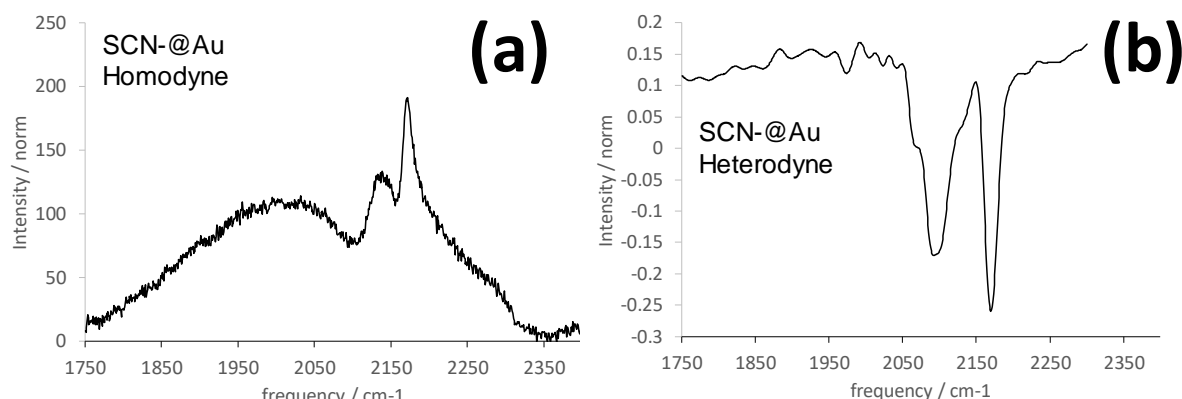
Central Laser Facility

K Saeed, AM Gardner, AC Cowan

University of Liverpool

O Al Bahri, JM Cole

University of Cambridge



**Figure 1.** A comparison of SCN- ions on a gold substrate measured with homodyne (a) and heterodyne (b) detected IR-Visible SFG spectroscopy. (a) was recorded with a 2 second accumulation of signal. (b) was recorded with a 20 second accumulation of signal. Heterodyne signal fringes were recovered from a spectrum recorded with a 4 ps delay between the local oscillator and the SFG signal.

Surface specific IR-Visible Sum frequency generation (SFG) has the ability to measure vibrational spectra of monolayer level buried interfaces. The provision of IR-Vis SFG spectroscopy at CLF-Ultra has been driven by successful studies of catalysis at electrochemical interfaces.<sup>1–3</sup> Detection of the SFG signal in-quadrature on a camera (known as ‘homodyne’ detection) is the simplest means of acquiring data, however field level interferences of overlapping signals on top of the electronic SFG signal (known as the nonresonant background) make it difficult to identify and interpret the vibrational signals of interest. In previous years, CLF-Ultra relied on IR-Visible pulse delayed time gating to remove the nonresonant background. This method is useful on long-lived vibrational species, but at the expense of reduced signals sizes. It also introduces non-physical shifts on peak positions, as well as artefacts on the lineshapes observed.<sup>4</sup>

A more powerful and robust means of detecting IR-Visible SFG signals is to interfere them with a phase stable reference (local oscillator) field. Known as heterodyne detection, the SFG signal is measured at the field level, eliminating the interferences inherent to in-quadrature detection, allowing determination of the sign of the response (giving molecular orientation) and also allowing the removal of the nonresonant background.

CLF-Ultra have recently experimented with heterodyne detected IR-Visible SFG on several user experiments (App 19139946 and 19130066). The optical scheme of Petersen and coworkers<sup>5</sup> was implemented and studied carefully with regards to optimising signal-to-noise and signal recovery. The data in Figure 1 illustrates the current status. The Petersen scheme as implemented at CLF-Ultra works correctly. 1(b) clearly shows the elimination of the dispersive character of the lineshapes caused by interference of signals, as well as elimination of the nonresonant background. Developments are now focused on why the signal-to-noise is compromised in the heterodyne scheme, where a factor of 10x increase in averaging is necessary to achieve acceptable signal-to-noise compared with homodyne measurements.

## References

- (1) Neri, G.; Donaldson, P. M.; Cowan, A. J. The Role of Electrode–Catalyst Interactions in Enabling Efficient CO<sub>2</sub> Reduction with Mo(Bpy)(CO)<sub>4</sub> As Revealed by Vibrational Sum-Frequency Generation Spectroscopy. *J. Am. Chem. Soc.* **2017**, *139* (39), 13791–13797. <https://doi.org/10.1021/jacs.7b06898>.
- (2) Neri, G.; Walsh, J. J.; Teobaldi, G.; Donaldson, P. M.; Cowan, A. J. Detection of Catalytic Intermediates at an Electrode Surface during Carbon Dioxide Reduction by an Earth-Abundant Catalyst. *Nat. Catal.* **2018**, *1* (12), 952–959. <https://doi.org/10.1038/s41929-018-0169-3>.
- (3) Neri, G.; Donaldson, P. M.; Cowan, A. J. In Situ Study of the Low Overpotential “Dimer Pathway” for Electrocatalytic Carbon Dioxide Reduction by Manganese Carbonyl Complexes. *Phys. Chem. Chem. Phys.* **2019**, *21* (14), 7389–7397. <https://doi.org/10.1039/c9cp00504h>.
- (4) Laaser, J. E.; Xiong, W.; Zanni, M. T. Time-Domain SFG Spectroscopy Using Mid-IR Pulse Shaping: Practical and Intrinsic Advantages. *J. Phys. Chem. B* **2011**, *115* (11), 2536–2546. <https://doi.org/10.1021/jp200757x>.
- (5) Vanselous, H.; Petersen, P. B. Extending the Capabilities of Heterodyne-Detected Sum-Frequency Generation Spectroscopy: Probing Any Interface in Any Polarization Combination. *J. Phys. Chem. C* **2016**, *120* (15), 8175–8184. <https://doi.org/10.1021/acs.jpcc.6b01252>.