

Microsecond Resolved Infrared Spectroelectrochemistry using Dual Frequency Comb IR Lasers

Erick Lins,¹ Stuart Read,² Bipinlal Unni,¹ Scott M. Rosendahl² and Ian J. Burgess^{1,*}

¹Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 5C9 Canada

²Canadian Light Source, Saskatoon, Saskatchewan, S7N 0X4, Canada

*corresponding author: email (ian.burgess@usask.ca)

Abstract

A dual infrared frequency comb spectrometer with heterodyne detection has been used to perform time resolved electrochemical attenuated total reflectance surface enhanced infrared absorption spectroscopy (ATR-SEIRAS). The measurement of the potential dependent desorption of a monolayer of a pyridine derivative (4-dimethylaminopyridine, DMAP) with time resolution as high as 4 μ s was achieved without the use of step-scan interferometry. An analysis of the detection limit of the method as a function of both time resolution and measurement co-additions is provided and compared to step-scan experiments of an equivalent system. Dual frequency comb spectroscopy is shown to be highly amenable to time-resolved ATR-SEIRAS. Microsecond resolved spectra can be obtained with high spectral resolution and fractional monolayer detection limits in a total experimental duration that is two orders of magnitude less than the equivalent step-scan experiment.

Keywords

Dual frequency comb spectroscopy, time resolved spectroelectrochemistry, attenuated total reflectance surface enhanced infrared absorption spectroscopy (ATR-SEIRAS), 4-dimethylamino pyridine (DMAP), RC constant, detection limit, noise analysis.

Introduction

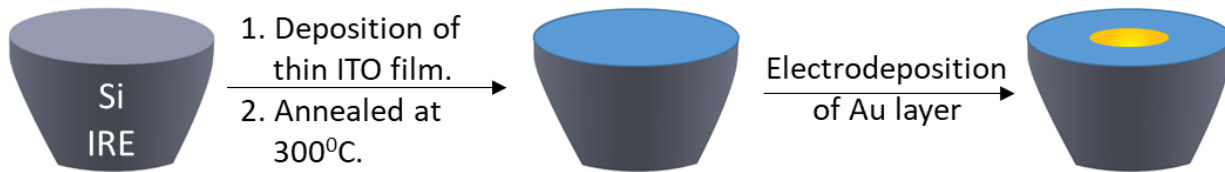
Time resolved infrared spectroelectrochemistry is a powerful tool for monitoring the kinetics of electrochemical processes and electrocatalytic reactions.¹⁻⁵ Conventionally, fast (sub millisecond) infrared spectroelectrochemistry (SEC) requires the use of step-scan spectroscopy, whereby the moving mirror in the interferometer is stopped at a given retardation position, δ , and the transient IR response of a time dependent chemical/physical process is measured. Data cubes of time resolved interferograms are constructed by repeating the process at different δ values.⁶⁻⁷ The co-addition of many data cubes (replicate measurements) is typically needed to improve the S/N to acceptable levels, such that, paradoxically, the total duration of a step-scan measurement is often very long. For example, a subset of these authors recently performed a step-scan experiment that needed more than 10^5 potential steps to measure the time resolved spectrum of the transient adsorption of a pyridine derivative. Additionally, the electrochemically triggered event must be robust enough to give a consistent response for a total number of transients defined by the product of the number of mirror positions and the number of co-added data blocks.

The advent of quantum cascade lasers and laser frequency combs has led to a paradigm change in time resolved IR spectroscopy.⁸⁻¹⁰ The heterodyned detection of two IR laser combs covering the same optical bandwidth but with different free spectral ranges yields a radio frequency interference signal.¹¹⁻¹² This GHz signal can be digitized using a fast data acquisition card and eventually Fourier transformed to provide interferograms with microsecond level resolution. This negates the need to construct an interferogram through successive mirror movements as is done in step-scan IR spectroscopy. Herein, we report the first demonstration of microsecond-resolved ATR-SEIRAS (attenuated total reflectance surface enhanced infrared spectroelectrochemistry)

using dual comb IR laser spectroscopy by measuring the potential-dependent desorption of a physisorbed pyridine derivative.

Experimental

The internal reflection element (IRE) was a 60° face angled Si crystal (PIKE technologies) with anti-reflection coatings on its two face angled surfaces. A 20 nm thick layer of indium tin oxide (ITO) was sputtered on the principal reflecting plane of the IRE and the modified crystal was then annealed under vacuum for 1 hour at 300 C° (see Scheme 1). The IRE was assembled in a JackfishSEC J1 cell (Jackfish SEC) and a gold island film was electrodeposited on the ITO from a solution of 0.25 mM KAuCl₄, 50 mM NaF and 0.1 mM 4-methoxypyridine.¹³ The SEC cell was disassembled, thoroughly washed and reassembled with fresh electrolyte (50 mM KClO₄) containing 0.1 mM 4-dimethylaminopyridine (DMAP) in D₂O. The geometric area of the working electrode in contact with the electrolyte was 0.32 cm². IR measurements were made on an IRis-F1 mid-IR dual comb spectrometer (IRSweep) with nominal 6 μm quantum cascade laser sources. The SEC cell was mounted on a VeeMAX III specular reflection accessory (PIKE) that had been modified to accept collimated laser light (Figure 1). The angle of incidence was 60°. An SRS EC301 potentiostat (Stanford Research Systems) was used to control the working electrode potential. A coiled Au wire served as the counter electrode and all potentials were measured *versus* a Ag/AgCl (saturated KCl) reference electrode. Post-acquisition data processing was performed using tools from the open source software project, Quasar [<https://doi.org/10.5281/zenodo.1188775>].



Scheme 1 : Preparation of a Si face-angled crystal internal reflection element (IRE) with a thin layer of indium tin oxide and subsequent modification through the electrodeposition of a gold nanoparticle film.

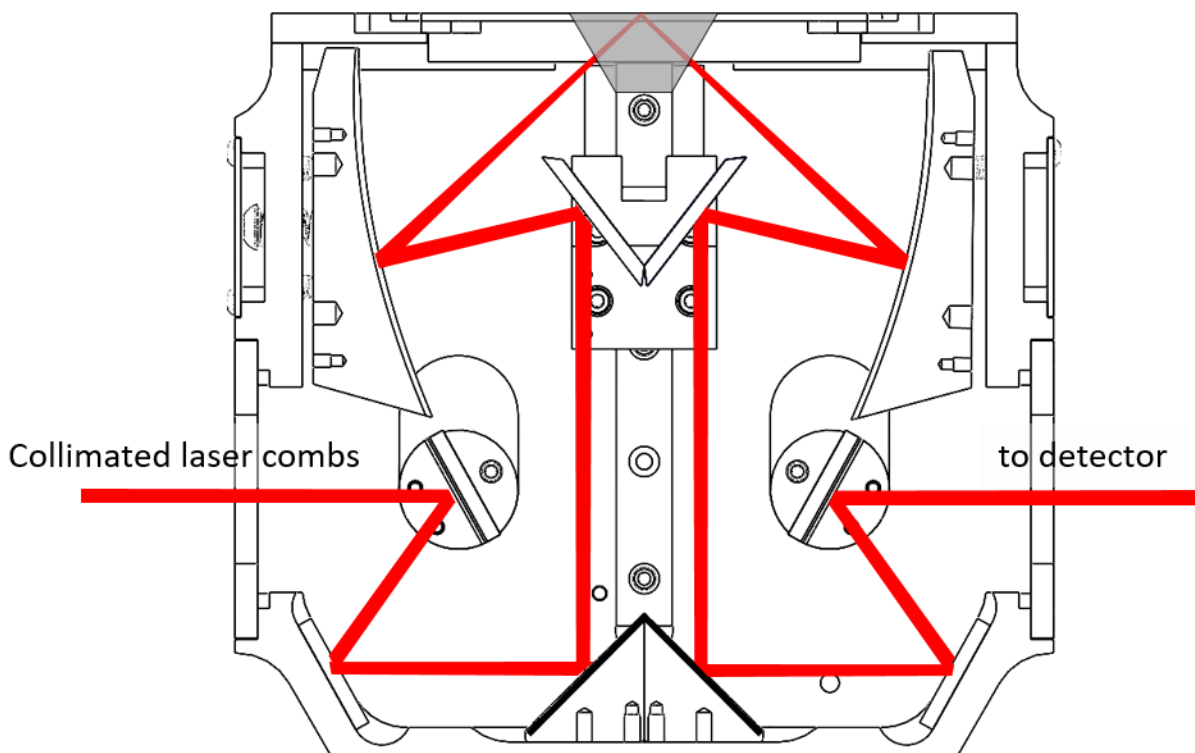


Figure 1 : Optical configuration for performing ATR-SEIRAS with a laser based source.

Results and Discussion

The minimum response time of an electrochemical interface is controlled by the RC or cell constant which is the product of the electrolyte resistance and the working electrode capacitance. External reflection based IR techniques, such as infrared reflection absorption spectroscopy (IRRAS), require the working electrode to be pushed very close to an IR transparent window. The presence of a highly-resistive, thin electrolyte layer makes IRRAS incompatible with sub-second resolved IR spectroelectrochemistry. In contrast, the Kretschmann configuration used in ATR-SEIRAS removes the need for the thin electrolyte layer¹⁴⁻¹⁵ and allows for time resolved SEC with millisecond resolution.¹⁶⁻¹⁷ In these experiments, the RC constant of the gold island film in the spectroelectrochemical cell containing 50 mM KClO₄ was determined from electrochemical impedance spectroscopy to be 10-20 ms.

The potential dependent adsorption of DMAP on gold surfaces has been previously studied with both electrochemical¹⁸⁻¹⁹ and spectroelectrochemical²⁰ techniques. Briefly, DMAP adsorbs on polycrystalline gold from neutral and basic solutions through the lone pair of electrons on the endocyclic nitrogen. This phase of adsorption is stable on the metal surface in the approximate potential range $-0.8 \text{ V} < E < 0.5 \text{ V}$.¹⁸ The pyridine derivative is totally desorbed by application of potentials more negative than -0.8 V. The broad-band ATR-SEIRAS spectrum of DMAP consists of several, strong absorbance peaks corresponding to A' ring modes,²⁰ the most prominent of which is centred at approximately 1628 cm^{-1} which conveniently lies within the approximately 100 cm^{-1} comb bandwidth. Measurements of DMAP desorption were made by initially biasing the working electrode at +0.30 V for 15 seconds to allow a complete monolayer to form and then stepping the potential to -0.90 V. The absorbance transient was measured for a total of 33 ms with the first 3 ms being recorded before the potential step and serving as a reference spectrum. The potential step

and IR data acquisition were repeated a total of 128 times. The resulting time-dependent spectra are dominated by the emergence of a single negative absorption band at 1628 cm^{-1} (Figure 2) which reaches a maximum magnitude of 7.5 mAbs by the end of the recorded transient and a final value of 11.1 mAbs after prolonged polarization at -0.90 V . Of additional note is the positive shift in the baseline, which has been noted in previous SEIRAS studies²¹ and has been observed to be more prominent when conductive metal oxide films are used as supports for metal island films.¹³

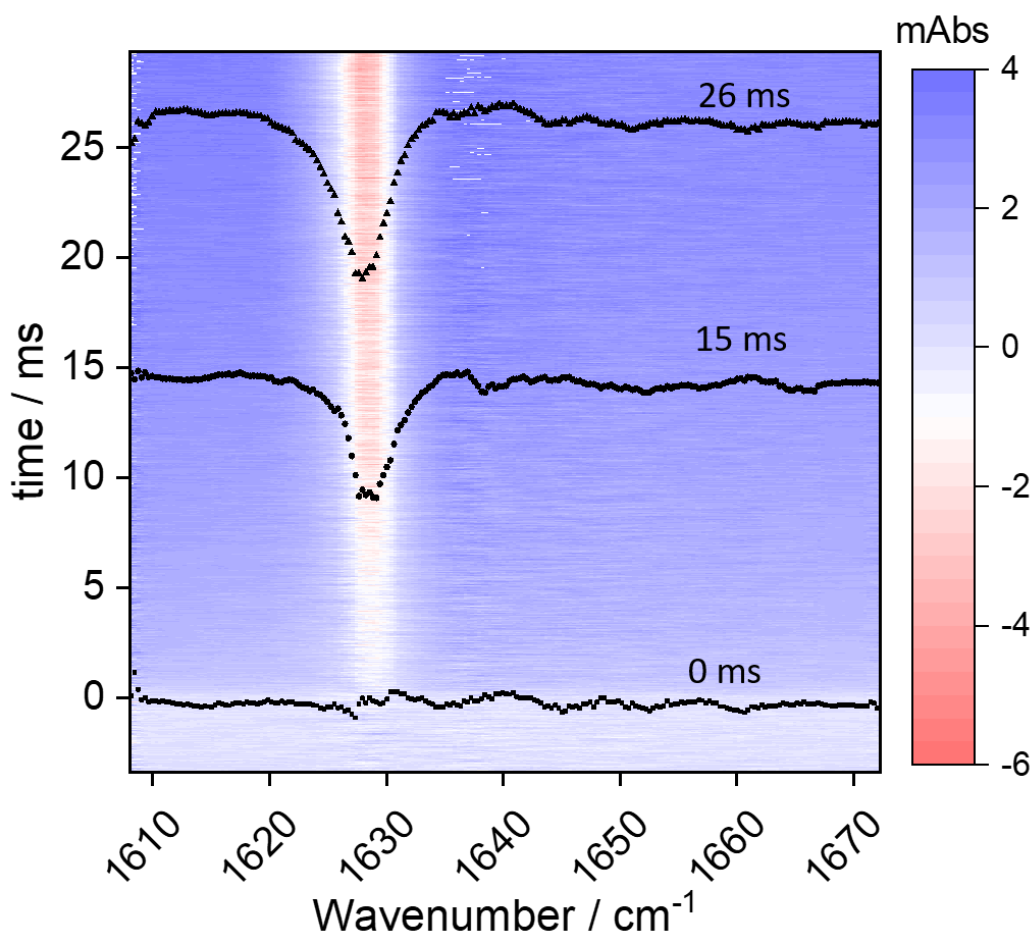


Figure 2 : Time resolved evolution of the ATR-SEIRAS absorbance change upon a potential jump from $+0.30\text{ V}$ to -0.90 V using the dual-comb IR spectrometer. Spectral processing conditions were 128 co-additions with $20\text{ }\mu\text{s}$ time binning. Spectral resolution was 3.3 cm^{-1} .

Figure 3 shows the transient evolution of the integrated 1628 cm^{-1} band with either 20 μs or 200 μs time binning. In both cases the time resolution greatly exceeds the time scale of the changes in the molecular absorption band and the apparent time required for desorption of the pyridine derivative is surprisingly large. Fitting the experimental transients to an empirical double exponential function (red line in Figure 3) yields time constants of 1.5 ms and 42 ms. Given the high solubility of DMAP in aqueous solutions, the expected time needed for the desorbed monolayer to diffuse from the electrode surface to a distance, x , where the electromagnetic enhancement is negligible (approximately 5 nm)²²⁻²³ can be estimated as $t = x^2/D \approx 1 \mu\text{s}$ for a

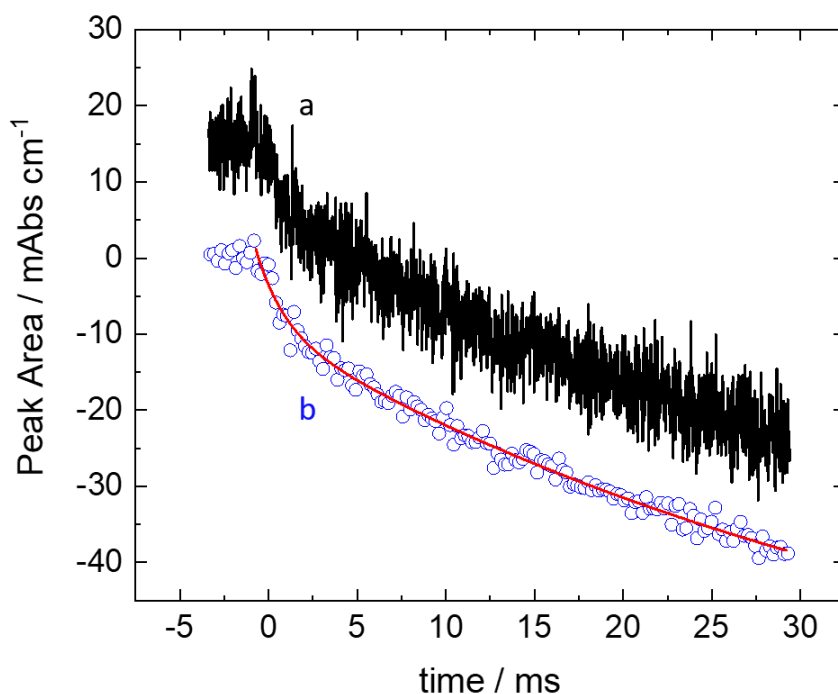


Figure 3: Integrated peak area for the A' ring mode of DMAP (peak frequency 1628 cm^{-1}) as a function of time using a) 20 μs and b) 200 μs time binning. The two curves are offset along the ordinate for clarity. Spectra are the result of 128 co-additions with 3.3 cm^{-1} spectral resolution. The red line is the result of a fit of the 20 μs resolved data to a double exponential decay.

diffusion coefficient of $10^{-6} \text{cm}^2 \text{s}^{-1}$. The results of more sophisticated treatments of the diffusion of a desorbed monolayer²⁴ gives comparable time scales. Thus, even the smaller of the two

experimentally observed time scales is roughly three orders of magnitude larger than expected. This is most likely a consequence of the RC constant of the spectroelectrochemical cell.

Although the relatively sluggish response of the spectroelectrochemical cell prevents a meaningful interpretation of the absorbance transient, the time resolved ATR-SEIRAS data provide extremely useful information for quantifying the limits of detection and the minimum time binning requirements of the dual frequency comb heterodyne detection method for future time resolved spectroelectrochemical experiments with cell constants in the microsecond regime. The noise level of the experiment can be quantified by analyzing the spectra collected prior to the potential step. Although the entirety of the first 3 ms of the transient measurement is averaged to make the reference spectrum, this data is actually composed of individual, $\sim 4 \mu\text{s}$ resolved, “single shot” spectra. A 0% absorbance line can be calculated by binning single-shot spectra over a range of Δt and dividing the result by the reference spectrum. The rms noise (in absorbance units) in the region of the DMAP peak (i.e. $1620 \text{ cm}^{-1} - 1635 \text{ cm}^{-1}$) was determined using this approach and quantified through Equation 1,

$$\text{Noise} = \sqrt{\frac{\sum_{i=1}^N \Delta_i}{N-1}} \quad \text{Equation 1}$$

where N is the number of spectral points in the region, and Δ_i is the square of the absorbance difference between successive points. The noise level is a function of both time-binning and the number of co-added repeat measurements (the equivalent of ensemble averaging).¹⁰ Figure 4a shows the Allan plot for four co-added measurements with variable time binning, Δt . The noise level is $\sim 2 \text{ mAbs}$ at $\Delta t = 4 \mu\text{s}$ and an order of magnitude lower for $\Delta t = 800 \mu\text{s}$. Increasing the number of co-added measurements to 128 provides an approximately five-fold systematic lowering in the noise level. Alternatively, the rms noise is plotted as a function of the number of

co-adds in Figure 4b for both $\Delta t = 4 \mu\text{s}$ and $\Delta t = 800 \mu\text{s}$. In all cases, the slopes of the lines in Figure 4 are $-0.5 \pm 10\%$ which indicates the noise is dominated by random noise and obeys the basic assumptions of Nyquist averaging.

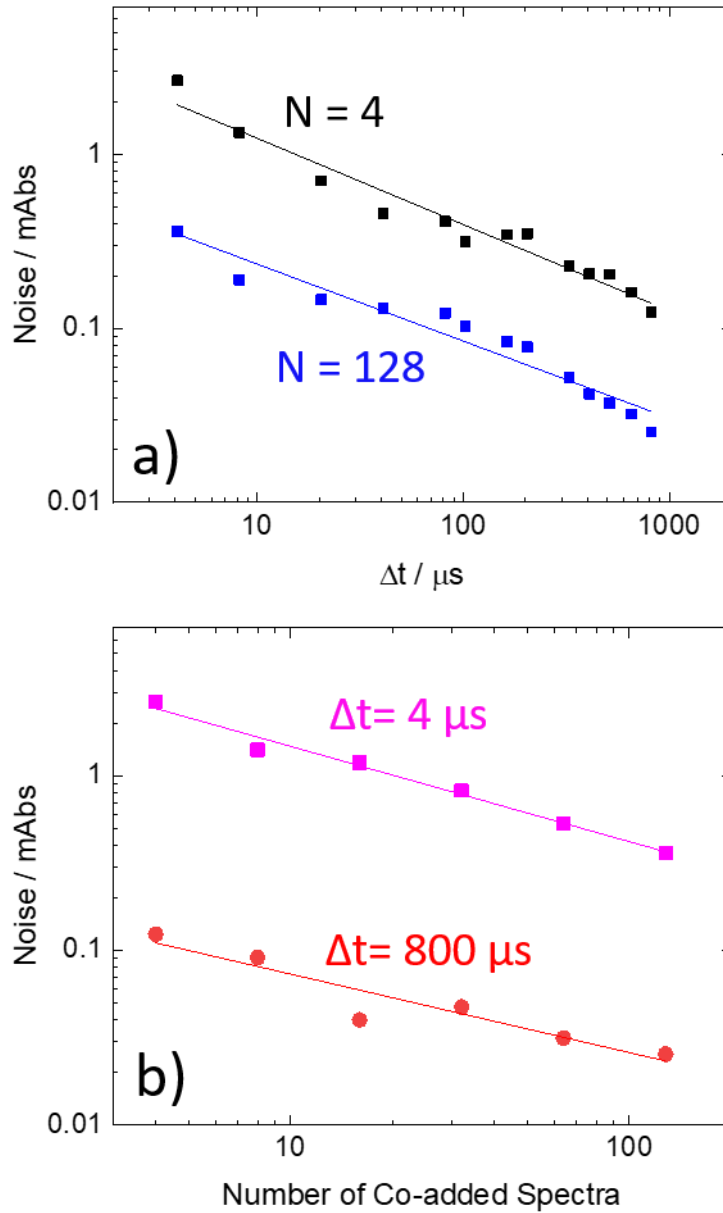


Figure 4 : Allan plots for noise analysis of the dual comb ATR-SEIRAS data as a function of a) the time binning interval and b) the number of co-added measurements. The number of co-added spectra, N , and the time binning intervals, Δt , for the respective plots are labelled accordingly.

The Allan plots allow the detection limit of a time-resolved ATR-SEIRAS measurement to be established. Defining the minimum detectable signal as three times the noise level of the measurement, a signal as low as 0.6 mAbs can be discerned from a time resolved experiment with ~ 10 μs time binning and 128 co-adds. As the maximum absorbance signal from the DMAP monolayer ($\Gamma_{\text{max}} = 7.4 \times 10^{-10}$ moles cm^{-2})¹⁸ is 11.1 mAbs, the limit of detection under these conditions is 5% of a monolayer which can be improved to 0.7% by increasing the time binning to 800 μs . For comparison, the noise from the same ATR-SEIRAS configuration was evaluated using a conventional IR source and spectrometer working in step-scan mode and found to be 0.5% of the DMAP monolayer signal after 128 co-additions and 1 ms time binning at 8 cm^{-1} resolution. Although the noise level is comparable to that of the dual comb spectrometer, the lower resolution step-scan experiment required more than two days of continuous total measurement time. For comparison the measurement of 128 co-added spectra using the dual comb spectrometer was completed in 32 minutes.

Conclusions

Dual frequency comb IR spectroscopy has been used for the first time to measure time-resolved electrochemical ATR-SEIRA spectra. In a proof of concept experiment, the desorption of a monolayer of a pyridine derivative was monitored with 10 μs time resolution and a detection limit of 5% of a monolayer. Relative to a step-scan IR experiment, the dual frequency comb ATR-SEIRAS measurement required 2 orders of magnitude less experiment time to provide comparable S/N and temporal resolution but with better spectral resolution. The applications of the method are potentially immense for the study of short lived adsorbed species during electrocatalysis. Of critical importance for future applications is the need to further reduce the spectroelectrochemical

cell constant. We are currently developing the means to perform analogous experiments on microband electrodes with RC constants in the microsecond regime.

Acknowledgements

The authors are grateful to Kaiyang Tu, Tyler Morhart, Ian Andvaag and Burke Barlow for their assistance. This work was funded by Discovery (RGPIN-2019-04032) and Research Tools and Instruments Grants from the Natural Science and Engineering Research Council (NSERC) of Canada. Research described in this paper was performed at the 01B1-1 (mid-IR) beamline at the Canadian Light Source (CLS). The CLS is a national research facility of the University of Saskatchewan, which is supported by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council (NSERC), the National Research Council (NRC), the Canadian Institutes of Health Research (CIHR), the Government of Saskatchewan, and the University of Saskatchewan.

Conflict of Interest

The authors report no conflicts of interest.

References

1. Zhou, Z.-Y.; Lin, S.-C.; Chen, S.-P.; Sun, S.-G., In situ step-scan time-resolved microscope FTIR spectroscopy working with a thin-layer cell. *Electrochem. Commun.* **2005**, *7*, 490-495.
2. Zhou, Z.-Y.; Sun, S.-G., In situ step-scan time-resolved microscope FTIR spectroscopy applied in irreversible electrochemical reactions. *Electrochim. Acta* **2005**, *50*, 5163-5171.
3. Jin, B.; Tao, F.; Liu, P., Rapid-scan time-resolved FT-IR spectroelectrochemistry - Study on the electron transfer of ferrocene-substituted thiophenes. *J. Electroanal. Chem.* **2008**, *624*, 179-185.
4. Jin, B.; Liu, P.; Wang, Y.; Zhang, Z.; Tian, Y.; Yang, J.; Zhang, S.; Cheng, F., Rapid-Scan Time-Resolved FT-IR Spectroelectrochemistry Studies on the Electrochemical Redox Process. *J. Phys. Chem. B* **2007**, *111*, 1517-1522.
5. Bellec, V.; De Backer, M. G.; Levillain, E.; Sauvage, F. X.; Sombret, B.; Wartelle, C., In situ time-resolved FTIR spectroelectrochemistry: study of the reduction of TCNQ. *Electrochem. Commun.* **2001**, *3* (9), 483-488.
6. Manning, C. J.; Palmer, R. A.; Chao, J. L., Step-scan Fourier-transform infrared spectrometer. *Rev. Sci. Instrum.* **1991**, *62*, 1219-1229.
7. Johnson, T. J.; Simon, A.; Weil, J. M.; Harris, G. W., Applications of Time-Resolved Step-Scan and Rapid-Scan FT-IR Spectroscopy: Dynamics from Ten Seconds to Ten Nanoseconds. *Appl. Spectrosc.* **1993**, *47*, 1376-1381.
8. Chen, Z.; Hänsch, T. W.; Picqué, N., Mid-infrared feed-forward dual-comb spectroscopy. *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 3454-3459.
9. Schnee, J.; Bazin, P.; Barviau, B.; Grisch, F.; Beccard, B. J.; Daturi, M., Coupling a Rapid-Scan FT-IR Spectrometer with Quantum Cascade Lasers within a Single Setup: An Easy Way to Reach Microsecond Time Resolution without Losing Spectral Information. *Anal. Chem.* **2019**, *91*, 4368-4373.
10. Klocke, J. L.; Mangold, M.; Allmendinger, P.; Hugi, A.; Geiser, M.; Jouy, P.; Faist, J.; Kottke, T., Single-Shot Sub-microsecond Mid-infrared Spectroscopy on Protein Reactions with Quantum Cascade Laser Frequency Combs. *Anal. Chem.* **2018**, *90*, 10494-10500.
11. Villares, G.; Hugi, A.; Blaser, S.; Faist, J., Dual-comb spectroscopy based on quantum-cascade-laser frequency combs. *Nat. Commun.* **2014**, *5*, 5192.
12. Wang, Y.; Soskind, M. G.; Wang, W.; Wysocki, G., High-resolution multi-heterodyne spectroscopy based on Fabry-Perot quantum cascade lasers. *Appl. Phys. Lett.* **2014**, *104*, 031114.
13. Andvaag, I. R.; Morhart, T. A.; Clarke, O. J. R.; Burgess, I. J., Hybrid Gold-Conductive Metal Oxide Films for Attenuated Total Reflectance Surface Enhanced Infrared Absorption Spectroscopy. *ACS Appl. Nano Mater.* **2019**, *2*, 1274-1284.
14. Osawa, M., Surface-enhanced infrared absorption. *Top. Appl. Phys.* **2001**, *81*, 163-187.
15. Osawa, M., Surface-Enhanced Infrared Absorption Spectroscopy. In *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Ltd: 2006.
16. Ataka, K.; Nishina, G.; Cai, W.-B.; Sun, S.-G.; Osawa, M., Dynamics of the dissolution of an underpotentially deposited Cu layer on Au(111): a combined time-resolved surface-enhanced infrared and chronoamperometric study. *Electrochem. Commun.* **2000**, *2*, 417-421.
17. Noda, H.; Wan, L.-J.; Osawa, M., Dynamics of adsorption and phase formation of p-nitrobenzoic acid at Au(111) surface in solution. A combined surface-enhanced infrared and STM study. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3336-3342.

18. Barlow, B. C.; Burgess, I. J., Electrochemical Evaluation of 4-(Dimethylamino)pyridine Adsorption on Polycrystalline Gold. *Langmuir* **2007**, *23*, 1555-1563.
19. Vivek, J. P.; Burgess, I. J., Crystallographic dependence of 4-dimethylaminopyridine electrosorption on gold. *Electrochim. Acta* **2013**, *88*, 688-696.
20. Rosendahl, S. M.; Danger, B. R.; Vivek, J. P.; Burgess, I. J., Surface Enhanced Infrared Absorption Spectroscopy Studies of DMAP Adsorption on Gold Surfaces. *Langmuir* **2009**, *25*, 2241-2247.
21. Priebe, A.; Sinther, M.; Fahsold, G.; Pucci, A., The correlation between film thickness and adsorbate line shape in surface enhanced infrared absorption. *J. Chem. Phys.* **2003**, *119*, 4887-4890.
22. Wokaun, A., Surface-Enhanced Electromagnetic Processes. In *Solid State Physics*, Ehrenreich, H.; Turnbull, D.; Seitz, F., Eds. Academic Press: 1984; Vol. 38, pp 223-294.
23. Osawa, M.; Ikeda, M., Surface-enhanced infrared absorption of p-nitrobenzoic acid deposited on silver island films: contributions of electromagnetic and chemical mechanisms. *J. Phys. Chem.* **1991**, *95*, 9914-9919.
24. Pesika, N. S.; Stebe, K. J.; Searson, P. C., Kinetics of Desorption of Alkanethiolates on Gold. *Langmuir* **2006**, *22*, 3474-3476.

For Table of Contents Only

