

Attenuated total reflection mid-IR-spectroscopy for electrochemical applications using a QCL

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Abstract: A setup is presented for ATR-IR spectroscopy based on a pulsed tunable external-cavity QCL. The electronic detection system integrates the detector signal during laser emission. Repeatable measurements of absorption spectra have been achieved.

OCIS codes: (300.6360) Spectroscopy, laser; (300.6340) Spectroscopy, infrared; (240.6490) Spectroscopy, surface

Introduction

After demonstration of the first QCL [1], further development and consistent improvement effected that QCLs became a suitable light source for spectroscopic experiments. High power output, room temperature operation, and tuneability make QCLs well-suited for various applications. In addition to high resolution spectroscopy, stand-off detection of explosives, and non-linear spectroscopy, QCL devices are widely used for time-resolved spectroscopy [2-4]. The in situ characterization of reactions is indispensable for verifying suggested reaction mechanisms. Recent publications report about the detection of short-lived species down to a picosecond or even femtosecond timescale, depending on the experimental setup and progress [5]. Most of these works use transmission geometries. In a reflection geometry, the challenge is to detect small changes near a surface. To facilitate detection, multiple reflection setups with thin ATR crystals can be used [6]. Using this principle in classical Fourier transform (FT) IR spectroscopy, small amounts of functional groups on colloidal particles can be detected [7]. The use of QCLs offers additional advantages over FT-IR spectrometers, as due to the highly collimated beam, the loss when coupling the light into the thin crystals is low, resulting in a high light intensity at the detector.

Frequently the application of QCL in IR spectroscopy uses lock-in amplifier to acquire detector output and in turn verification with oscilloscopes [5,8]. However, lock-in amplifiers are not well suited for low duty cycles and oscilloscopes need long processing time. Therefore, in such setups the digitized detector output present only spot tests of all detected pulses. Furthermore most oscilloscopes are equipped with 8-bit ADC which causes high quantization noise. The measurement setup presented here enables the recording of all single emitted laser pulses and the output of averaged signals without delay caused in signal processing and converting. The setup is based on a low-priced and slowly working analog digital converter (ADC) which results in low noise IR spectra with high resolution, and good reproducibility.

Experimental setup

In this setup we present the application of an EC-QCL in ATR-IR spectroscopy for the detection of intermediates in electrochemical reactions on semiconductor surfaces. The general setup is schematically illustrated in figure 1.

The EC-QCL (Model 11090-UT, Daylight Solutions, Inc.), exhibits a tunable wavenumber between 1010 cm^{-1} and 1235 cm^{-1} with a total resolution of 0.5 cm^{-1} . The pulse rate can be selected from 100 Hz to 100 kHz while pulse width has a tuning range from 40 ns to 500 ns. For these measurements the duty cycle was set to 5% at a 500 ns pulse width. The deployed TE-cooled photoconductive MCT detector (Daylight Solutions, Inc.) has a response time below 3 ns. A self-made spectroelectrochemical cell made of PTFE is used in which the bottom side consists of a semiconductor (usually germanium) crystal (52 mm x 20 mm x 0.5 mm, prism angle: 30° , angle of incidence 60°) that is well connected to a copper base and used as working electrode. The laser radiation is directed into the semiconductor crystal, where it undergoes multiple internal reflection. Afterwards the radiation which passed through the crystal is directed to the detector. For electrochemical studies, a platinum electrode is used as counter electrode and Ag/AgCl/KCl (3 M) electrode is used for reference.

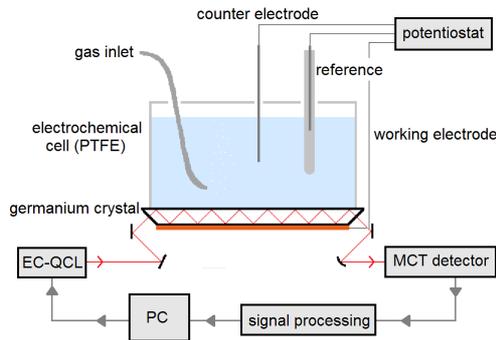


Fig. 1. Experimental setup.

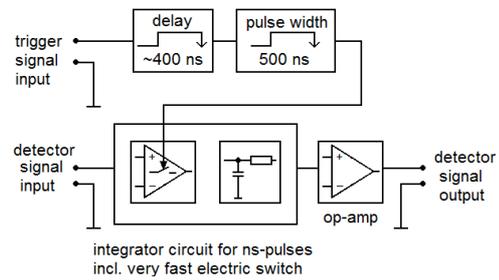


Fig. 2. Schematic circuit of the integration device for ns-pulses.

The main idea for this type of measurement device was to use a pulsed QCL for scanning successively all wavelengths of the selected range and record a high number of pulses for each wavelength to get reduced noise and well averaged data. Measurement control is based on an electric circuit which affords the integration of the signals of detected pulses. As the integration over the total period leads to an decreasing integrated signal, an electric circuit was developed that collects only the information of the detected laser pulses (pulse width 500 ns) during the active state and stops transferring data during the inactive state when no laser light is emitted. This device requires an electric circuit with a very fast electric switch (response time on nanosecond timescale) which controls the collection of data. The use of the very fast and amplifier together with a sample-and-hold circuit (OPA615) from Texas Instruments leads to realization of an integration device for ns-pulses schematically depicted in figure 2. The hold command delay time of the attached switch amounts to 2.5 ns, while the used operational amplifiers have a band width up to 710 MHz. The next step was to trigger the switch, which should close the circuit when a detected laser pulse arrives and operate signal integration whereas it should open again after the pulse is over. To trigger this fast switch using the trigger signal of the laser directly was not possible because of a high delay time to the detected pulse of nearly 400 ns. For compensation of this delay, two dual monostable multivibrators were used, with resets connected in series. The internal RC-circuit of the first multivibrator is set to the delay time to trigger the second monostable multivibrator, while the RC-circuit in the second multivibrator is set to the laser pulse width (500 ns) to trigger the electric switch. Propagation delay is also adjusted by fine-tuning of these RC-circuits. With this circuit the detected laser signals of the MCT detector directed to the OPA615 are transported to the subsequent capacitor and collected in there while the switch is closed. After integration of these collected signals their averaging results in a smoothing of the peakshape. Finally the processed signals are output after amplification to the ADC. For the recording of data, an in-house written Agilent VEE program is used. At each wavelength, the averaged intensity of 20000 pulses was found to yield satisfactory results. Therefore, a measurement time of 0.2 s per wavelength is sufficient. Between two wavelengths, a delay of 1.5 s ensured a stable laser operation at the new wavelength.

Results

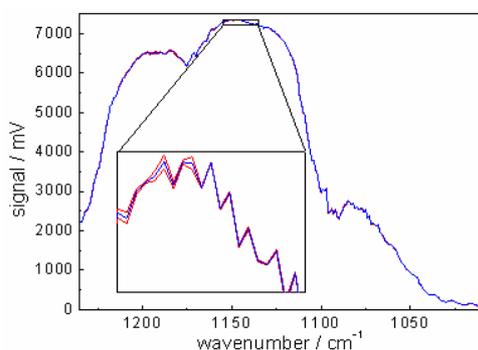
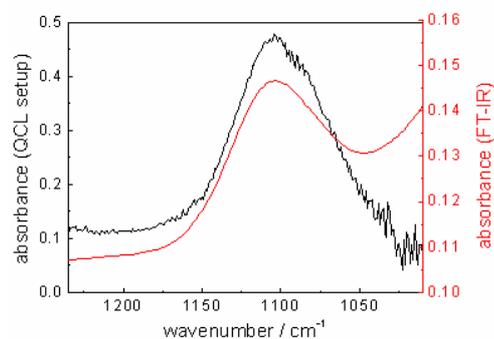


Fig. 3: Spectrum (blue) with standard deviation (red).

Fig. 4: Absorbance spectrum of NaClO₄ solution measured in the setup introduced here (black, left) and measured with an FT-IR (red, right).

As initial result, figure 3 shows a plot of the average spectrum in the total wavenumber range in steps of 1 cm^{-1} . To test the repeatability of the output IR spectrum, 6 spectra were recorded consecutively, averaged to yield the graph in figure 3, and a standard deviation was computed, which is shown as the red lines around the spectrum in figure 3. Average standard deviation was 0.3 %.

The absorption spectrum of a 1 mol/L NaClO_4 solution in contact with a germanium (100) crystal is shown in figure 4. For comparison, an FT-IR spectrum from the same spectral range of a NaClO_4 solution of 0.1 mol/L is also shown in figure 4. The comparison shows that especially the spectral repeatability of the pulses is sufficient for the width of the absorption bands encountered in liquid phase.

A comparison of cyclic voltammograms measured in the same setup as used to record infrared spectra in argon and oxygen atmosphere in 0.1 mol/L NaClO_4 is shown in figure 5. The strong increase in cathodic current with increasing cathodic potentials in oxygen atmosphere are attributed to the onset of oxygen reduction. Concurrent stationary experiments using FT-IR spectroscopy show the presence of absorption bands of oxygen-related species. Especially the kinetics of the evolution of these species should be investigated using the QCL-based setup, which at one particular wavelength can measure considerably faster with good signal/noise ratio compared to FT-IR systems.

The results show that the setup which was realized is promising for detailed kinetic studies of electrochemical reactions.

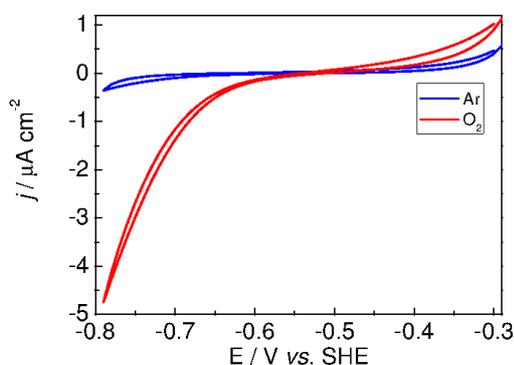


Fig. 5: Cyclic voltammogram of germanium(100) in NaClO_4 solution purged with argon and oxygen.

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