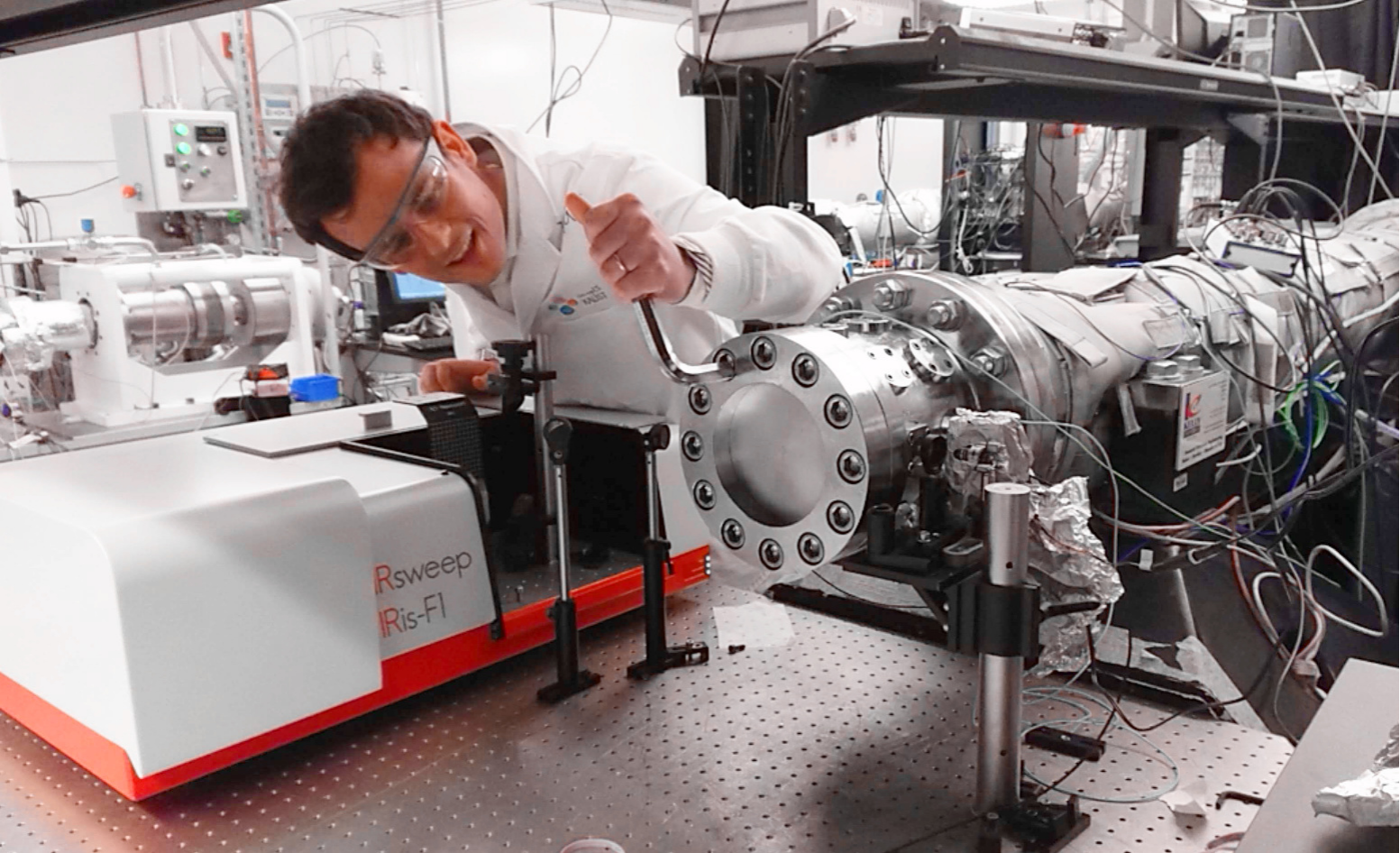


IRsweep

It's all about time

*Providing the next generation of
mid-IR dual-comb spectrometers*



IRis-F1 at Aamir Farooq's Chemical Kinetics and Laser Sensors Laboratory (KAUST, Saudi Arabia)

IRsweep brings high-performance mid-IR sensing to field applications

IRsweep's vision is to revolutionize optical sensing by introducing an ultrafast laser spectrometer in the mid-infrared: the IRis-F1.

Our goal is to provide solutions allowing specialists in research and industry to be faster and more precise in their mid-IR absorption spectroscopy measurements.

The IRis-F1 spectrometer is the backbone of IRsweep's commercial activities, and represents the technological basis for further integration into process analytics and possibly portable applications.

The IRis-F1 is based on quantum cascade laser frequency combs invented by IRsweep's co-founders in 2012 at ETH Zurich.



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IRsweep 2020

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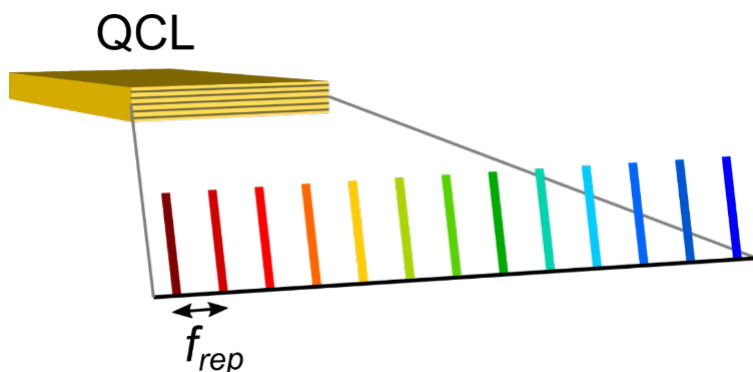
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Technology

Frequency combs

IRsweep employs frequency comb laser sources. These are broadband lasers that emit not at one but at many discrete wavelengths, making them distinct from both classical single-line as well as supercontinuum sources.

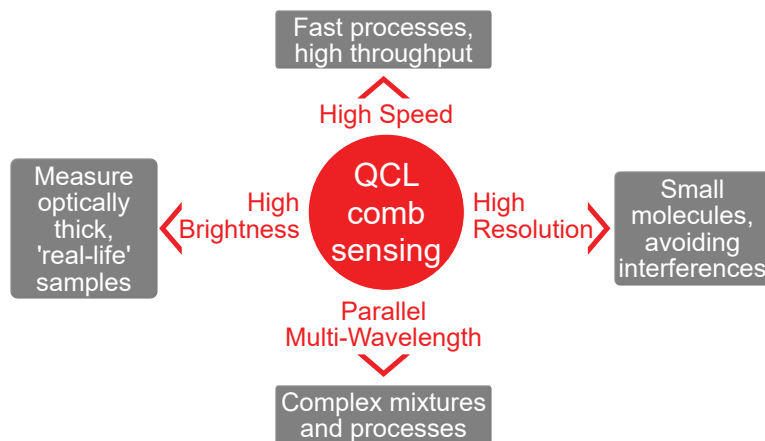


Such a source is depicted in the schematic. Importantly, the line-spacing (or f_{rep}) of frequency combs is extremely well defined, and this is one of the properties that makes them useful for spectroscopy.

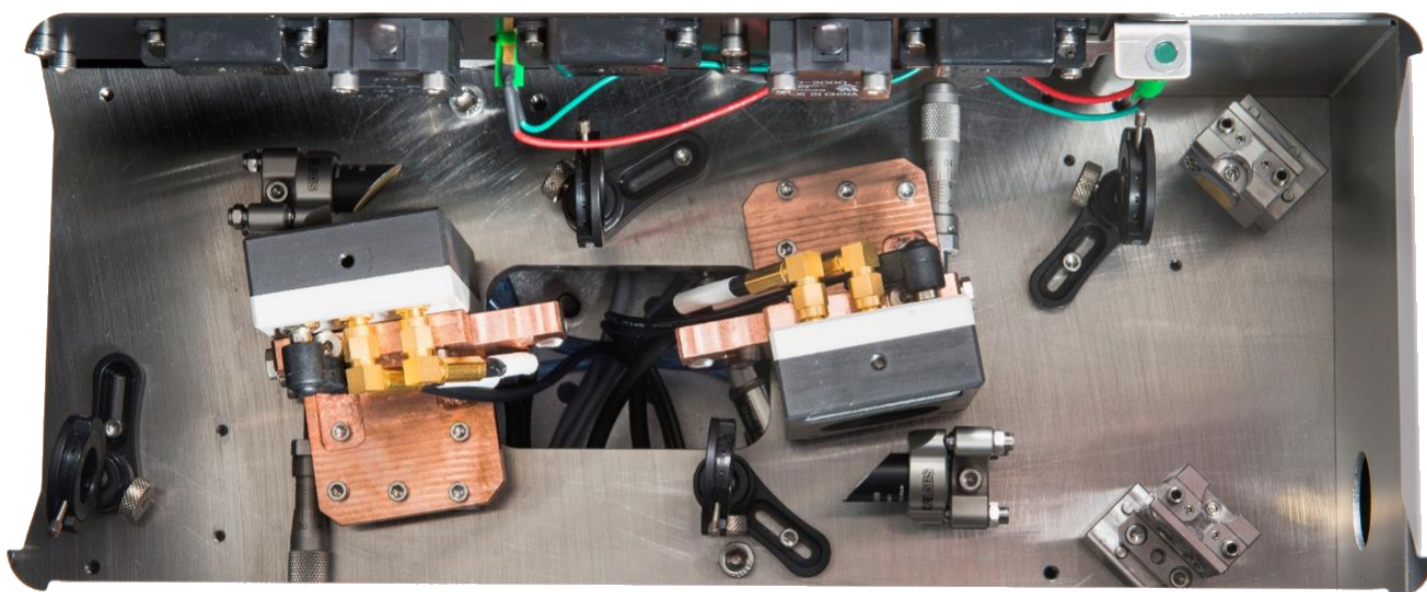
The frequency comb sources used in our spectrometers are based on quantum cascade lasers (QCLs).

These are electrically-pumped semiconductor devices, which are robust and straightforward to use by our end-users.

As co-discovered by one of IRsweep's founders, it is the engineering of the devices that allow them to behave as frequency combs. Their output powers can be many hundreds of milliwatts and the exact spectral profile and f_{rep} of each laser can be carefully controlled by changing the current and device temperature.



The QCLs in the IRis-F1 come pre-aligned and pre-set, requiring little to no maintenance.

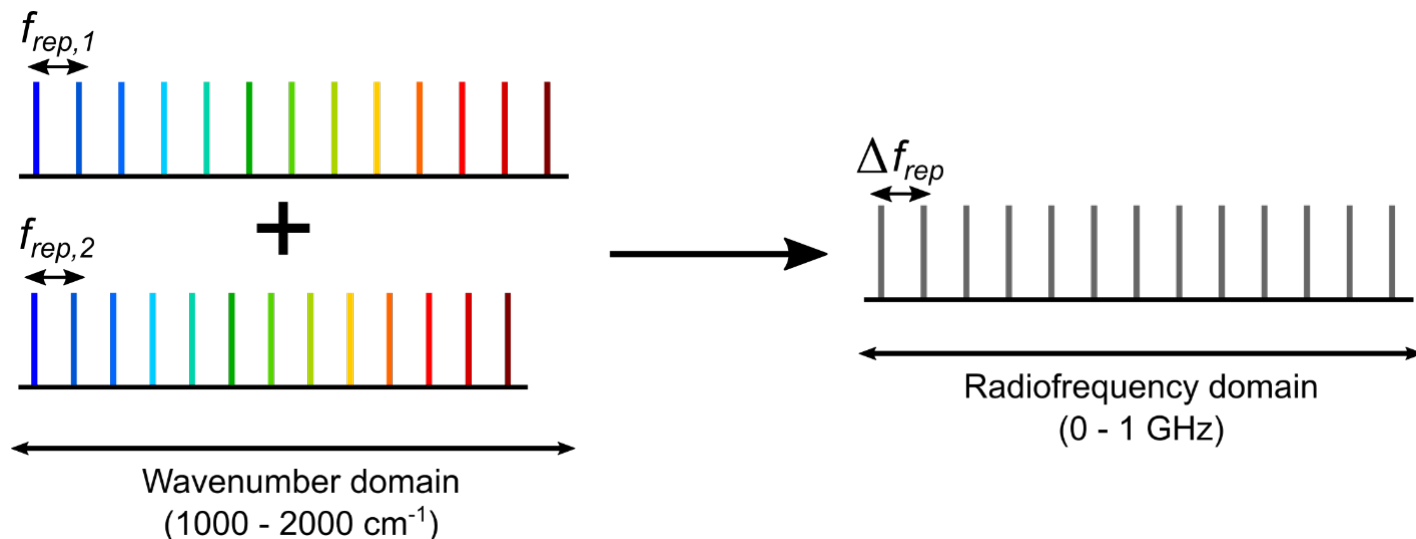


The IRis-F1 is equipped with two high sensitive, fast TE-MCT (thermoelectrically cooled mercury-cadmium-telluride) detectors, making the use of LN_2 obsolete.

Heterodyne detection

Two frequency comb lasers are used for spectroscopy. As shown in the schematic below, their line-spacings (in this case $f_{rep,1}$ and $f_{rep,2}$) are chosen to be similar but not the same. When overlaid on a detector, this produces a heterodyne beating, equivalent to the difference of the two spacings:

$$\Delta f_{rep} = f_{rep,1} - f_{rep,2}$$



Pairs of comb teeth generate beating signals that are separated by Δf_{rep} . We detect these signals by choosing $f_{rep,1}$ and $f_{rep,2}$ in such a way that Δf_{rep} is on the order of 1 to 5 MHz; therefore, the entire heterodyne beating pattern can be recovered from a high-bandwidth detector. Crucially, this detection method requires no scanning, and the entire spectrum is recorded in a time-frame of $1/\Delta f_{rep}$ (ca. 1 μ s).

Improved measurements compared to FTIR

Aside from being completely solid-state, there are many other advantages dual-comb spectroscopy has to offer over other approaches.

Speed

Making good use of being a solid-state device, the IRis-F1 measures at 4 μ s per spectrum, with the potential to go to 1 μ s with manual post-processing.

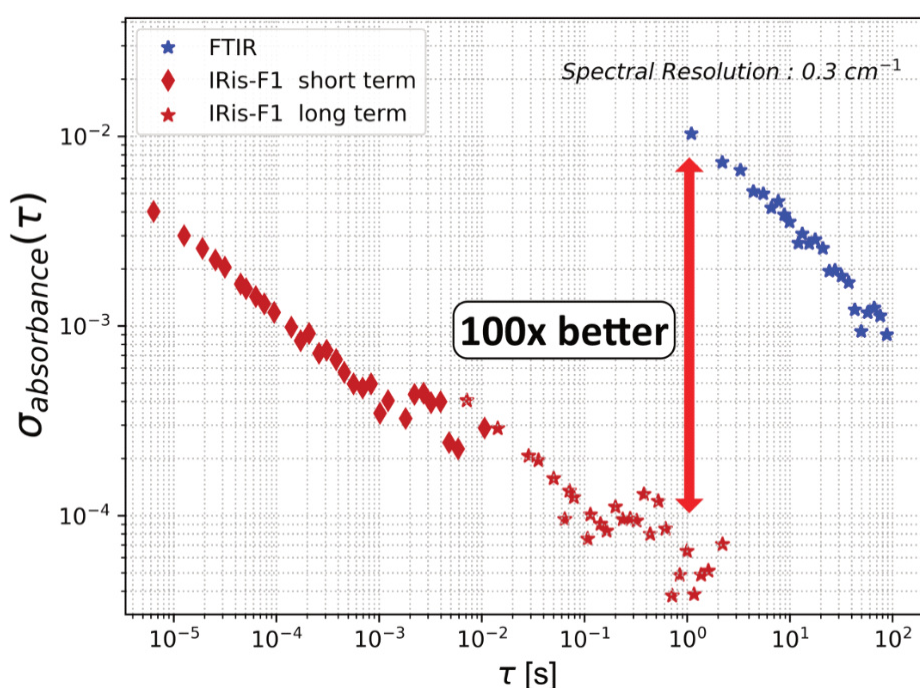
Importantly, in a single measurement block (up to ca. 130 ms) the measurement-to-measurement dead time is zero. This means that, in the case of a 130 ms measurement, more than 33,000 spectra are recorded sequentially in this time frame.

It is possible to carry out rapidly repeating measurements, with shorter measurement blocks, compared to access timescales of sub-seconds to minutes. This allows repetition rates of 220 spectra per second to be achieved with good signal-to-noise ratios in the application on the monitoring of rapid curing reactions.

Brightness

Frequency comb QCLs are laser sources and are well suited to photon-hungry applications. For example, measurements of optically dense samples become possible. Importantly, many time-resolved applications are photon-limited and in this case a higher brightness means higher signal to noise ratios. See below for a graph that shows how noise levels of a single spectral element of the IRis-F1 compares to a leading FTIR instrument. Even though a high-sensitivity liquid nitrogen cooled detector is used in the FTIR, the laser source enables far lower deviations in signal to be reached.

IRis-F1 vs FTIR noise comparison



*100x better SNR
compared to FTIR at
 0.3 cm^{-1} resolution*

Bandwidth

Compared to single-mode laser systems and distributed feedback QCLs, the IRis-F1 is relatively broadband, with a spectral bandwidth of $>60 \text{ cm}^{-1}$. This enables the simultaneous observation of several species, the accurate correction of baseline artifacts and gives more data for fitting, turning many questions in chemistry into overdefined problems. The spectrometer's spectral coverage can be readily changed by swapping the laser module.

Rapid full-spectrum acquisition

Since the whole spectrum is recorded in microseconds, any environmental changes in the sample can be observed, monitored and used to improve the analysis.

For instance, sample degradation can be evaluated with every shot, changes in the baseline can be tracked, there is no spectral hysteresis, and drifts due to heating are not simply averaged out and do not distort the overall spectra as is the case with step-scan FTIR measurements.

Products: IRis-F1

Dual-comb spectrometer

Want to speed up your spectroscopic measurements?



Does Fourier-Transform Infrared (FTIR) spectroscopy limit your measurement capabilities in terms of speed, signal-to-noise ratio or spectral resolution?

The IRis-F1 spectrometer overcomes these limitations and offers an unmatched combination of speed, brightness and resolution. A complete spectrum can be acquired in one microsecond, and the high brightness laser source enables high signal-to-noise ratios >1000 in $100 \mu\text{s}$ measurement time. These parameters are achieved with a default spectral resolution of 0.25 cm^{-1} to 0.5 cm^{-1} .

Spectral and temporal resolution are recorded simultaneously, avoiding massive experiment repetition as sometimes required in step-scan FTIR. A high-resolution version, offering $<0.001 \text{ cm}^{-1}$ spectral resolution, is also available.

The dual-comb light sources are packed into laser modules which are user exchangeable without tools and with minimum realignment. Modules are available with different center wavenumbers throughout the mid-IR and typically cover $>60 \text{ cm}^{-1}$.

The sample compartment is large and versatile, allowing coupling of most existing accessories such as ATR units, transmission cells and reflection setups. The beam can also be extracted to couple to external experiments.

The IRis-F1 is based on quantum cascade laser frequency combs, which are broadband mode-locked mid-IR lasers. Spectral resolution is generated by the dual-comb technique, where one comb acts as a dispersive element for the other. The resulting interferogram is typically recorded in less than a microsecond.



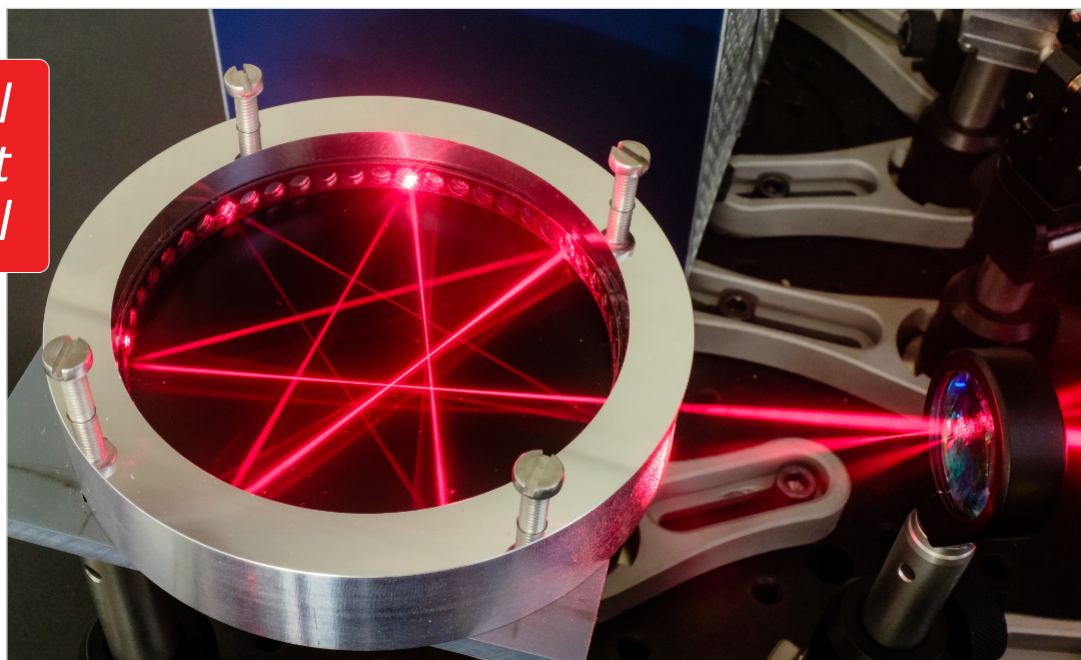
Easy laser module exchange, done within a few seconds, allows you to cover several bandwidths with $>60 \text{ cm}^{-1}$ spectral coverage.

Products: IRcell-S

Multipass cell without absorption mask

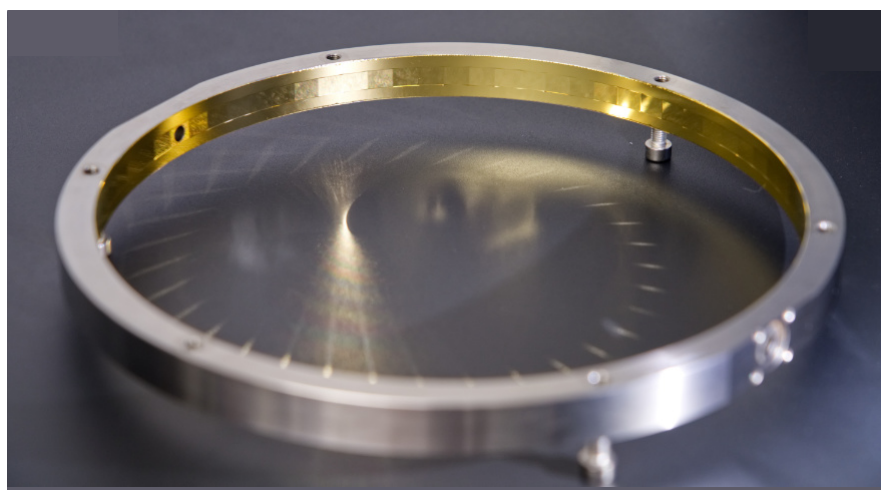
The IRcell-S - small volume, robust multipass cell

Multipass cells are used to fold a long optical path into a small volume to increase the sensitivity of an optical measurement. Such cells are regularly used for gas phase spectroscopy of trace species in several applications, e.g. environmental air quality or breath analysis.



A key parameter of multipass cells is the ratio of path length to volume, because smaller volumes result in shorter system response times and lower sample consumption. The IRcell-S has a particularly low volume due to its planar star-shaped beam pattern and outperforms most White- and Herriott-based designs in terms of path length per volume.

The IRcell-S has a substantially improved optical design compared to IRsweep's previous IRcell: the rotationally symmetric ring mirror is replaced with a series of individually curved mirror segments, yielding a more stable beam pattern. As a result, the alignment is substantially simplified, no absorption mask is required, no teflon is exposed to the inside of the cell and there is more freedom on the coupling angle.



The IRcell-S features a sample volume of only 31 ml at a 4 meters path length

The beam profile of the transmitted beam is also improved compared to the previous IRcell. The IRcell-S additionally offers two separate ports for coupling light in and out, which simplifies placement of optical components.

The cell comes with three gas ports by default, which are typically used as inlet, outlet and pressure sensor. It has also been used without top and bottom to directly measure a flow through the ring, e.g. as part of a tube.

Products: IRis-core

Turnkey mid-IR dual-comb source

The advantages of dual-comb spectroscopy, now also in your application

Dual-comb spectroscopy is increasingly employed in stand-off detection, open path detection and other applications due to its merits in speed, suppression of background radiation and high optical powers.

The IRis-core is an ideal basis for the setup of such a system in the mid-IR range: it offers two overlapping free-running QCL-based frequency comb lasers in a single system. The system outputs already co-aligned beams and comes with a set of drive instructions with factory-characterized heterodyning conditions. The system comes complete with drive electronics and a control computer with a graphical user interface.



IRis-core, with one of the compatible laser modules

The IRis-core is a receiving bay and driving and control electronics for IRsweep laser modules. In this modular approach, it is possible to exchange the dual-comb laser modules to switch laser wavelength.

The laser modules are compatible with the laser modules of IRsweep's IRis-F1 dual-comb spectrometer and ensure maximum flexibility in future applications. Suitable detection systems with data-processing capabilities that are integrated can also be provided with the system.

Optional Detection System

The IRis-detect is an optional detection system that is available for the IRis-core. It consists of two high bandwidth thermoelectrically cooled MCT detectors for sample and reference channel along with a fast sampling system to collect, process and store the multi-heterodyne data. Data can be processed and represented as transmission or absorption by the system and triggering and typical measurement schemes are readily available. Examples are short time-resolved acquisitions covering time ranges from microseconds to tens of milliseconds and time-averaged data that can be acquired over longer time scales.

Processing is done live on the detection system, which is a requirement to achieve long measurements beyond tens of milliseconds, due to very large raw data rates. Data processing includes a proprietary coherent averaging algorithm optimized to reduce systematic errors, including QCL specific drift correction and comb state analysis. The final data is stored in the open HDF5 format. The detection system is controlled through a graphical user interface allowing live inspection of the data in time and frequency domain. The graphical user interface can also control the IRis-core dual-comb emitter system.

Applications

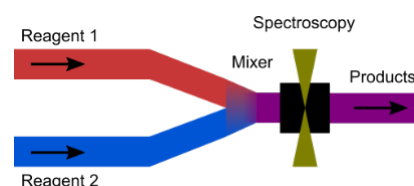
Stopped Flow Technique

Understanding the mechanism of a chemical reaction is an important step away from trial-and-error-based reaction optimization. By studying the structures of intermediates, for how long they exist, and the ways in which they can and cannot react, reactions can be intelligently designed, controlled and where required, optimized.

This application explores the use of the IRis-F1 spectrometer in IR stopped-flow experiments. Firstly, we investigate the hydrolysis of methyl chloroacetate (MCA) and this will be followed by the refolding of ubiquitin, which is expected to be a more challenging measurement.

Stopped-Flow

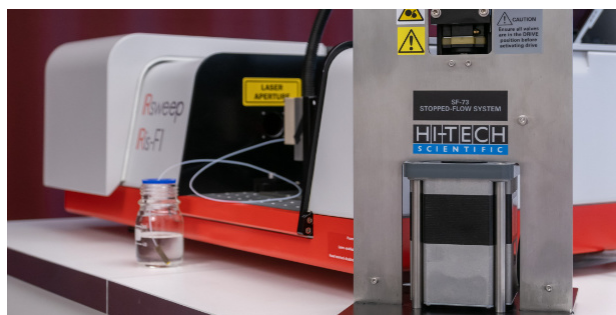
Stopped-flow is a powerful technique to study reactions on a millisecond to minute timescale. Simply speaking, it works by rapidly mixing reagents before a spectroscopic cell, as depicted in the figure.



When the flow is stopped, the chemical reaction initiated by mixing can be analyzed using a variety of techniques. IR spectroscopy is powerful in this regard because it is sensitive to chemical and structural changes of the analytes.

Experimental Setup

For this set of experiments, we partnered with TgK Scientific, a leader in stopped-flow IR equipment. The syringe drive unit of the SF-73 stopped-flow system is shown in the picture below. It connects via an umbilical to a spectroscopic cell with CaF_2 windows and a path-length of 100 μm .

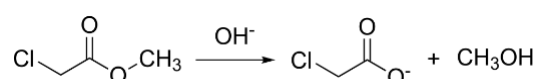


For the MCA experiment, a background was acquired of the pure solvent and for the ubiquitin experiment a background was acquired of the already reacted mixture. This was necessary to subtract the signal from the changing solvent environment.

The IRis-F1 was triggered from the SF-73 through a TTL signal sent through a BNC connection and user control happened through KinetaDrive. This way, shots are synchronized to data collection providing a consistent reference to time zero and the convenience and reassurance of not missing data. Typically, spectra are integrated for 0.5 ms and acquired every 4.5 ms.

Hydrolysis of methylchloroacetate

The scheme for the hydrolysis of MCA is shown below.

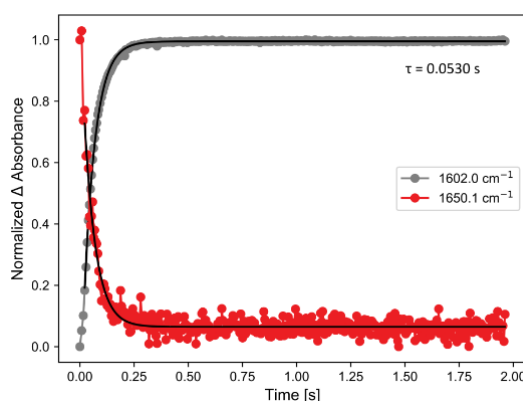
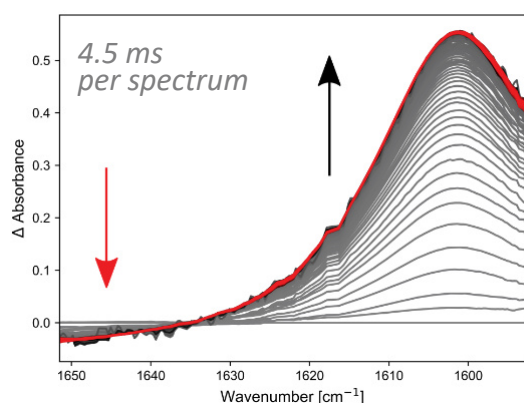


This reaction is often carried out as a test for stopped flow systems and typically hydroxide concentrations of 0.1 M or less are used. Here, we used a concentration of KOH of 0.5 M to speed up the reaction (in D_2O).

The results of a single shot of the hydrolysis reaction are shown in the figures. The spectra (next page, top left) show the disappearance of a weak MCA band around 1650 cm^{-1} and the appearance of a new band belonging to the formed acetate salt at 1602 cm^{-1} . Excellent signal to noise (S/N) ratios are seen throughout the spectra and despite the low intensity of the MCA band, it can be fitted well with a mono-exponential decay. A lifetime of 53 ms is found for this process at room temperature.

Applications

Stopped Flow Technique

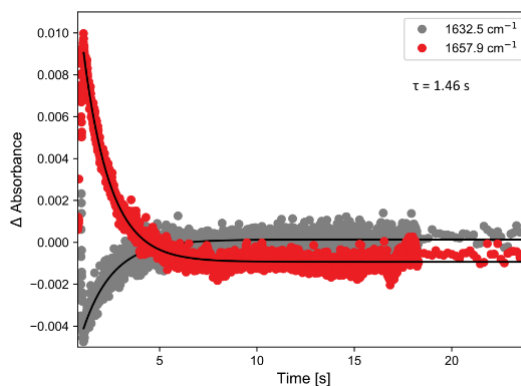
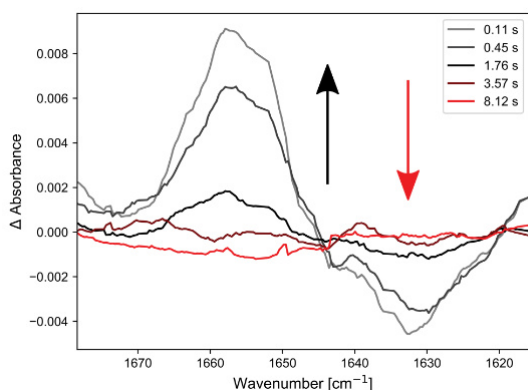


Hydrolysis reaction of MCA: spectra (left) and kinetics (right) at two spectral points

Folding of ubiquitin

The example of MCA shows a strong absorbance response. A more challenging experiment, inspired by the work of Lendl and coworkers (2003), involves the exposure of the protein ubiquitin to a change in solvent (20:80 methanol:D₂O → 55:45 methanol:D₂O). The resulting β-sheet to β-turn folding can be observed in the Amide I region of the IR spectrum. We used CH₃OD for this experiment, to avoid the strong background absorption associated with the OH stretch of methanol in this spectral region.

The difference spectrum shows a depletion at ca. 1635 cm⁻¹ and a new band, with two features around 1660 and 1650 cm⁻¹ and a lifetime of 1.46 s. These band positions are consistent with values in the literature, where a shift was reported rather than a difference spectrum. Here the time resolution is approximately 20 ms and even for the small spectral changes observed, the S/N ratios remain good.



Refolding of ubiquitin: difference spectra (left) and kinetics (right) at two spectral points

The reproducibility of the reagent delivery by the SF-73 and the synchronization of time by triggering, allow the averaging of multiple shots to further improve the S/N ratio. Alternatively, the improved S/N provides the opportunity to rapidly repeat a reaction under different conditions, such as temperature, enabling wider reaction parameter space to be mapped in shorter times and with low sample consumption.

Conclusion

Stopped-flow is a powerful tool to investigate the IR spectra of evolving and transient species and the monitor reactions on the timescale of milliseconds to minutes. It allows for precise, efficient and rapid mixing of a wide range of samples at low volumes, controlled temperatures and, if necessary, at anaerobic conditions.

We have successfully investigated chemical and biochemical reactions with this technique and have shown that good S/N ratios can be obtained even for weak signals and with single repetitions. Combining dual comb spectroscopy with stopped-flow opens up investigations of new reactions and processes that were previously difficult or impossible to measure in the IR.

Applications

Measurement of Optically Dense Samples

There are several reasons why users may want to measure infrared spectra of optically dense samples or on strongly absorbing backgrounds. For instance, scientifically relevant samples in heterogeneous catalysis or biology often consist of an analyte embedded in a complex matrix.

Removing the analyte from this matrix to make it amenable to spectroscopic investigations can alter its behavior. Similarly, in-situ process monitoring can be difficult if the materials surrounding the spectroscopically relevant species is strongly absorbing.

Another reason is to increase the sensitivity of a solution-phase measurement by increasing the optical path length. For most commonly used spectroscopic solvents, this method is limited by solvent absorption. This application explores the use of long path length transmission samples to increase the sensitivity in solution-phase measurements. It is made possible by using the high-intensity laser source of the IRis-F1 spectrometer, which can be used to conduct spectroscopic measurements through backgrounds with optical densities greater than 2.



The IRis-F1 dual-comb spectrometer, with its large sample compartment

Experiment

Experiments were carried out on the IRis-F1 dual-comb mid-infrared spectrometer. An important difference of the IRis-F1 compared to traditional mid-infrared spectrometers is the use of a pair of frequency comb lasers as a light source. It allows much higher light intensities to be achieved, and therefore more optically dense samples to be probed when compared to traditional globar sources.

Measurements were conducted in transmission mode with an optical path length of 100 μm , an acquisition time of 2 minutes and a spectral resolution of 4 cm^{-1} .

The analyte acetylsalicylic acid (aspirin) has a band centered at 1202 cm^{-1} and was measured in water at a range of concentrations, starting from a saturated solution (3 mg/ml).



The laser power was adjusted to achieve the maximum possible throughput with the background sample in place. The upper limit for the path length was determined to be approximately 100 μm of water at 1180 – 1240 cm^{-1} ; above this, the laser power is insufficient to penetrate the solvent background.

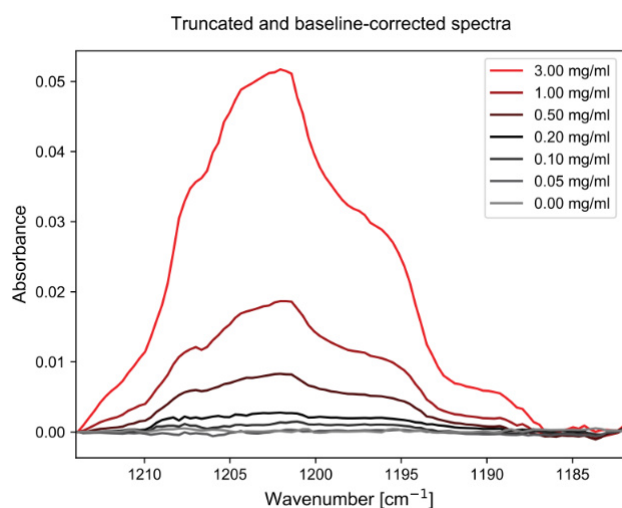
Applications

Measurement of Optically Dense Samples

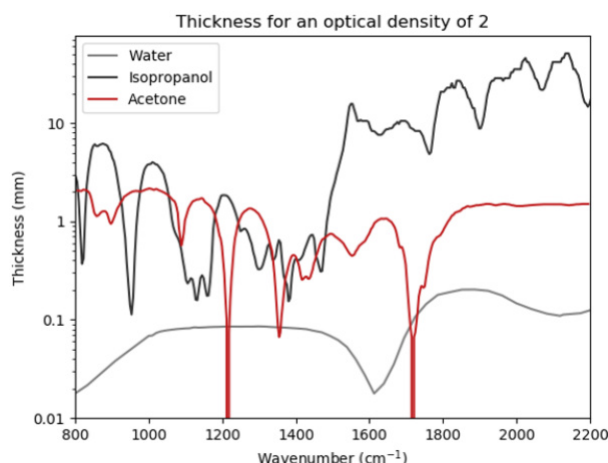
Results and Discussion

The analyte peak can clearly be seen to concentrations as low as 0.10 mg/ml, even on top of a very large background absorption. Baseline correction improves the result since the large ratio of solvent background to signal intensity can lead to somewhat larger baseline offsets than would be observed with a more transparent sample medium.

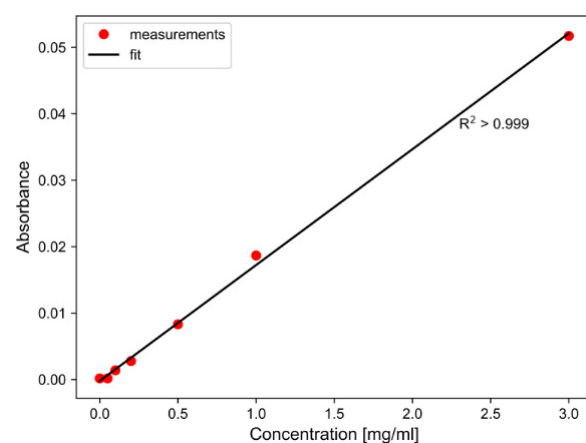
By using a linear baseline correction, the band can be isolated, and a regression analysis shows a good fit to very low concentrations of analytes.



DCS in Transmission through 100 μm Aspirin in Water with LOD (limit of detection) of 0.10 mg/ml



Recommended maximum sample thickness for different solvents

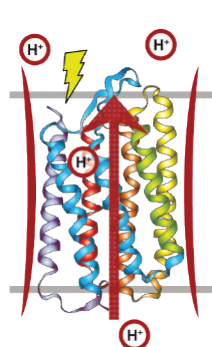


The resulting regression analysis at 1202 cm⁻¹ confirms the LOD of 0.10 mg/ml

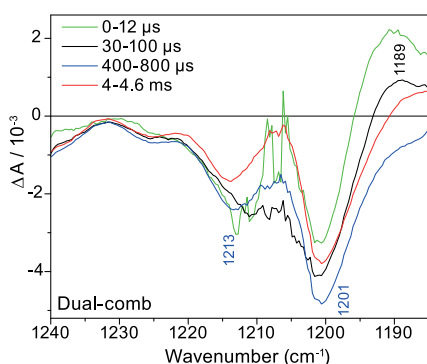
Bacteriorhodopsin Photocycle

Observation of the bacteriorhodopsin photocycle in a single shot

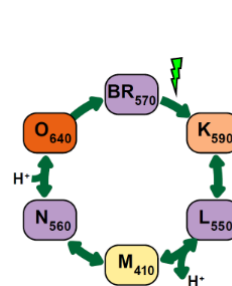
Protein structure



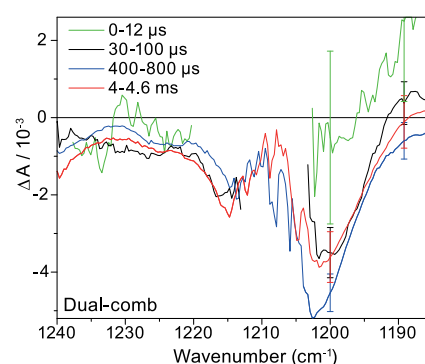
500 averages



Photocycle



Single shot



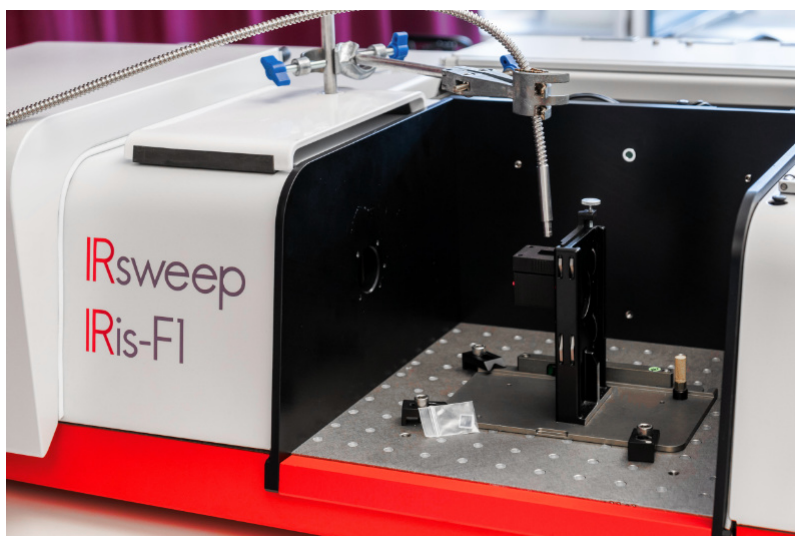
Applications

Polymer Chemistry

Fast spectroscopic monitoring is a proven tool in R&D and production environments, where it is used to gain insight into chemical reactions.

The IRis-F1 dual-comb spectrometer can be used to monitor curing reactions, where it can provide invaluable insight on the performance of coatings and adhesives.

Infrared spectroscopy is in many ways an ideal measurement technique for this application as it is capable of performing non-invasive in-situ measurements that provide direct information about the structure and bonding of the sample. However, many high-performance adhesives possess fast curing rates and the speed of off-the-shelf spectroscopic techniques is the limiting factor in their analysis.



The IRis-F1 is based on quantum cascade laser (QCL) frequency comb technology, which allows for measurements on microsecond to minute timescales to be carried out.

Experiment

Measurements were conducted with a single-reflection diamond Golden Gate ATR accessory (Specac). The sample is a UV-activated adhesive, which was kindly provided by DELO Industrial Adhesives (Germany). When uncured it has an infrared band at 1613 cm^{-1} and a new band at 1638 cm^{-1} after curing.

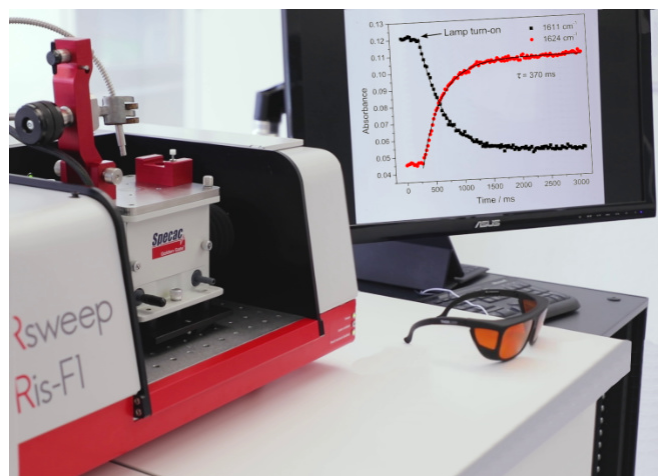
The spectrometer was set to a resolution of 4 cm^{-1} and the acquisition time was 1 ms, with a repetition rate of 220 spectra per second. Curing was triggered using a mercury lamp (LC8, Hamamatsu), via an optical fiber. After starting the measurement, the lamp is turned on to initiate the curing reaction. For each measurement a rapid series of measurements spanning before, during, and after curing was taken.

Results and Discussion

Difference spectra can be generated by subtracting a spectrum of the uncured glue (defined as a negative-time spectrum) from each of the subsequent positive-time spectra. The figure (next page, large) shows the resulting difference spectra, which highlight the changes produced by the curing reaction in 5 ms increments. Negative bands show that a feature has disappeared, while positive bands show that a new feature has grown in. Here it is evident that not one, but two new bands grow in, at ca. 1638 and 1624 cm^{-1} .

The fringing, expected when using a laser-based instrument with an ATR prism, is caused by a change in the refractive index of the sample (i.e. glue vs air). Fringes could be removed with a simple Fourier transform (FT) filter.

The kinetic traces at two points in the spectra (inset) clearly show the time-point where the lamp was turned on. By fitting the growth and decay of these points, the kinetic properties of the curing process can be determined.



The experimental setup

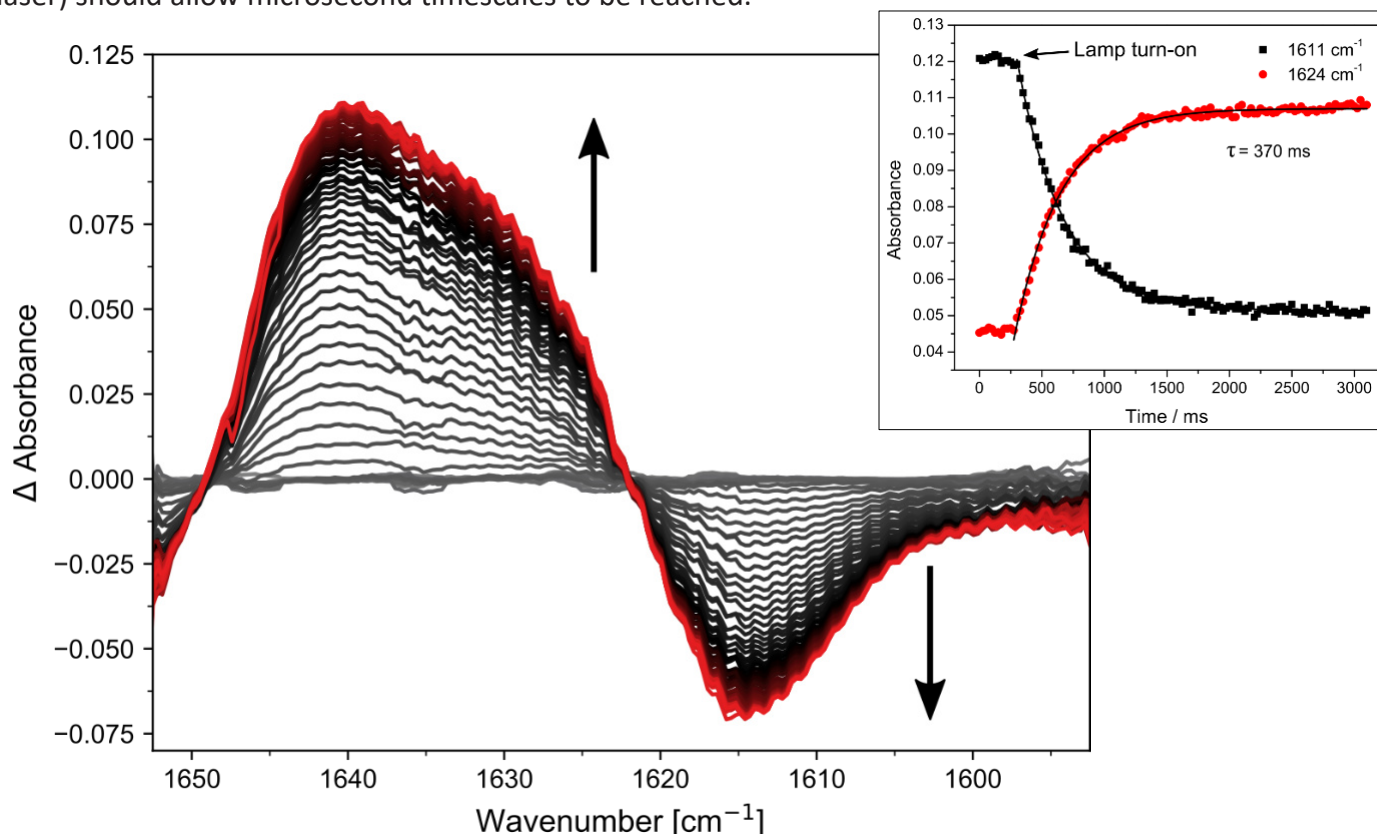
Applications

Polymer Chemistry

Conclusion

Rapid measurements with high signal to noise ratios were performed on a sample of glue during curing, giving insight on processes that happen on a millisecond timescale. This bridges the previously demonstrated capabilities of the IRis-F1 to measure on the microsecond timescale, with the second to minute timescale. It enables processes over many orders of magnitude in time to be studied.

Faster measurements are possible from the point of view of the spectrometer, however, the present setup appears to be limited by the lamp turn-on time and brightness. A different curing source (e.g. a laser) should allow microsecond timescales to be reached.



Formation and Characterization of Macromolecules

Polymers are used as plastics, paints, elastomers, dental compounds, composites and more, giving them a wide range of applications. The polymerization process is typically monitored with infrared spectroscopy.

The IRis-F1 spectrometer offers high signal-to-noise ratios at time resolutions from microseconds to seconds. It can be used to monitor the polymerization and help understand polymer formation and stabilization, as well as unwanted processes such as cross-linking, aging, contamination or decomposition. Due to its high time resolution, intermediates can be resolved as well.

Typical sample interfaces such as ATR can still be used. In addition, the sensitivity can be increased compared to FTIR-based systems, by increasing the sample interaction length.

The IRis-F1 achieves its superior performance by employing dual-comb spectroscopy based on broadband lasers. The lasers are detected in a so-called multi-heterodyne regime – the acquisition time is not restricted by moving parts.

Applications

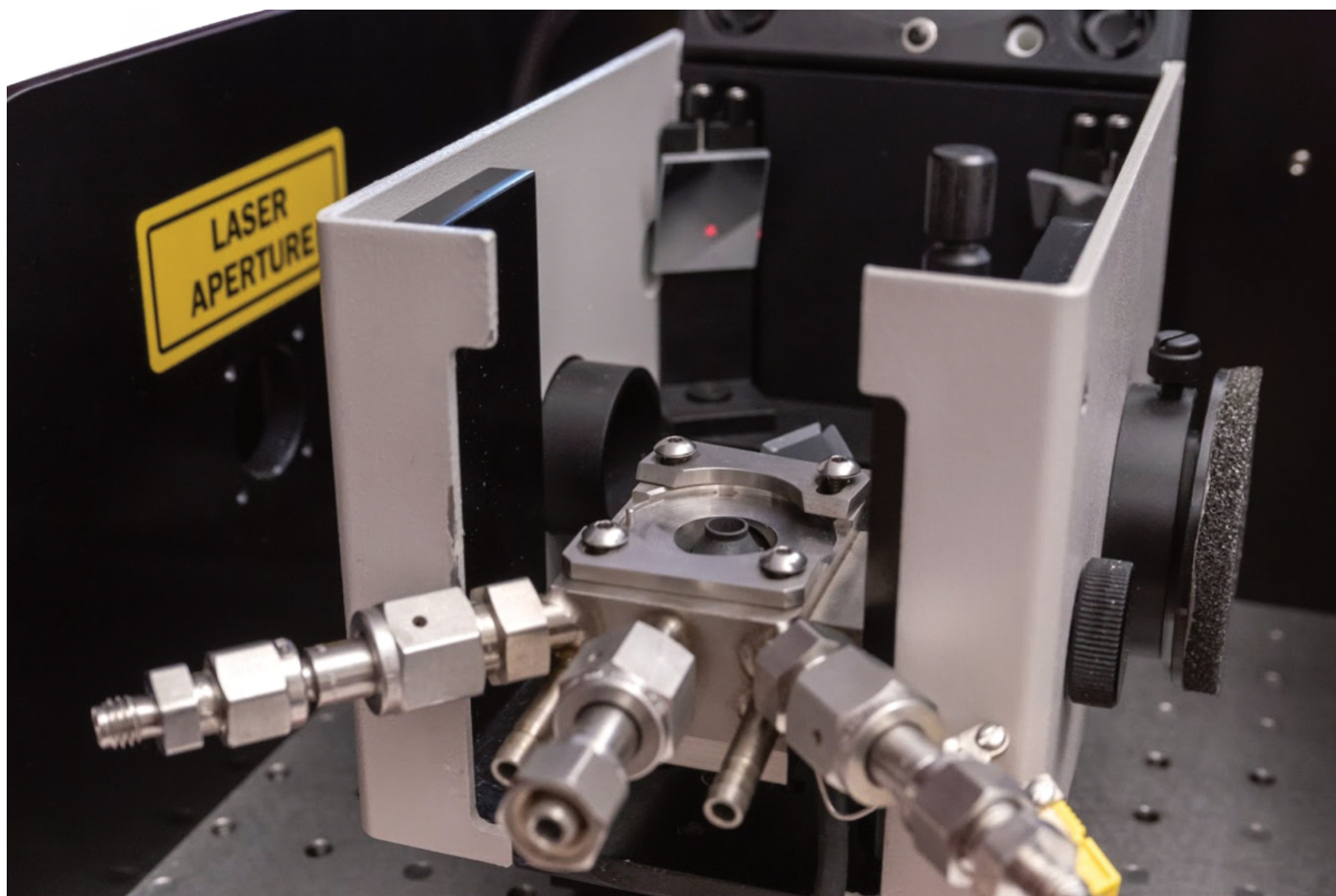
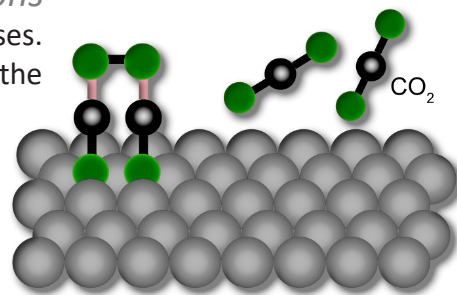
Heterogenous Catalysis

Diffusion and Gas Adsorption Studies of Low Concentrations

Heterogenous catalysis is an important step in many industrial processes. Changes to both the catalyst and the efficiency and pathway of the catalyzed reaction must be probed on a molecular level to elucidate the processes, and allow for the development of improved catalysts and processes.

The current method of choice to study catalysts under dynamic conditions is (operando) spectroscopy. Conventional FTIR is sometimes too slow, while other techniques, such as EXAFS, do not provide information on the state of the whole molecule or require difficult experiments.

Studying catalyst changes, diffusion processes, or surface effects – all these are necessary for a good understanding of catalysis and for future design improvements of both catalysts and reactors. These studies are now available with unmatched time resolution, signal-to-noise ratio, and IR spectral coverage in our table-top setup: the IRis-F1. It is compatible with standard FTIR accessories and can be coupled to DRIFTS cells.



Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy: IRis-F1 and Praying Mantis from Harrick with temperature control in the sample compartment allow investigations on these surface effects with high time resolution.

Applications

Protein Dynamics

Spectroscopy on proteins

Understanding the kinetics of proteins and enzymes is key in life science applications in research and industry. Infrared spectroscopy is well suited to meet this challenge.

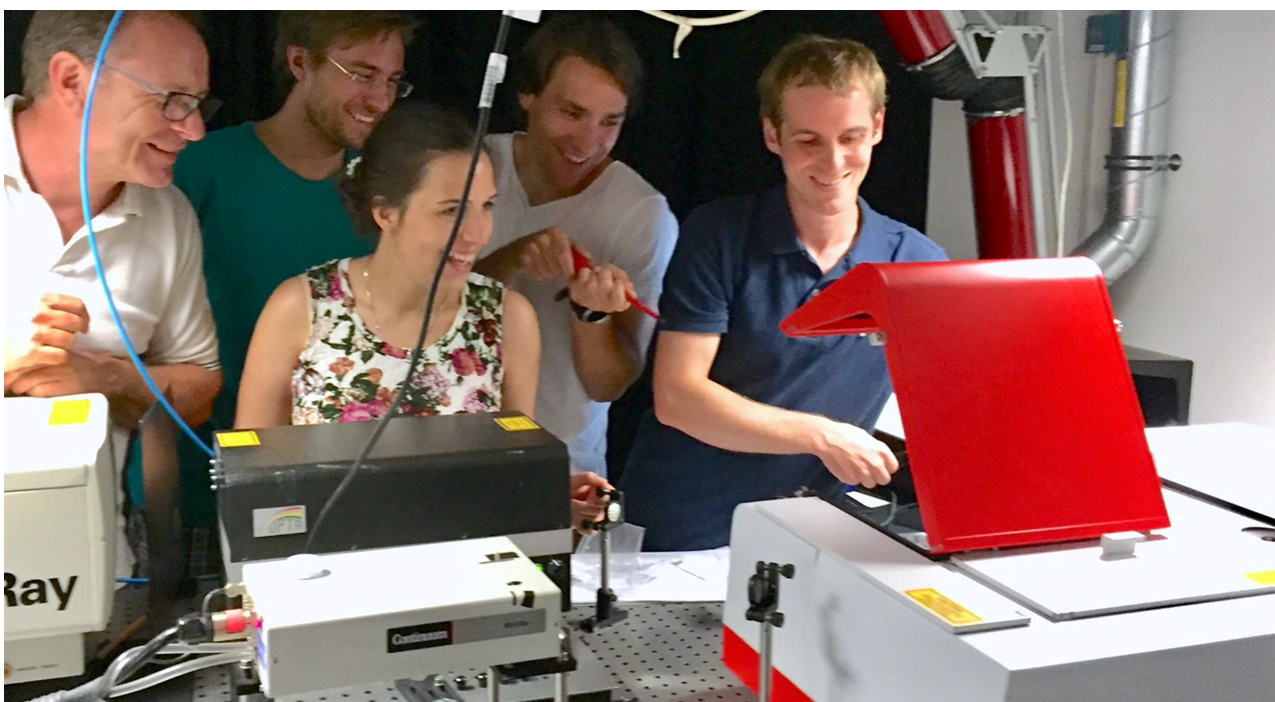
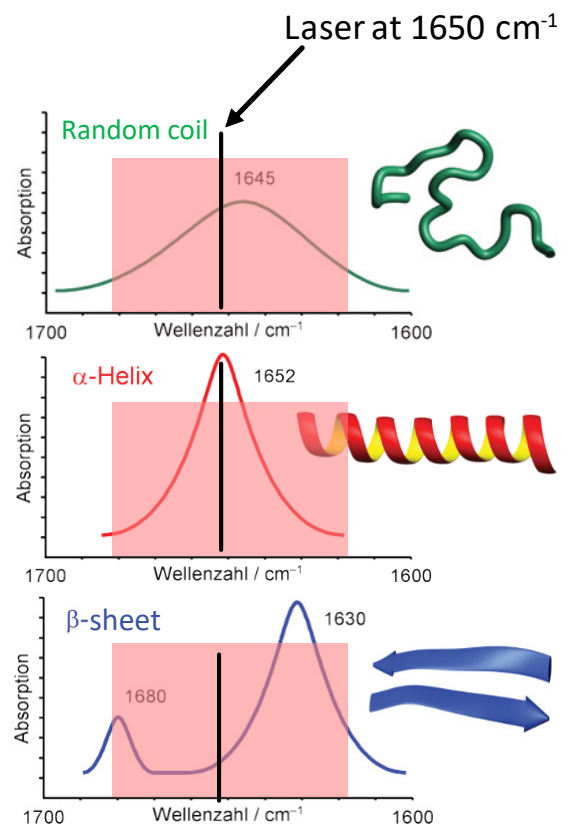
Using the industry standard of step-scan FTIR measurements to analyze protein reactions by mid-IR spectroscopy is challenging and at times frustrating, as having to repeat kinetic protein reactions thousands of times can be burdensome to impossible.

Proteins age, making reproducible measurements difficult. Even worse, many biochemical processes are non-repeatable, putting a large portion of proteins out of reach of investigation.

A new, more effective technology

The single-shot capability of the IRis-F1 enables study of dynamics of the class of non-reversible protein reactions, such as in vertebrate rhodopsins. Challenging research on proteins such as GPCRs becomes much easier because of improved signal-to-noise ratios compared to current state of the art.

The publication “Single-Shot Sub-microsecond Mid-infrared Spectroscopy on Protein Reactions with Quantum Cascade Laser Frequency Combs” in *Analytical Chemistry* by IRsweep together with the Kottke group from the University of Bielefeld (Biophysical Chemistry and Photochemistry) and the operational IRis-F1 in Prof. Heberle's lab at the FU Berlin (Experimental Molecular Biophysics) both illustrate IRsweep's commitment in the field.



The IRis-F1 in Prof. Heberle's lab at the FU Berlin

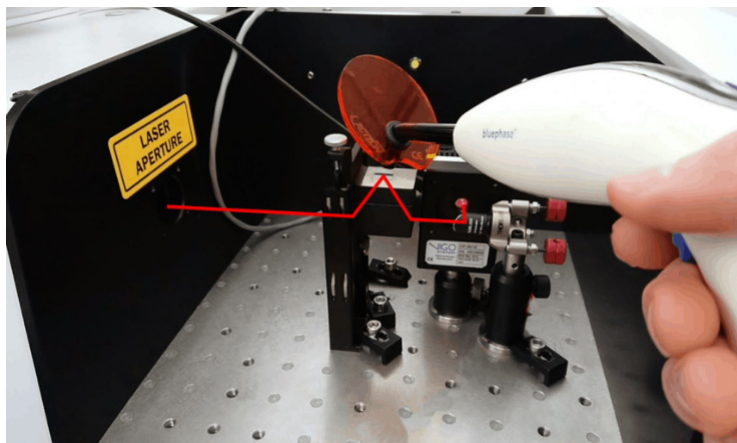
Applications

Dental Curing

Dentistry employs many advanced materials and methods. Many adhesives and fillings are on the forefront of polymer science since they are expected to handle many years of physical stress in the rather chemically harsh environment that is in our mouths.

On top of this, they have to be non-toxic and be easily applied in a pain-free and convenient manner, where they are expected to solidify and set at exactly the right time.

Photochemistry is the method of choice for this, generally making use of short-wavelength visible or UV-A light to ensure that the curing process can be triggered exactly when wanted. This way, the chemical reactions that create our dental fillings can be completed in seconds.



Monitoring Advanced Reactions

Observing chemical reactions in real time is difficult. Mid-infrared spectroscopy offers the possibility to non-destructively monitor bond-specific changes at high speeds.

Currently, rapid-scan FTIR is used for similar investigations. This technique has three main limitations for such experiments: brightness, time resolution and spectral resolution. Learn more here about how the technology of IRsweep's IRis-F1 can give better signal to noise ratios for faster measurements while retaining a very high effective spectral resolution.

IRsweep's IRis-F1 spectrometer can measure a spectrum with a 60 cm^{-1} spectral width in $1 \mu\text{s}$. Here we measured the curing of dental resins and binders at a repetition rate of 220 spectra per second and a spectral resolution of 4 cm^{-1} .

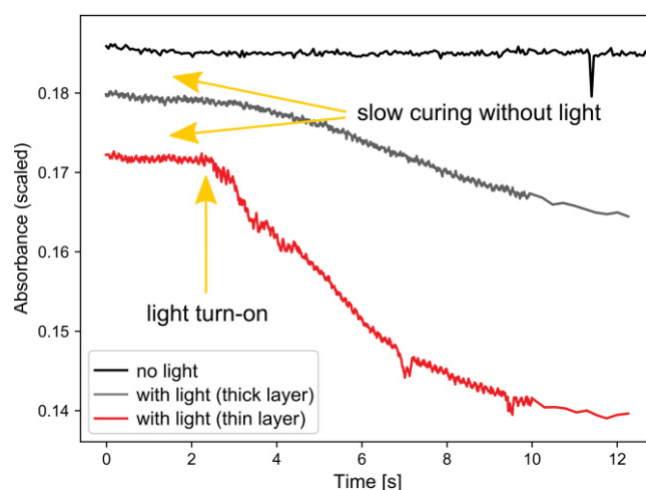
An IRUBIS silicon attenuated total reflection (ATR) crystal was used as a sensing substrate in the IRis-F1 spectrometer. This means the material directly on the surface of the crystal is measured. The reactions were initiated using a handheld fiber-optic coupled bluephase® curing light (Ivoclar Vivadent), which irradiated the substrate with light at wavelengths between 380 and 500 nm.

Results

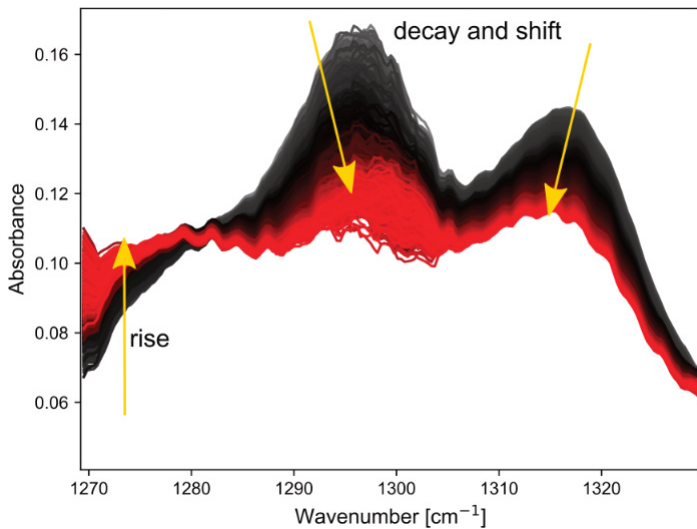
The experiment investigated the Duo-Link two-component luting cement (BISCO). Clear spectral changes are seen during curing, manifesting in a decay and shift of the bands at 1295 and 1316 cm^{-1} and a rise at lower wavenumbers.

Plotting these changes as a function of time shows the true power of using fast infrared spectroscopy for the analysis.

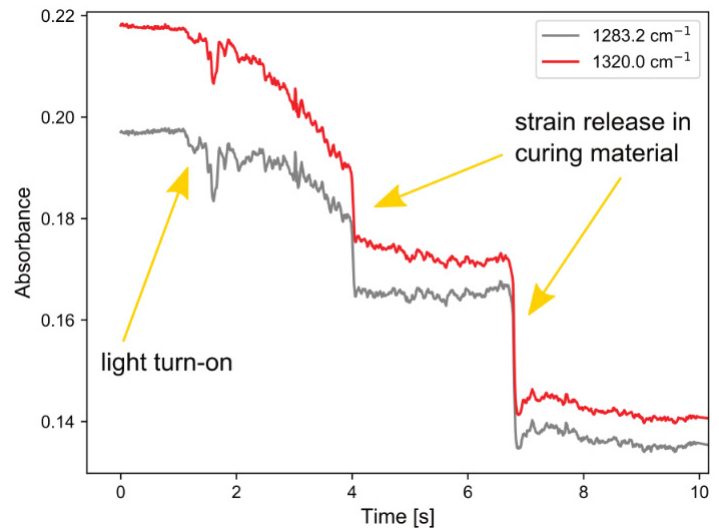
Two different thicknesses were investigated and it is clear from the time traces that the thin layer (red line) cures much faster than the thick layer (grey line).



Curing of the thin (red line) and thick layers (grey line)



Curing of Duo-Link cement measured with a repetition rate of 220 spectra per second shows strong spectral changes.



Physical changes in the material can be followed with IR spectroscopy. Here we see internal strain release due to curing, which affects the contact with the IR probe.

Ten seconds into the experiment the thick layer is still relatively uncured and light treatment would have to be continued to get a good result. The rate of curing strongly depends on the thickness of the layer.

The adhesive also shows some curing without light (top left, black line), which is expected due to the "dual cure" feature of this product. Once the light is switched on, the spectral changes are rapid.

Not just chemical changes can be seen using IR spectroscopy but also physical changes, as shown in the following experiment (top right figure). Normally this cement is used with an adhesive. Here it is intentionally left out, and no or incomplete binding to the substrate occurs.

This means that changes in the material, for example contraction/hardening, can lead to large changes on the measurement interface. These events are easily followed with fast mid-IR spectroscopy.

Conclusion

With the IRis-F1 it is possible to monitor fast reactions, ranging from timescales of milliseconds to minutes.

Curing of dental materials is an exciting field that can benefit from faster and brighter measurements. Chemical and physical changes have an effect on the resulting infrared spectra, meaning advanced analysis can be done even if no chemical changes are involved.

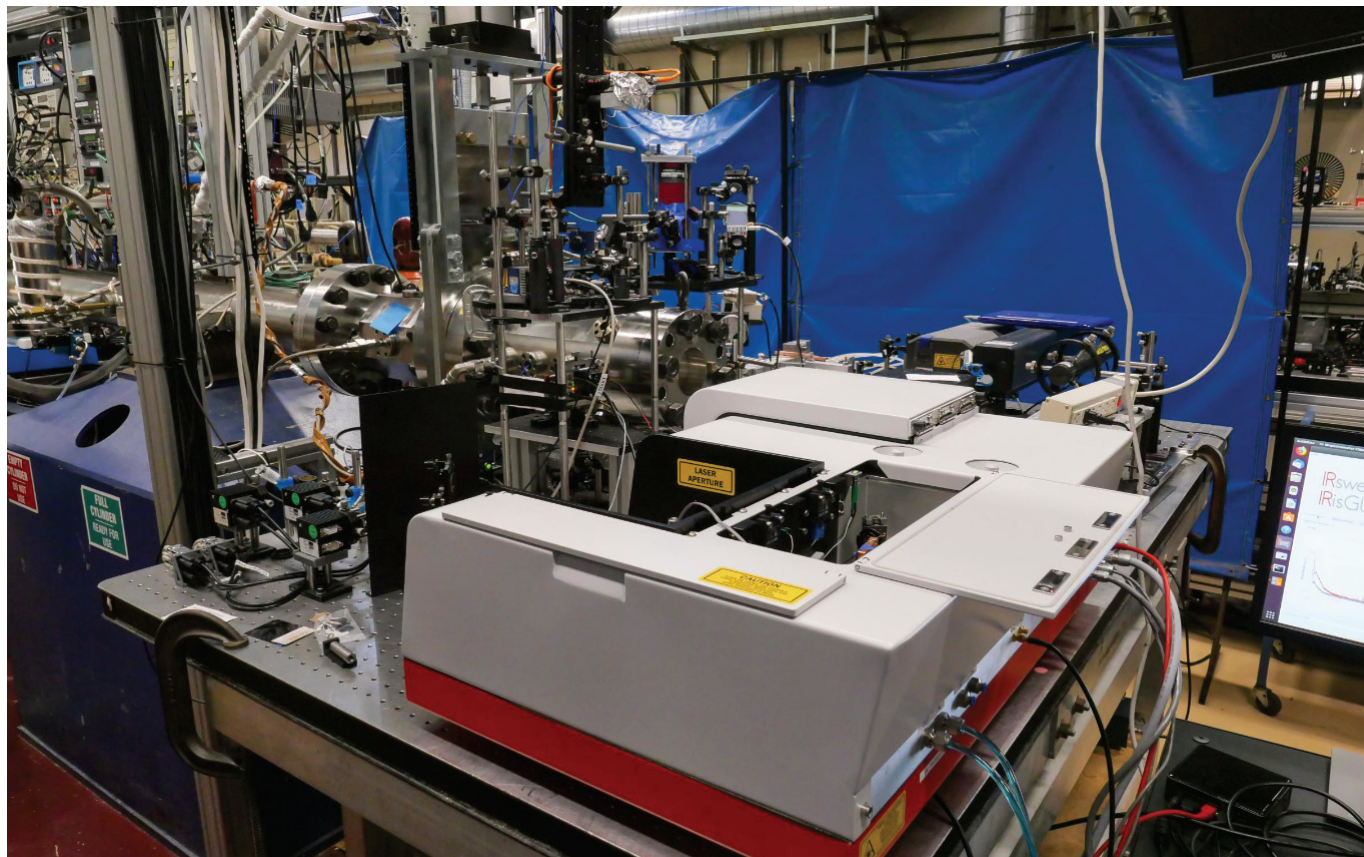
The technique is also non-destructive and can be adapted to many methods of sampling. This means it is possible to test these materials in realistic environments that are similar to where they will be used.

Applications

Combustion Diagnostics

Shock Tubes and Rapid Compression Machines

Absorption spectroscopy is an important tool for studying combustion processes. The mid-IR range, where the fundamental vibrational excitations can be studied, is especially interesting.



At the Hanson Group Lab, Stanford University

A common challenge in combustion absorption spectroscopy is the simultaneous observation of multiple species on short time scales. This is often done with a dedicated laser system per species, which limits the number of observable molecules to very few, due to overall system complexity. Broadband laser systems are a possible solution to this problem, but swept sources are often too slow to capture the dynamics, especially in shock tubes.

With the IRis-F1 dual-comb spectrometer, all laser modes are detected simultaneously with a single line of sight, allowing to observe multiple species at sub-microsecond time scales. Speciation with up to four species has been done, as well as the measurement of activation energies and reaction rates.

Dual-comb spectroscopy is an interferometric technique that works without moving parts. It is available for the first time as an integrated commercial solution in the mid-IR by IRsweep as the IRis-F1. Due to the use of Quantum Cascade Laser frequency combs, high-power mid-IR light is available.

The IRis-F1 has been used by a number of renowned combustion research labs, specifically on shock tubes, including the Hanson Lab at Stanford University where a paper published in March 2020 (Pinkowski et al., 2020) shows the pyrolysis of a fuel (Propyne, broadband absorber) and the subsequent oxidation with the generation of water (narrowband absorber).

Applications

Combustion Diagnostics

The measured absorption as a function of wavelength and time is shown in Figure 1 and the corresponding speciation is shown in Figure 2, where it is also compared to a suite of dedicated analysis lasers, where one laser and detector are needed per species.

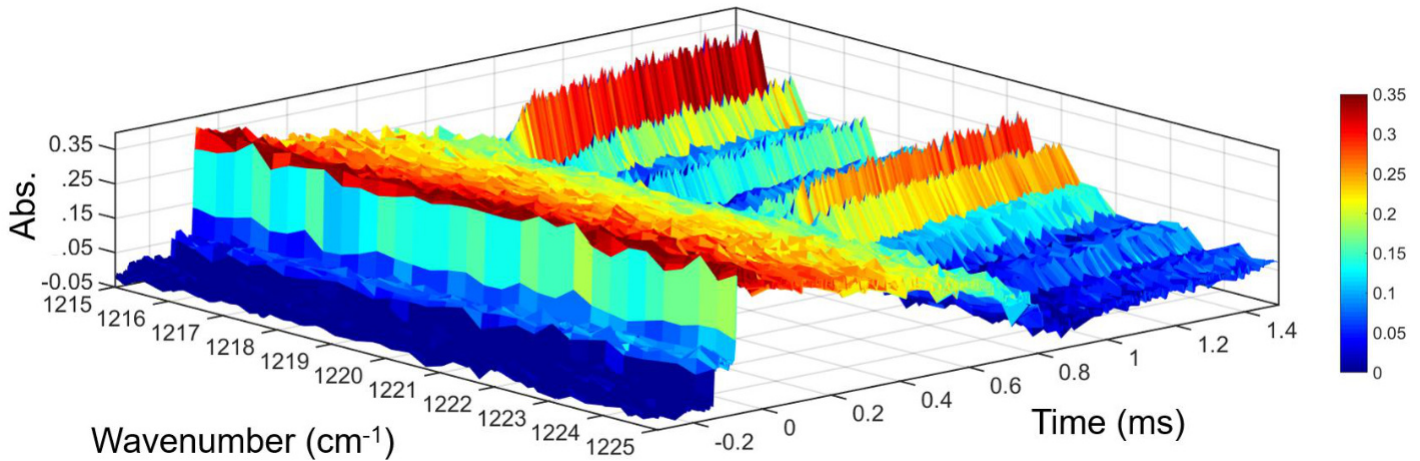


Figure 1. ©Pinkowski et al., 2020. DCS data from 1215 cm⁻¹ to 1225 cm⁻¹ of propyne oxidation (2% p-C₃H₄, T₀ = 1225 K, P₀ = 2.8 atm) illustrating the arrival of the incident and reflected shock before time-zero. The broadband absorption feature of propyne is visible from 0 to 0.6 ms and can be seen transforming into a finely featured spectrum (water) after 0.8 ms. The DCS data demonstrates good SNR during the passage of each shock wave, occurrence of a combustion reaction, and temperature/pressure increase of roughly 2500 K/60x over only 1 ms.

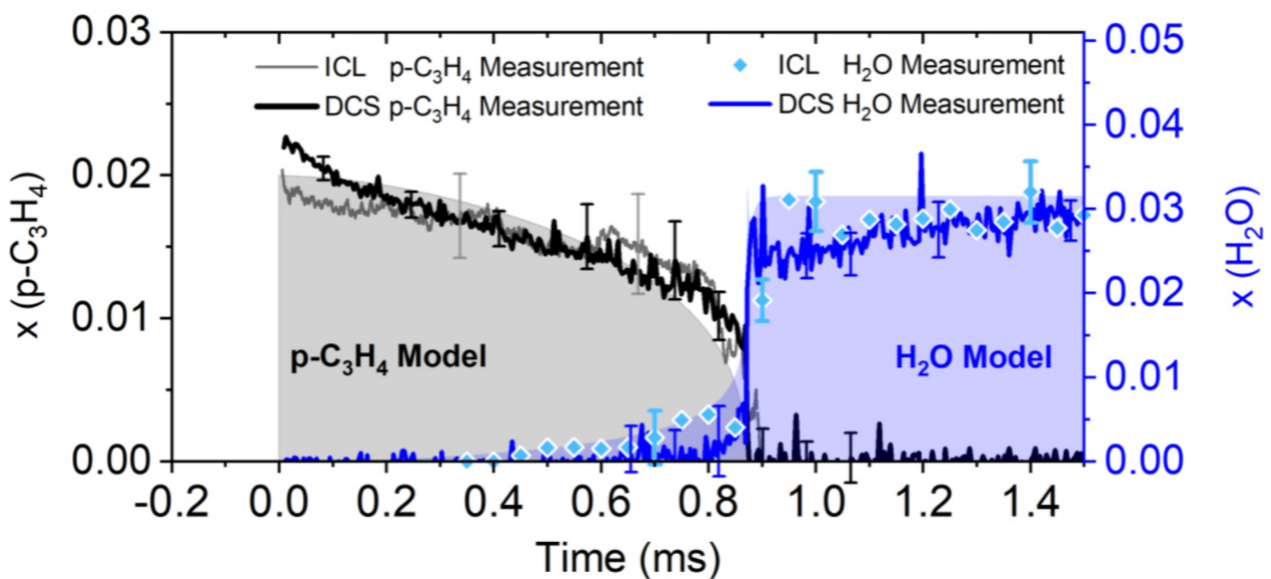


Figure 2. ©Pinkowski et al., 2020. DCS measurements of propyne oxidation with time-zero conditions of 2% p-C₃H₄/ 18% O₂ in Ar, 1225 K, and 2.8 atm. Speciation measurements at a 95% confidence interval and simulated results for propyne and water. Agreement at a 95% confidence interval is observed between the DCS and supporting laser measurements. While overall agreement exists between the DCS measurements and USC Mech II, key differences are visible at early times and just after ignition.

Applications

High-Resolution Gas Phase Spectroscopy

High-Resolution (0.001 cm^{-1}) Gas Phase Spectroscopy

The mid-infrared spectral range hosts the fundamental ro-vibrational transitions of many molecules and is therefore extensively studied with high spectral resolution in fundamental and applied research. Stabilized frequency combs and the concept of dual-comb spectroscopy have revolutionized this field as honored with the 2005 Nobel Prize in Physics. Since then, frequency combs have been ever improving and their spectral coverage has been expanded (Gianella et al., 2020).

Covering the mid-IR spectral range has been a challenge and more recently, QCL-based frequency combs (Villares et al., 2014) have become available as a powerful mid-IR frequency comb source. Based on those sources, IRsweep offers a fully integrated laboratory spectrometer with a spectral resolution $<0.001\text{ cm}^{-1}$ and a flexible center wavenumber between 2200 cm^{-1} and 900 cm^{-1} .

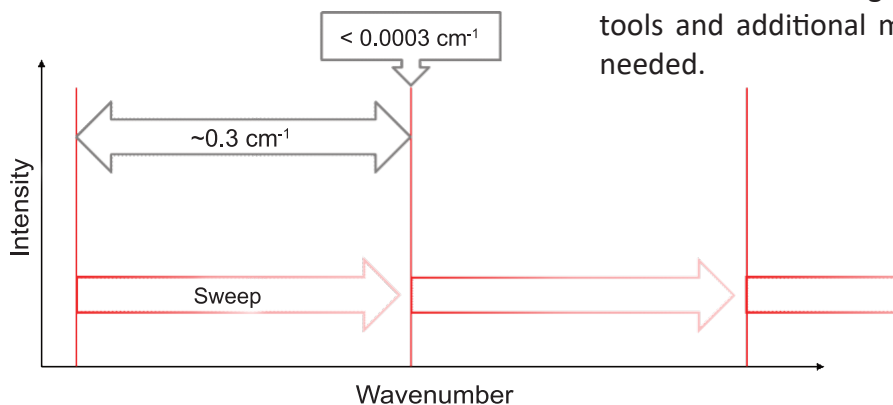
Beyond FTIRs

To achieve such a resolution with Michelson-interferometer based instruments (FTIRs), a large mirror movement distance is required. Large mirror translations result in very low available brightness from the typically used globar sources and long scan times. Low signal-to-noise ratios per time are a consequence.

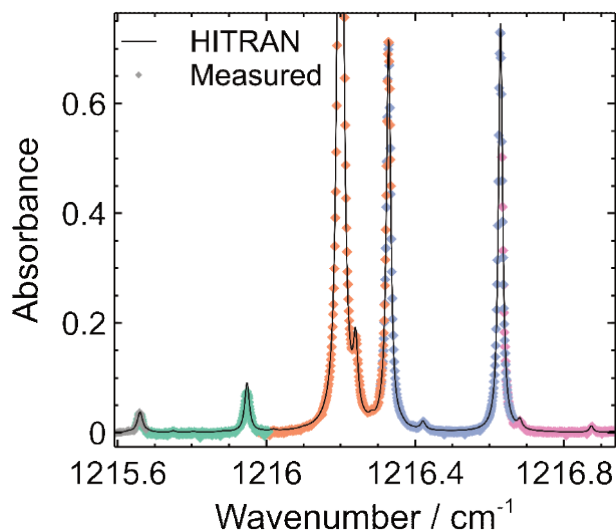
Turnkey Dual-Comb Spectroscopy with QCLs

The IRis-F1 HR dual-comb spectrometer overcomes this limitation: high spectral resolutions $<0.001\text{ cm}^{-1}$ can be achieved while the laser sources use the full dynamic range of the detection system resulting in high signal-to-noise ratios in short measurement times. A noise equivalent absorbance $\text{NEA}=7\times 10^{-5}\text{ Hz}^{-1/2}$ has recently been published (Gianella et al. 2020) with the system.

The resolution is achieved by simultaneously sampling a spectral band of typically 60 cm^{-1} with highly resolved ($\sim 1\text{MHz}$ wide) laser lines that are spaced by typically 0.3 cm^{-1} . The spacing between the laser lines is covered by sweeping all lines simultaneously over the distance between the lines. The center wavelength can be moved by switching the laser module in the IRis-F1 HR. Changing center wavelength does not require tools and additional modules can be purchased as they are needed.



Sweeping of the frequency comb over the spectral distance between the laser lines (point spacing, or free spectral range) results in a continuous spectrum.



Spectrum of CH_4 acquired with spectral resolution $<0.001\text{ cm}^{-1}$

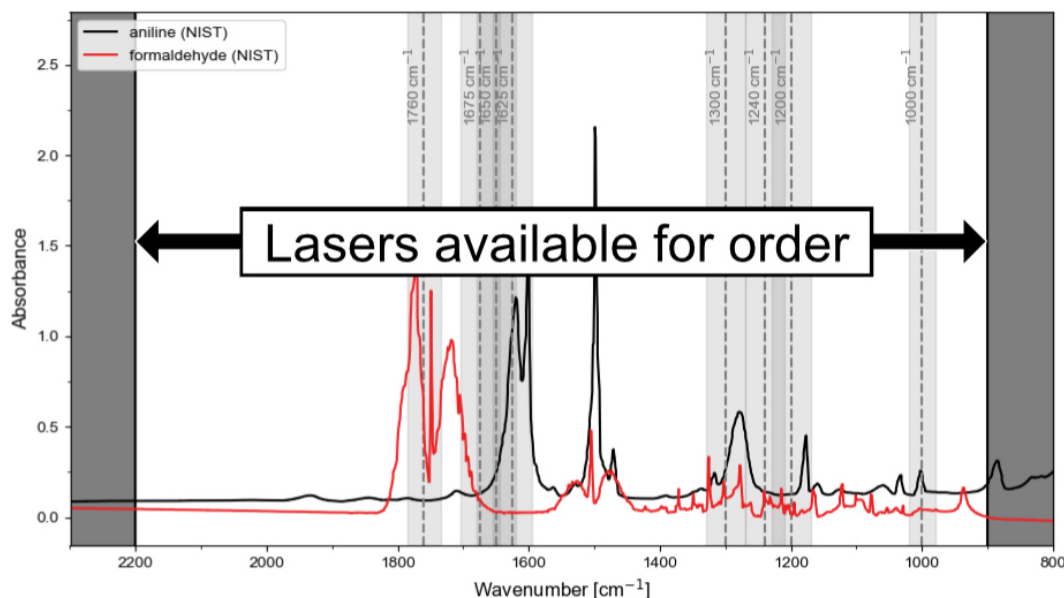
Flexibility

IRis-F1 HR is based on the IRis-F1 dual-comb spectrometer, retaining the possibility of high speed measurements with $<1\mu\text{s}$ time resolution (at a point spacing of $\sim 0.3\text{ cm}^{-1}$) for kinetics studies and reaction monitoring.

Laser Availability

*Lasers in stock
as of May 2020:*

Please ask about other center wavenumbers (2200 – 900 cm^{-1}) required by your application, we will inform you about expected lead-times.



Selected List of Publications

Microsecond Resolved Infrared Spectroelectrochemistry Using Dual Frequency Comb IR Lasers

E. Lins, S. Read, B. Unni, S. M. Rosendahl, I. J. Burgess,
Analytical Chemistry (2020)

"Microsecond resolved spectra can be obtained with high spectral resolution and fractional monolayer detection limits in a total experimental duration that is 2 orders of magnitude less than the equivalent step-scan experiment."

High-resolution and gapless dual comb spectroscopy with current-tuned quantum cascade lasers

M. Gianella, A. Nataraj, B. Tuzson, P. Jouy, F. Kapsalidis, M. Beck, M. Mangold, A. Hugi, J. Faist, L. Emmenegger,
Optics Express (2020)

"We present gapless, high-resolution absorption and dispersion spectra obtained with quantum cascade laser frequency combs covering 55 cm^{-1} ."

Dual-comb spectroscopy for high-temperature reaction kinetics

N. H. Pinkowski, Y. Ding, C. L. Strand, R. K. Hanson, R. Horvath, M. Geiser,
Measurement Science and Technology (2020)

"In the current study, a quantum-cascade-laser-based dual-comb spectrometer (DCS) was used to paint a detailed picture of a 1.0 ms high-temperature reaction between propyne and oxygen."

Vibrational Stark Spectroscopy on Fluorobenzene with Quantum Cascade Laser Dual Frequency Combs

U. Szczepaniak, S. H. Schneider, R. Horvath, J. Kozuch, M. Geiser,
Applied Spectroscopy (2019)

"Measurements performed on fluorobenzene with the dual-comb spectrometer (DCS) were compared to results obtained using a conventional FT-IR instrument ... The dual-comb spectrometer provided similar qualitative and quantitative data as the FT-IR setup in 250 times shorter acquisition time."

Single-shot sub-microsecond infrared Spectroscopy on Protein Reactions with Quantum Cascade Laser Frequency Combs

J. Klocke, M. Mangold, P. Allmendinger, A. Hugi, M. Geiser, P. Jouy, J. Faist, T. Kottke,
Analytical Chemistry (2018)

"The kinetic analysis of irreversible protein reactions requires an analytical technique that provides access to time-dependent infrared spectra in a single shot. We present a spectrometer based on dual-frequency-comb spectroscopy using mid-infrared frequency combs generated by quantum cascade lasers."



IRsweep

It's all about time



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