3D-Printing for Low-Cost and Versatile Attenuated Total Reflection Infrared Spectroscopy

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ABSTRACT: In this work, we present a fully 3D-printed module for attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy ready for use in commercial FTIR spectrometers. The developed setup stands out in terms of robustness and ease of sample application. Rapid prototyping paired with theoretical considerations were employed to design and fabricate the module. Cost-efficient commercial available silicon and germanium ATR crystals prepared from double-side polished wafers were mounted in the setup. While low-noise levels and stability bear comparison with commercial systems, the multibounce ATR crystal’s long interaction pathlengths as well as their interchangeability turns the presented ATR module into an even more sophisticated tool. The versatility of the proposed setup is demonstrated for various spectroscopic challenges: Curing of a cyanoacrylate and a two component epoxy based adhesive was monitored by tracking polymerization processes at room and high temperatures. To emphasize potential applications of the disposable ATR module in life science studies exploring potential bio-hazardous samples mid-IR spectra of Escherichia coli and bovine serum albumin were recorded. The total printing time of the ATR module is 10.5 h enabling overnight fabrication at a total cost ranging from 150-613 € making the high versatility of ATR spectroscopy accessible to a broader audience. This proves the potential of 3D-printing to generate optical instruments tailored to the needs of individual analytical problems.

Fourier transform infrared spectroscopy (FTIR) is a rapid analytical technique providing molecule-specific qualitative and quantitative information in a label-free and non-destructive manner.1 The most prominent probing technique for the acquisition of IR spectra is in attenuated total reflection (ATR) configuration. It allows for quick and robust measurements of liquids, solids and pastes or other troublesome samples, by requiring hardly any sample preparation. In this technique, the light is totally reflected in the optical denser ATR element, generating an evanescent field interacting with the sample at penetration depths typically up to 2 μm per reflection.2 The strong absorption of water in the mid-IR region restricts the optical pathlength to 6-8 μm for classic FTIR transmission experiments, leading to difficult sample handling. The inherent surface layer probing character of ATR spectroscopy, as the evanescent wave interacts only with few micrometer of the sample at the ATR crystal’s interface, makes aqueous samples more amenable in this configuration.3 These advantages of ATR spectroscopy have been exploited in a wide variety of fields including forensic science,4 on-line monitoring5 and biofilm studies.6 Combination of ATR with novel high power IR light sources,7,8 optimized liquid handling,8,9 as well as divers modification of the ATR element indicates the potential of this technique.10-13 Complementary to commercial, costly ATR prisms, crystals prepared from double-side polished Silicon wafer have emerged.14 Besides an increased number of active reflections and hence effective pathlength, these crystals allow for fast screening by parallel preparation or complete disposal due their low-costs and availability. In addition, ATR spectroscopy was further enhanced by microstructures for e.g. nanofluidic sensing,15 or electrochemical investigations.16 Furthermore, microstructured single-bounce ATR crystals make use of the easy access to Si fabrication, while allowing to extending the IR transmission of Si beyond multireflection elements.16 All these emerging systems can be further exploited by custom-made and fit-for-purpose scientific instrumentation.

Since its introduction in the 1980s, 3D-printing has evolved into a versatile platform for rapid manufacturing of customized parts made of metals, ceramics and polymers. Nowadays commercially available 3D-printers cost less than 500 €, enabling fabrication at home or in every lab.17 Scientific instrumentation has been improved due to the freedom of design typical for 3D-printing. High performance laboratory equipment like a flexure translation stage microscope,18 enhanced sample handling for analytical ultracentrifugation,19 complex liquid handling20,21 innovative chemical reactionware22 and acoustic lenses23 are among a vast amount of examples hardly producible with common manufacturing techniques. Several application of 3D-printing auxiliary optical equipment like chopper wheels, rail24 and cage systems25 have been reported. Parts of optical setups e.g. gas cells,26,27 electrochemical
cells,\textsuperscript{30} entire ultra-violet/visible (UV/VIS) spectrometers\textsuperscript{31} as well as active optical components in the UV-VIS, IR\textsuperscript{32} and terahertz\textsuperscript{33} regime have already been 3D-printed. In this work we demonstrate the combination of 3D-printing with hand-crafted and commercial available low-cost silicon and germanium ATR elements for FTIR-ATR spectroscopy. The 3D-printed module was designed to fit in commercial FTIR spectrometers. Its figures of merit bear comparison with commercially available ATR units. The high quality spectroscopy and the great versatility enabled by the 3D-printed module is showcased for a variety of fields such as monitoring polymerization processes at high temperatures, recording spectra of potentially hazardous biological samples and performing quantitative liquid investigations using a 3D-printed liquid compartment. To the best of our knowledge this is the first time that a 3D-printed setup in combination with low-cost ATR elements have been utilized for ATR-IR spectroscopy.

\textbf{Experimental}

\textbf{Reagents and Samples.} Ethanol (99 \%, Sigma) was used as received. Superglue (Loctite 495) was purchased from RS components. Two-component epoxy resin (Polytec PT, Germany) was mixed in 10:1 ratio and subsequently applied on a Si ATR crystal by spin coating using a spin velocity of 4000 rpm, \textit{Escherichia coli} (\textit{E.coli}) pellets were a gift from Consiglio Nazionale delle Ricerche, Avellino, Italy. Bovine Serum Albumin (99 \%, Sigma Aldrich) was used as received and dissolved in deionized water.

![Figure 1. 3D-exploded-view drawing of 3D-printed ATR module mounted on the spectrometer adapter plate using custom-built ATR elements.](image)

\textbf{Experimental setup.} The 3D-printed ATR setup is fixed with two M2 countersunk screws and nuts countersunk into the ATR body, to fit on a commercial spectrometer adapter plate (universal transmission unit, Bruker, Germany) allowing to be embedded into the beam path of any Bruker spectrometer. The 3D-printed body with a footprint of length \( \times \) width \( \times \) height = 70 \( \times \) 70 \( \times \) 105 mm\(^3\) was designed to be printed in one piece and is equipped with dove-tail rails with 10 mm width allowing for adjustment of the mirror mounts. The mirror mounts have triangular recesses that allow their fixture using M3 screws.\textsuperscript{19} Gold-sputtered microscope slides, attached to the mirror mount using double-sided tape, were used to direct the IR beam to the ATR crystal’s facets. The groove (21 \( \times \) 11 \( \times \) 0.4 mm\(^3\)) on the top of the body allows for reproducibly exchange the ATR crystals. A 14 \( \times \) 1 mm FKM O-ring sealed the ATR crystal and the fixture mounted with four M6 screws (the holes on top of the body are designed to easily cut the M6 thread into the PLA material). In addition, a small adapter was designed to host the IRUBIS ATR crystals (IRUBIS GmbH, Germany, 11 \( \times \) 9 mm) in the same body.

ATR crystals were cut from double-side polished Si and Ge wafers (Microchemicals, Germany, 20 \( \times \) 10x0.525 mm\(^3\)) and the narrow facet were polished to an angle of 45\(^\circ\). The used Ge wafer was coated with 20 nm SiO\(_2\). To this end, cleaved pieces were glued to angled aluminum holder and polished using diamond polishing wheels (15 \( \mu \)m - 0.1 \( \mu \)m grain size). Although this geometry would allow for 20 active bounces, only 15 mm of the ATR crystals surface are accessible due to the O-ring sealing and hence, the number of active bounces equals to 15.

The assembled ATR module was placed in the sample compartment of a high-performance Vertex 80v FTIR spectrometer as well as in a routine measurement Tensor 37 FTIR spectrometer (both Bruker, Germany) both equipped with liquid-nitrogen cooled detectors. For comparison, a Platinum ATR unit (Bruker, Germany) was used. The aperture was optimized to maximum signal and was set to 8 mm. Spectra with a resolution of 4 cm\(^{-1}\) were recorded and 32 scans were averaged per spectrum (4 s acquisition time). Spectra were calculated using a Blackmann-Harris 3-term apodization function and a zero-filling factor of 2. All spectra were acquired at room temperature and analyzed using the software package OPUS 8 (Bruker, Germany).

\textbf{3D Printing of the ATR module.} Following the blueprints of the ATR module developed in Inventor Professional 2017 (Autodesk, USA) the components were sliced using Slic3r Prusa Edition v1.40.1 software (Prusa Research, Czech Republic). A Prusa i3 MK3 3D printer (Prusa Research, Czech Republic) was used for additive manufacturing. The hotend of the extruder was equipped with a 0.4 mm brass nozzle. PLA with a diameter of 1.75 mm sourced from Prusa (Prusa Research, Czech Republic) was printed at 200 °C (First layer 220 °C). The layer height was set to 0.15 mm (0.2 mm for the first layer). Lifting of the Z axis, when filament retraction is triggered was set to zero to avoid stringing, therefore post processing of the printed ATR module was mainly required for visual impression. The infill was set to 20 \% using a honeycomb pattern. No support structures were used when printing the ATR module. Further printing parameters were chosen as suggested by Slic3r for Prusa PLA. The overall printing time for the ATR module including the mirror mounts is 10.5 h with the proposed settings using ~27 m filament. The .stl files ready for slicing and reprinting can be found in the supporting information.

\textbf{Results and Discussion}

\textbf{Setup Performance.} The 3D-printed ATR setup was placed in the beam path of a FTIR spectrometer and the gold mirrors were adjusted to maximum signal at the detector. The ATR body was designed to avoid stray light from direct reflection...
of lower surface of the ATR crystal. This was verified by blocking the crystal’s rear facet. Thereby, the detector signal was completely suppressed, hence, only light passing through the ATR crystal is reaching the detector. To showcase the versatility of the setup, three different ATR crystals were inserted and the corresponding single channel spectra are given in Figure 2A. The single-bounce ATR crystal (IRUBIS) and the Ge ATR crystal provides the highest transmission down to 700 cm⁻¹, while the Si crystal is transparent to 1200 cm⁻¹. Bands at 1447 cm⁻¹, 1385 cm⁻¹ and 1296 cm⁻¹ are associated with phonons in silicon. Band at 1066 cm⁻¹ stems from Si-O-Si vibrations. The carbonyl stretching vibration of the polymeric acid of the filament is located at 1732 cm⁻¹ and it is visible in the spectra because it is the supporting surface for the ATR crystals. The RMS noise of all crystals for 4 s integration time (32 scans) are between 3 - 5 x 10⁻⁵ A.U. obtained from 100 % lines between 2000 cm⁻¹ to 1300 cm⁻¹. Furthermore, the effective pathlength dₑ of the home-built Si and Ge ATR crystals, comparable with the thickness of a transmission measurements can be derived from the absorbance of water by inserting into Lambert-Beer’s law A = ε c dₑ N. With the absorbance A, the absorption coefficient ε, and the concentration c. For multireflection ATR crystals, as used in this study, the absorbance increases linearly with the number of active bounces N (see Experimental section for further details). For weakly absorbing samples, dₑ can be approximated by

\[ dₑ = \frac{2\theta}{n_1} \frac{\sin n_1 \cos^2(\theta)}{2 \sin^2(\theta)(1 - n_1^2)} \] (1)

\[ dₑ = \frac{2\theta}{n_1} \frac{\sin n_1 \cos^2(\theta)}{2 \sin^2(\theta)(1 - n_1^2)} \] (2)

where \( n_1 \) and \( n_2 \) are the refractive indices of the ATR crystal and the sample, respectively \( n_{eff} = n_1 n_2 \). For an unpolarized IR beam, as generated with the thermal emitter of the FTIR spectrometer, it is the average of parallel and perpendicular effective pathlength (Equation 4). For the blank Si and Ge ATR crystal with \( N = 15 \), \( \theta = 45^\circ \), \( n_1 = 3.42 \) or \( n_1 = 4.01 \), respectively, \( n_2 = 1.32 \) (water) and \( \lambda_0 = 6.1 \) μm. Equation 2 yields N-dₑ (1640 cm⁻¹) = 6.91 μm and 4.57 μm for Si and Ge, respectively. Note that the special microstructured geometry of the IRUBIS ATR crystals did not allow for this calculations.

Figure 2. (A) Single Channel spectra of a Germanium crystal, silicon crystal and Si IRUBIS ATR crystals, all shown for angle of incidence = 45°. *Spectra of IRUBIS is divided by 5. (B) Water spectra on corresponding ATR crystals. Absorbance is highly affected by the number of active bounces, material of the ATR element and the microstructured geometry of the ATR element.

Water spectra recorded using different ATR crystals are given in Figure 2B and nicely illustrate the material and number of active bounces dependent depth of penetration: While the single-bounce ATR crystal from IRUBIS shows the lowest absorbance, the high number of bounces for the Ge and Si ATR crystal lead to considerably higher absorbance. These spectra can be further used to characterize the 3D-printed ATR module and determine the effective pathlength experimentally. To this end, the absorbance of the bending vibration of water at 1640 cm⁻¹ (compare Table 1), the corresponding absorption coefficient ε = 21.4 L cm⁻¹mol⁻¹ (obtained from a water transmission spectrum obtained with a defined pathlength), and c = 55.56 mol L⁻¹ inserted into Lambert-Beer’s law. This yielded a dₑexp(Si ATR) = 5.97 μm and dₑexp(Ge ATR) = 3.95 μm, which is equivalent for both films to 86.4 % of the theoretically obtained values reported above. To determine the source for this intriguingly reproducible deviation, the same ATR crystals and ATR fixture were used in the ATR setup built from commercial available optomechanics including xyz-stages and rotation mounts allowing for precisely adjusting the angle of incident, used in our previous studies. From this experiment, we found that the dₑexp values for both crystals in combination with the 3-D printed liquid compartment exactly match the theoretically obtained values (absorbance for the Si ATR is given in Table 1). For this reason and due to the exact same deviation for both ATR materials, we assumed the small inaccuracies in dimension of the 3D-printed mirror mounts to result in a deviation of the angle of incidence, which highly affects the effective pathlength. If inserting into Equation 1-3, the obtained dₑexp values correspond to \( \theta = 48.8^\circ \) if holding all other parameter fixed. Here, the rapid prototyped nature of 3D-printing easily allowed for correction by adapting the angle of the facet of the mirror mounts.

Table 1. Calculated and theoretical derived effective pathlength for different ATR crystals. * for \( N = 15 \); \( \theta = 45^\circ \). * 3D printed setup, b obtained with optomechanic setup.

| Material | Si ATRᵃ | Ge ATRᵇ | IRUBIS ATRᵇ | Si ATRᵇ | Bruker ATR Unit |
|----------|---------|---------|-------------|---------|----------------|
| A(1640 cm⁻¹) first print | 0.71 | 0.47 | 0.12 | 0.86 | 0.15 |
| A(1640 cm⁻¹) final print | 0.84 | 0.50 | 0.11 | - | - |
| dₑ | 0.48 | 0.39 | 0.48 | - | - |
| dₑexp * | 7.24 | 4.57 | 7.24 | - | - |
| dₑexp first print | 5.97 | 3.95 | 1.01 | 7.24 | 1.26 |
| dₑexp final print | 7.07 | 4.49 | 0.95 | - | - |

This adjustment and reprint of the mirror mount, enabled to account for the printer-induced deviations and dₑexp were in very good agreement with theory, being just 0.5° off. In addition, the mechanical stability of the 3D-printed ATR module was tested by removing the entire system from the spectrometer’s sample compartment, removing the ATR crystals and as well as pushing the mirror mounts by hand while recording water spectra. For all three test situations, the deviation of the
intensity of the water band was < 4%. Lastly, the entire ATR setup was inserted into another spectrometer (Bruker Tensor 37). Owing to the standardized sample compartment dimensions and beam height, no adjustments were needed and the ATR module was immediately ready to use. However, in contrast to the high-end spectrometer, here a slightly higher RMS noise of 8·10^{-5} A.U. was obtained. The RMS noise of the commercial ATR unit of 9·10^{-5} A.U. was obtained in the same spectrometer. For comparison, absorbance of water and corresponding de obtained on the commercial Bruker ATR unit is also given in Table 1.

The excellent mechanical stability and the high quality spectra obtained with the 3D-printed ATR module, will be further explored in the following sections. The disposable character of the entire setup as well as the possibility to remove the ATR crystals is demonstrated for samples that are otherwise hardly accessible with commercial ATR units.

**Biological Samples.** Handling of biogenic samples typically involves cumbersome instrument cleaning protocols to avoid cross-contamination and therefore often relies on disposable equipment. Additionally, such samples often feature hazardous characteristics. In the presented setup, the only parts getting in contact with the sample are either the low-cost commercial IRUBIS ATR crystals or hand-crafted ATR crystals made from wafers as well as the fully 3D-printed ATR fixture. Therefore, cross-contaminations can be avoided due to the disposable nature of the proposed setup.

![Figure 3](image-url)  
**Figure 3.** FTIR spectra of *E. coli* dried on IRUBIS ATR crystal. Bands for different species found in biological samples are highlighted: (A) lipids, (B) protein, (C) phosphates of the DNA backbone and carbohydrates (D).

Potential hazardous samples were mimicked by an *E. coli* suspension pipetted on an IRUBIS ATR crystal, dried over-night at room temperature and re-placed in the 3D-printed ATR setup. The resulting IR spectrum is given in Figure 3, showing a high quality bacteria spectrum including bands typically found in biological samples. Bands associated with lipids (region A Figure 3), protein at 1641 and 1536 cm⁻¹ (region B) and bands corresponding to the DNA backbone at 1237 cm⁻¹ (region C) and carbohydrates at 1070 cm⁻¹ (region D) are in good accordance with literature.³⁹

**Figure 4.** (A) FTIR spectra of BSA solutions with different concentration recorded on a Si ATR crystal. Background spectrum was recorded one for all spectra using pure water. (B) Calibration curve using amide II band height.

Besides for bacteria, IR spectroscopy is frequently employed for spectroscopic studies of proteins.³⁸ The typically employed ATR configurations with only one active bounce however impede the application of ATR spectroscopy for low concentration protein measurements. The herein presented multi-bounce ATR crystals have effective pathlengths of up to 7 µm at 1640 cm⁻¹, being in the range of transmission cells employed for the same purpose but being difficult to handle.⁴¹ In Figure 4A, the spectra of the model protein Bovine Serum Albumin (BSA) in aqueous solutions for different concentrations are depicted. The amide I at 1653 cm⁻¹ and the amide II band at 1543 cm⁻¹ are well resolved. The height of the amide II band as a function of BSA concentration is given in Figure 4B demonstrating linearity down to a concentration of 2 mg mL⁻¹. This underlines the potential usage of the setup for investigation in biological matrices e.g. blood or milk.

**Curing of Adhesives.** IR spectroscopy has proven a great tool to study polymerization processes as it probes the characteristic vibrations of the molecule.⁴²,⁴³ Since the curing processes is strongly influenced by the applied film thickness, the possibility of reproducible deposition of the probed film is highly desired. In contrast to fiber optics or commercial single-bounce ATR setups, the presented exchangeable ATR crystals provide this degree of freedom. Due to their small footprint and low weight, they can be inserted into spin or dip-coating devices allowing for controlled film deposition. In addition, these ATR crystals can be heated to 400 °C overnight without decrease in performance, as shown in a previous study.⁴⁴ This is a crucial requirement as many adhesive cure upon heat treatment. By means of spin coating, a commercial two-component epoxy resin was applied to a Si ATR crystal and spectra were recorded immediately after deposition, after 30 min of curing at 100 °C as suggested by the supplier and after further curing for 24 h (see Figure 5).
After 30 min of curing, the band at 912 cm\(^{-1}\) associated with the epoxy ring has almost vanished, while the bands associated with the anhydride hardener at 1770 cm\(^{-1}\) and 971 cm\(^{-1}\) are not visible anymore (Figure 5). After 24 h of curing, no band at 912 cm\(^{-1}\) is visible and a full conversion of the epoxy group can be concluded.

In addition to the heat curing adhesive, the ionic polymerization of a cyanoacrylate adhesive (“super glue”) initiated by water in ambient air was monitored. To this end, the adhesive was applied to a Si ATR crystal into the open sample compartment with ca. 40% relative humidity. As the polymerization progressed, the vinyl group was consumed leading to decreasing bands that are associated with the C=C stretching vibration of this group at 3126 cm\(^{-1}\) and 1613 cm\(^{-1}\), respectively (compare Fehler! Verweisquelle konnte nicht gefunden werden.A). The area of the C-H stretching vibration was used to monitor the polymerization process and the evolution of the band area over time is given in Fehler! Verweisquelle konnte nicht gefunden werden.B. The reaction proceeded faster within the first 30 min, after which the reaction slowed down and the profile flattened out. In addition, the band of the adjacent nitrile moiety was shifted to higher wavenumbers from 2237 cm\(^{-1}\) to 2251 cm\(^{-1}\) due to the change in the chemical environment. All these findings are in good agreement with a previous report on a similar adhesive.\(^3\)

**Conclusions and Outlook**

In this work we demonstrate the combination of a 3D-printed ATR module using different low-cost and easily exchangeable ATR crystals embedded into commercial FTIR spectrometers. The low-noise levels and high pathlengths of the multibounce ATR crystals allow for high quality spectra acquisition beyond commercial ATR units. Processing a wide variety of samples, with the setup underlined the versatile nature of 3D-printed instrumentation: The ATR crystals withstand high temperatures, allowing for monitoring of polymerization processes. The easiness of exchanging the ATR elements indicates the implementation in applications requiring high sample throughput or complex sample handing. Moreover, the disposable character of the ATR elements and the overall ATR suggest the use in studies involving hazardous samples. Thus, the proposed setup may be used in further biological or life science applications.

**Table 2. Summary of costs for the 3D-printed ATR module.**

| Supplier                                      | Price [€] |
|-----------------------------------------------|-----------|
| Si: Double-side polished Si wafer, e.g. microchemicals, 100 mm | 24\(^a\) |
| Ge: Double-side polished Ge wafer, e.g. from university wafer, 50 mm | 200\(^\) |
| IRUBIS                                       | 70        |
| 27 m filament                                 | 2         |
| Adapter plate                                 | 223       |
| 2 x Gold mirrors\(^b\)                        | 108       |
| 4 x M6x10 mm screw                            | 1         |
| 4 x M3x5 mm screw                             | 1         |
| 2 x M2 nuts                                   | 1         |
| FKM O-ring                                    | 1         |
| **Total**                                     | **361 - 537\(^\)** |

\(^a\)up to 50 ATR crystals can be prepared from one wafer

\(^b\)in this study, gold-sputtered microscopy slides were used

\(^\)depending on used ATR crystal and availability of the adapter plate

Table 2 summarizes the costs of the used components and if assuming a 3D-printer is available as well as the spectrometer adapter plate that is typically delivered with the FTIR spectrometer for transmission measurements, this setup can be rebuilt overnight for less than 150 €. This is about 50 times less than the price of a commercial ATR unit. This low-budget setup allows for making the high versatility of ATR spectroscopy accessible to a broader audience. In addition, we are confident that only minor alteration of the ATR module, should allow for its incorporation into FTIR spectrometers of other manufactures. Lastly, the combination with novel light sources like quantum cascade lasers or pulsed small-footprint thermal emitters coupled with novel detector systems such as Fabry-Pérot filters, would allow to further miniaturize and 3D-print entire IR spectrometers.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.
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