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Broadband terahertz heterodyne spectrometer exploiting synchrotron radiation at megahertz resolution

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A new spectrometer allowing both high resolution and broadband coverage in the terahertz (THz) domain is proposed. This instrument exploits the heterodyne technique between broadband synchrotron radiation and a quantum cascade laser (QCL) based molecular THz laser that acts as the local oscillator (LO). Proof of principle for exploitation for spectroscopy is provided by the recording of molecular absorptions of hydrogen sulfide (H₂S) and methanol (CH₃OH) around 1.073 THz. Ultimately, the spectrometer will enable to cover the 1–4 THz region in 5 GHz windows at Doppler resolution.

Driven by the rapid technological innovation and availability of system components, modern laboratory molecular spectroscopy is undergoing rapid changes towards broadband and high resolution capabilities. Frequency-comb spectrometers now allow spectra to be recorded with unprecedented spectral resolution and sensitivity from the mid-infrared (mid-IR) to the extreme ultraviolet (see the review paper from Picqué and Hänsch [1]), while chirped-pulse instruments enable broadband investigations at centimeter and millimeter wavelengths (see Brown et al. [2] and a recent review from Park and Field [3]). Such breakthroughs are yet to impact the less mature terahertz (THz) domains (arbitrarily defined as 1–10 THz). Indeed, despite significant efforts to improve the coverage of this so-called “THz gap”, molecular spectroscopy in this region usually entails a compromise between wide frequency coverage and high resolution. While high resolution capabilities are fast expanding toward the THz domain, both from lower and higher regions of the electromagnetic spectrum, the challenge of wide tunability remains. Quantum cascade lasers (QCLs), for instance, now enables high precision molecular spectroscopy in the THz range but tuning of the single-frequency THz QCLs is often limited to several GHz [4]. Improvement in high frequency electronic

technology permits harmonic generation using Schottky diodes to reach frequencies as high as 4 THz although at such frequency the components are not commercially available and only cover narrow parts of the spectrum with relatively low power [5]. Numerous opto-electronic solutions heterodyning two continuous wave optical sources have been exploited in the past decades (see *e.g.*, Ref. [6]). This category of instruments has allowed many crucial measurements of THz spectra owing to excellent high-resolution but lacks of instantaneous broadband capabilities. Broadband THz measurements can be undertaken by time domain spectroscopy (TDS) [7], asynchronous optical sampling (ASOPS) [8], or Fourier-transform (FT) spectrometers, however at limited spectral resolution. The achievable resolution of TDS is, in principle, set by the mechanical delay line, typically to around 1 GHz. For ASOPS, the recording of spectra with a resolution better than the laser repetition rate is somewhat cumbersome, time consuming and only provides low sensitivity at the present time. FT spectrometers are the most widely used solution and the commercial instruments can provide an ultimate resolution of 30 MHz [9]. As a consequence, the frequency metrology of molecular absorption is often limited by the apparatus function, defined by the optical path length

difference of the instrument, rather than by the natural width of the transition (the Doppler width is around few MHz in this part of the electromagnetic spectrum).

Achieving combined broadband and high resolution spectroscopy in the THz domain would open new opportunities for molecular spectroscopy. It would enable the observation of, among others, fine physical effects (couplings) involving high-lying energy levels of molecules, large amplitude motions, and the rotational structure of heavy molecules with dense spectra. For this latter point in particular, above 1 THz, high resolution (*i.e.*, rotationally-resolved) spectroscopy is currently limited to molecules of 10–20 atoms in size [10]. The broadband THz gas phase observation at Doppler-limited resolution of large molecular species entirely relies on significant breakthroughs in the performance of THz instrumentation. Spectrometers based on the heterodyne technique appear as a promising approach to achieve this goal. In particular, important benefits from radioastronomy instrumentation allow the multiplexing of intermediate frequency (IF) signals using Fast Fourier Transform Spectrometers (FFTS) increasing by orders of magnitude the attainable instantaneous spectral bandwidth and the signal-to-noise ratio (SNR) of the IF spectra [11]. Alternatively, modern synchrotron facilities provide a stable, broadband, and relatively intense THz and far-infrared (far-IR) continuum exploited for molecular spectroscopy (see *e.g.*, Ref. [9]) while the use of mid-IR QCL as the pump source of far-IR molecular lasers has tremendously increased the number of accessible far-IR lasing frequencies [12].

In this letter, we report on a significant advancement toward broadband, high resolution spectroscopy in the THz domain. We previously have exploited heterodyne techniques to characterize at high spectral resolution the synchrotron emissions in various operation modes of the machine [13]. Here, we demonstrate the successful development of a new generation of heterodyne instrument mixing the bright synchrotron continuum with a QCL-pumped molecular laser (local oscillator, LO) [12] and using a Hot Electron Bolometer (HEB, Scontel) mixer. As a proof of concept, we measured several pure rotation absorption lines of gas phase hydrogen sulfide (H_2S) and methanol (CH_3OH) around 1.073 THz. By tuning to various LO frequencies, this spectrometer will ultimately allow to cover the 1–4 THz region in few GHz windows.

This broadband THz heterodyne spectrometer exploits the synchrotron radiation extracted by the AILES beamline of the SOLEIL synchrotron facility, which serves as a far-IR continuum source, and a new generation optically pumped far-IR molecular laser acting as the LO (Fig. 1). In this study, the synchrotron radiation continuum was optically filtered by both a black polyethylene film and a 900–1100 GHz bandpass filter (Thorlabs) reducing the 3.4 mW full-range mean-power to about 1.6 μW in the spectral range of interest. The beamline chambers, which were kept under secondary vacuum, and our set-up for measurements at atmospheric pressure were separated by a 50 μm thick polypropylene window. After filtering, the beam was collimated using a 100 mm focal length plano-convex, aspheric polymethylpentene (TPX) lens and directed through a 55 cm long single-pass absorption cell equipped with 4 mm

thick polytetrafluoroethylene (PTFE) windows. A 300 mm focal length PTFE lens, placed near the cell output prevented large divergence of the synchrotron beam. The far-IR molecular laser is an optimized version of the prototype developed at IEMN [12] with an output power on the order of 0.5 mW thanks to a new waveguide and an optimized output coupler [14]. Using ammonia (NH_3) as a gain medium, this laser generates intense LO frequencies resulting from pure inversion transition in the $\nu_2 = 1$ vibrationally excited state. The upper level ($J = 3, K = 3$, symmetry "a") of the lasing transition is optically pumped by a free-running QCL laser (Ad-Tech Optics) using intense absorption lines from the ground state. Stimulated emission in the $\nu_2 = 1$ level is obtained using a 50 cm-long laser cavity built in a 6 mm-internal diameter copper tubing, a flat brass mirror with a 1.2 mm diameter hole in the center, and an optimized output coupler. In this study, the NH_3 pressure was set to about 15 μbar and a 1,073,049 MHz LO frequency was produced. The instantaneous laser linewidth was measured to be narrower than 100 kHz [15] and the laser power to be of a few hundreds of μW . The radiation was collected using a 200 mm focal length TPX lens and optically superposed to the synchrotron radiation exiting the absorption cell using a free-standing wire grid. Heterodyning of the two radiations was performed by the HEB optimized in the 0.3–4 THz range and exhibiting a double side band noise temperature ≤ 2000 K at 2.5 THz. Its low-noise cryogenically cooled high electron mobility high-electron mobility transistor (HEMT) intermediate frequency (IF) amplifier (25 dB gain) allows for 2.5 GHz instantaneous bandwidth. Owing to frequency refolding, the actual instantaneous frequency coverage is 5 GHz, and upper and lower sidebands can be discriminated by a slight tuning the laser frequency. The full IF bandwidth was amplified with an RF gain of 34 dB (Agile MwT AMT-A0032). The spectral analysis of the full IF bandwidth was realized using a FFTS (RPG-Radiometer Physics GmbH).

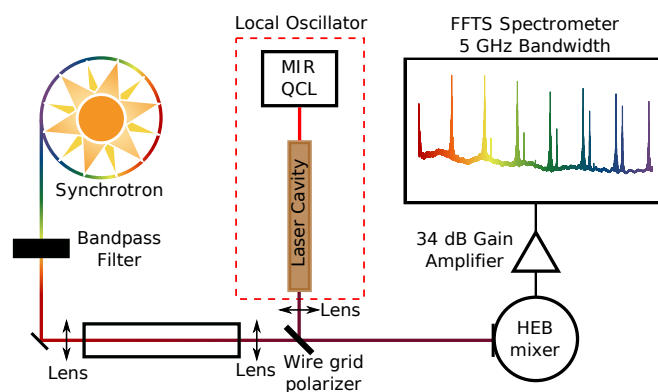


Fig. 1. Schematic representation of the broadband THz heterodyne spectrometer developed on the AILES beamline of the SOLEIL synchrotron.

In order to evaluate the performances of our spectrometer, the absorption spectra of hydrogen sulfide and methanol, two molecules exhibiting intense pure rotation transitions within a 5 GHz bandwidth around the 1,073,049.6 MHz LO frequency were recorded using a respective pressure of 30 and 70 μbar in

the absorption cell, and a 1 s acquisition time. Portions of the IF spectra showing the transitions recorded for each molecule are shown on Fig. 2. The spectra presented in Fig. 2 result from a post-processing adapted from Ref. [16] allowing to eliminate the contribution from the rectification (direct detection) of the modulation frequencies of the far-IR synchrotron continuum (Fig. 1). Due to this post-processing, intensity information can not currently be exploited. Several striking features of these plots have to be pointed out: i) the SNR ratio achieved in only 1 s of acquisition allows for the strongest transitions of both molecules to be observed; ii) the resolution of the instrument enables clearly the observation of two methanol transitions separated by 10 MHz (a third of the maximum resolution achievable using commercial FTIR interferometers); and iii) the linewidths are close to the expected Doppler widths allowing for accurate frequency determination. Two main spurious effects (laser frequency fluctuations and saturation of the HEB mixer), however, are worthy of improvements and are as discussed in the following paragraphs.

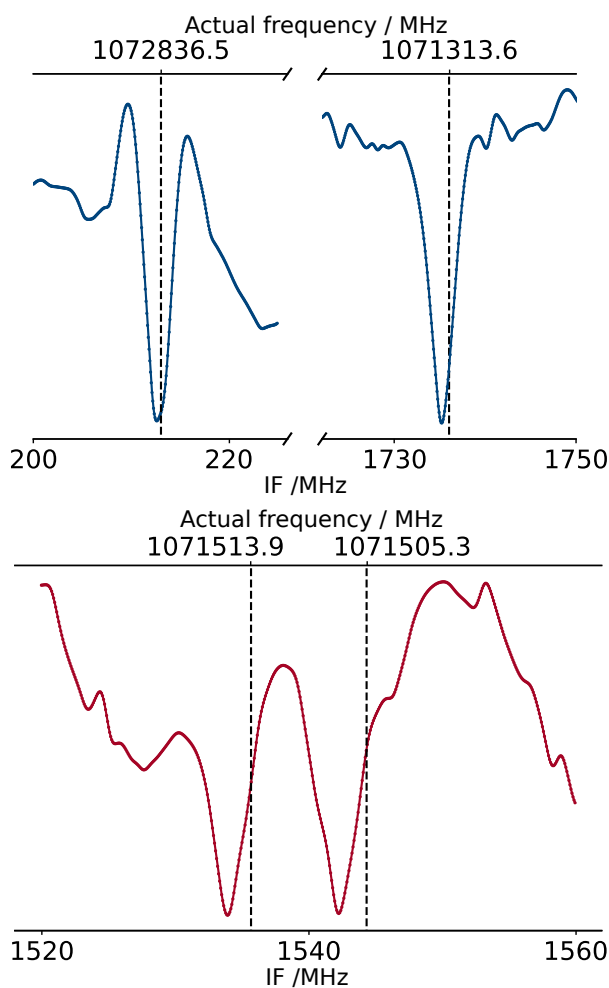


Fig. 2. Portions of the IF spectra extracted from the 2.5 GHz full bandwidth for the two test-molecules H₂S (top trace, in blue) and CH₃OH (bottom trace, in red). Both spectra were recorded in 1 s using the same 1,073,049 MHz LO frequency. The vertical dotted lines indicate the literature frequencies.

Because of rapid temperature changes, the free-running QCL suffered of frequency fluctuations inducing relatively large variations of the THz laser intensity and frequency (within the Doppler width of the THz transition). In these conditions, the mixer response was significantly affected yielding strong evolution of the baseline between consecutive scans. As a consequence, baseline compensation between two scans (*e.g.*, sample and reference spectra) is rather limited thus preventing from obtaining baseline flatness (Fig. 2). The actual noise level is very much smaller than it appears on the figure, but in the current configuration baseline fluctuations originating from the laser instability restrict the spectrometer performance. A second consequence of the THz laser frequency fluctuations is the observed shifts of the molecular transitions frequencies between successive scans. Since the center frequency of the successively recorded transitions can vary up to 1 MHz, averaging successive scans together yielded a broadening of the transitions. The FWHM of individual spectra is slightly larger the Doppler width of the transitions at room temperature, *e.g.*, 2.9 MHz measured for 2.2 MHz expected in the case of the hydrogen sulfide transitions.

Further insights in our frequency metrology can be provided by comparing the line frequencies of the measured transitions with accurate values from the literature [17, 18]. Because of their relevance to many scientific fields, the high resolution spectra of both H₂S and CH₃OH have been studied over a wide spectral region. Numerous articles have reported their pure rotation transitions that are summarized in databases such as the JPL [19] and CDMS [17] catalogs. In particular, H₂S pure rotation lines located above 1 THz have been measured with 100 kHz accuracy using a THz laser sideband spectrometer [20]. To the best of our knowledge the lines of methanol measured in the present work have not directly been measured. Xu *et al.* [21], however, reported a global treatment of a large data set including transitions observed at frequencies higher than 1 THz with an accuracy of 50 kHz thus frequency predictions reported in the CDMS database based on this work should be very accurate, to better than 100 kHz. The literature, when available, or predicted center line frequencies are reported in Fig. 2. Using our spectrometer, the line position accuracy is limited by the width of the absorption lines, their SNR ratio, and the LO frequency accuracy (both the numerical value used to convert IF into the actual frequencies and the laser frequency stability). Concerning the LO frequency value, Ref. [18] reported an experimental value of 1073049.5997 MHz accurate to 50 kHz. The deviation of our measurements from the literature values is about 600 and 300 kHz for the two lines of H₂S and 1.9 and 1.6 MHz for the CH₃OH ones. While the small frequency difference of the hydrogen sulfide transitions can be imputed to the laser frequency fluctuations, it is possible that the larger value observed for methanol is rather a reflection of the uncertainty in the frequency prediction. Since in the present configuration the limited LO frequency accuracy also yielded limited SNR ratio and broader transitions, stabilization of the LO frequency has to be undertaken before further assessments on the actual frequency accuracy of the measured transitions are made.

The line profile of the hydrogen sulfide transitions is worth

further discussion. While the line at 1,071,314 MHz displays close to a Gaussian profile, the second component at 1,072,387 MHz exhibits a second derivative-type profile. Since this line profile is only observed for one transition, we can exclude the Fourier Transform performed by the XFSTS or the baseline treatment to be responsible of it. Instead, we believe it may arise from saturation. Indeed, according to the JPL database [19], at room temperature this transition is supposed to be 6 times more intense than the lower frequency one. Since this intensity ratio is not reflected by our experimental measurements, such altered line profile of the stronger transition may be imputed to saturation effects.

Another source of noise in the spectra arises from the pulsed nature of the synchrotron emission which penalizes the operation of the spectrometer in two different aspects. First, direct detection of the pulse pattern provides intense frequency spikes on the IF spectrum. The rectification signal of the repetition rate (352 MHz) as well as the revolution frequency (846 kHz) give rise to two intense series of very sharp lines detected over the full IF bandwidth. Our post data treatment of the spectra was able to clean most of these spurious (see Fig. 1) but it prevents a rapid and more direct exploitation of the observations. Second, the relatively low average power (few hundreds of nW after filtering) translates into peak power of several watts for ps pulse duration. Such high power leads to rapid saturation of the HEB mixer and prevents the efficient mixing of the sources. Attenuation of such modulations of the THz continuum source is essential to improve further the sensitivity of the instruments.

Three major aspects of our spectrometer need to be upgraded: ultimate resolution, frequency coverage and SNR. From the LO side, it is clear that a better control of its frequency and intensity stability is highly demanded. Possibilities of locking the QCL frequency to standard frequencies is explored [15]. This new LO should provide the frequency metrology necessary to measure molecular adsorptions with sub-MHz accuracy on line position. It should also prevent the intense baseline variations detected on the IF spectrum which currently do not allow for longtime averaging and strongly decrease our ability to detect weak signals. A further benefit of the laser frequency stabilization will be the ability to finely tune its frequency over few MHz, enough to discriminate upper and lower contribution around the LO frequency. Additionally, a forthcoming laser cavity will soon permit to reach frequencies up to 6 THz, although the current HEB mixer will remain limited to 4 THz. A third important improvement should be performed to prevent HEB saturation. Time-stretching of the THz radiation by adapting technical concepts already developed for femto second lasers is currently under evaluation.

We demonstrated in this paper that the mixing of a pulsed source of THz continuum, here originating from synchrotron radiation, with a QCL-based molecular laser LO opens new possibilities for instantaneous broadband ultra-high resolution spectroscopy in this spectral region. The use of a HEB mixer together with a FSTS enables 5 GHz of instantaneous bandwidth to be recorded. This spectrometer displays broadband capacities in two aspects: its frequency coverage (provided by the numerous available LO laser lines) and its instantaneous

bandwidth. While all synchrotron-based far-IR spectroscopic stations over the world use FT spectrometers with an inherent limited spectral resolution, we demonstrated a new scheme of heterodyne detection for instantaneous broadband ultra-high-resolution spectroscopy, by gathering a set of non-usual equipment developed for radioastronomical THz studies. Specifications of this first prototype have been obtained from well-known molecules, and spectral resolution of the order of 1 MHz is clearly established, exceeding that of conventional FT instruments by at least one order of magnitude. Instrumental upgrades will enable an ultimate sub-MHz resolution (Doppler limited), a significant improvement in sensitivity (here, ability to record spectra over longer time period in order to improve the SNR and detect weaker signals), and a spectral coverage up to 4 THz. The 5 GHz instantaneous bandwidth, combined with the numerous THz LO frequencies, allow heterodyne spectroscopy to be performed over a wide spectral region covering most of the THz range. This spectrometer be complementary to current instruments available at synchrotron facilities, in a spectral region still difficult to access.

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