Unlocking synchrotron sources for THz spectroscopy at sub-MHz resolution

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Abstract: Synchrotron radiation (SR) has proven to be an invaluable contributor to the field of molecular spectroscopy, particularly in the terahertz region (1-10 THz) where its bright and broadband properties are currently unmatched by laboratory sources. However, measurements using SR are currently limited to a resolution of around 30 MHz, due to the limits of Fourier-transform infrared spectroscopy. To push the resolution limit further, we have developed a spectrometer based on heterodyne mixing of SR with a newly available THz molecular laser, which can operate at frequencies ranging from 1 to 5.5 THz. This spectrometer can record at a resolution of 80 kHz, with 5 GHz of bandwidth around each molecular laser frequency, making it the first SR-based instrument capable of sub-MHz, Doppler-limited spectroscopy across this wide range. This allows closely spaced spectral features, such as the effects of internal dynamics and fine angular momentum couplings, to be observed. Furthermore, mixing of the molecular laser with a THz comb is demonstrated, which will enable extremely precise determinations of molecular transition frequencies.

1. Introduction

Light sources in the THz spectral region, including globar and mercury lamps, quantum cascade lasers (QCLs), and harmonic or difference frequency generation sources, usually sacrifice either brightness or continuous coverage [1]. In comparison, synchrotron radiation (SR) maintains high brilliance over the THz range, resulting in a gain in signal-to-noise ratio (SNR) of spectroscopic measurements of up to 16, compared to laboratory continuum THz sources (globar, high-pressure mercury lamp) [2]. So far this source has been exploited for spectroscopy solely by Fourier-transform infrared (FTIR) techniques, due to the powerful multiplex advantage of interferometry. A major boundary for FTIR spectrometers, however, is their ultimate spectral resolution, which is constrained to about 30 MHz for commercial instruments. In comparison, transitions of room temperature gas-phase species in the THz range exhibit a Doppler full-width at half-maximum (FWHM) at least an order of magnitude lower than this (methanol transitions, for example, have a FWHM of about 2 MHz for frequencies around 1 THz). High-resolution THz spectroscopy has been demonstrated using a number of different techniques in the past, such as tunable far-IR spectroscopy [3], absorption spectroscopy using frequency multiplier chains [4–6] or difference frequency generation (DFG) [7,8], and, more recently, THz quantum cascade lasers (QCLs) used in direct absorption [9], hybrid comb [10], or dual-comb spectroscopy [11]. Using SR, an improvement in instrumental resolving power to match the best capabilities of other THz spectrometers, while maintaining the broadband advantage of SR, would enable a plethora of

new studies. Possible focuses include the couplings of angular momenta in molecules leading to fine and hyperfine splittings of rotational sublevels, intramolecular dynamics involving large amplitude motions, extensive and accurate linelists enabling detections of astronomical molecules, and metrological-grade measurements testing the validity of fundamental physics [12–14].

To reach the required level of precision for these studies with synchrotron-based spectroscopy, heterodyne detection provides a promising solution. Heterodyne detection relies on mixing the carrier light source (here the SR) with a local oscillator (LO). The frequency difference between the LO and the carrier light is the intermediate frequency (IF), which is the signal output by the mixer. In the heterodyne scheme, a key component is a stable, yet tunable, LO powerful enough to drive the mixer. High frequency electronics and QCLs routinely serve as LOs for THz heterodyne measurements (in particular for astrophysics), however they show limitations both in terms of emitted power and frequency coverage [1,12]. Difference frequency generation of THz light for heterodyne mixing is possible using photomixers fabricated on specific substrates [15,16], yet these schemes can suffer from low conversion efficiency and power instability. A recent breakthrough concerning optically pumped THz molecular lasers provides an attractive alternative LO: a continuous wave, mid-infrared (mid-IR), widely-tunable external cavity-QCL (EC-QCL) can pump a large number of molecular transitions, leading to a molecular laser with good coverage of the THz range [17–20]. The basic principle of the technique used in this work lies in mixing the intense THz SR (carrying molecular absorption information) with the THz output of a molecular laser in a superconducting hot electron bolometer (HEB). The IF signal is generated from DC to 2.5 GHz, where high-performance components such as low-noise amplifiers and fast Fourier transform (FFT) spectrometers are readily available. In the present work, the LO is a QCL-pumped molecular laser with drastically improved performance in terms of spectral coverage and stability (both frequency and intensity) compared to a prototype version that was used in a proof-of-concept demonstration of the heterodyne mixing technique [17,21]. The proof-of-concept instrument could only operate at the single, relatively low, frequency of 1.073 THz with a resolution limited to around 1 MHz. In contrast, the instrument presented here is a fully functioning spectrometer enabling sensitive sub-MHz resolution spectroscopy from 0.7 THz up to 5 THz. With the additional possibility of adding a THz comb for precise frequency metrology (to the kHz level), it could rapidly become the only instrument capable of advanced wide-range, ultra-high-resolution THz spectroscopic studies using SR. In this paper, the performance of the heterodyne instrument is discussed and compared with FTIR-based spectroscopy.

2. Methods

2.1. Synchrotron radiation

Both the THz heterodyne spectrometer and the FTIR spectrometer used in this work aim to record the spectral profile of THz SR after passing through an absorption cell containing a molecular species with pressure ranging from 1 to 50 µbar. These measurements were performed at the AILES beamline of the SOLEIL synchrotron facility [22]. In the synchrotron mode of operation in use for the work presented here, the synchrotron storage ring was filled up with 416 equally spaced electron bunches, for a total of 500 mA of current, which resulted in ~10 ps pulses of SR at a 352 MHz repetition rate.

2.2. THz heterodyne measurements

The working principle of the THz heterodyne spectrometer built for this study is shown in Fig. 1. A more detailed schematic can be found in the Supplement 1. In the mode of operation used for this work, SR passed through an absorption cell (60 cm length by 7 cm diameter with polypropylene windows), before it was mixed with the output of the molecular laser in a NbN

HEB (Scontel DU-RS 0.3-4T-0.1). This produced an IF signal from DC to 3 GHz, pre-amplified by a cooled high electron mobility transistor (HEMT) amplifier with +60 dB of gain. The molecular laser was pumped by a free-running mid-IR EC-QCL (MIRcat-1200, DRS Daylight Solutions) and was filled with 5-15 µbar (depending on the targeted pump transition) of either natural abundance NH_3 (Sigma-Aldrigh 99.98%) or isotopically enriched $^{15}NH_3$ (Eurisotop 99.6%). The wavelength of the pump laser was verified by rerouting the beam to a wavemeter (Bristol Instruments 771B-MIR). To optimize the HEB sensitivity, the output power of the molecular laser (100s of µW) was attenuated by a polarizing grid to a few µW. A diffraction echelette grating with 2.5 grooves per mm served to filter the incoming SR, which allowed bandpass tunability. This was implemented to avoid saturating the HEB with background noise from unused frequencies in the SR. The frequency band passing through the absorption cell was controlled by adjusting the angle of the grating.
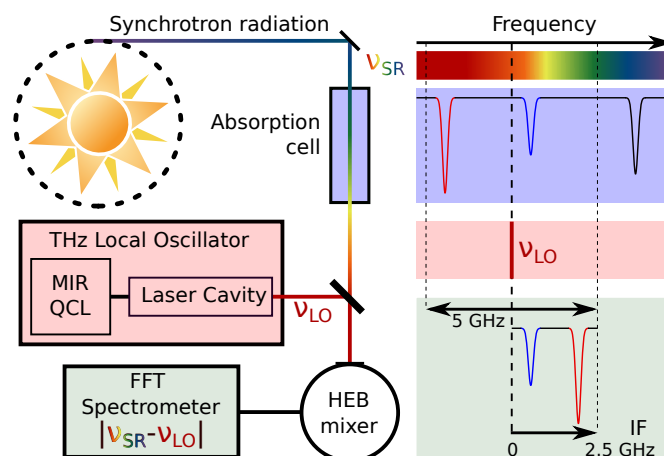
Fig. 1. Schematic representations of the THz heterodyne spectrometer (left) and recorded spectra (right). On the left-hand side, broadband SR passes through a gas-phase absorption cell before combining with the output of the mid-IR-pumped THz molecular laser in the HEB mixer. The IF output of the HEB, which contains both the upper sideband and the lower sideband of the mixing, overlaid from DC to 2.5 GHz, is analysed by the FFT spectrometer. The right-hand side shows the overlaid IF spectrum in the green box, which can be unfolded around the LO frequency in red, to give the original THz absorption spectrum in the blue box. The blue peak corresponds to an absorption originating from the upper sideband whereas the red peak represents an absorption originating from the lower sideband. Note that the beam path between instruments is at atmospheric conditions. More experimental details are given in the Supplement 1.

The laser beam and synchrotron beam were superimposed before the HEB by a 12 µm thick Mylar beamsplitter. Since the HEMT is prone to self-oscillation, a 6 dB attenuator (Mini-Circuits VAT-6+) was used as the first element in the IF signal chain to mitigate this behaviour. After the attenuator, the IF signal passed through a 34 dB gain amplifier (Agile MwT AMT-A0032), a 90-3000 MHz bandpass filter (Mini-Circuits SHP-100+), and a second amplifier of 20 dB gain (Mini-Circuits ZX60-V63+) before reaching the 2.5 GHz instantaneous bandwidth, 32,768 channel spectrum analyser (XFFTS, Radiometer Physics GmbH). Spectra presented in this work are an average of 105 repetitions of 1 s acquisition time each. The mixing produces an upper sideband and a lower sideband that are overlaid in the recorded spectrum, resulting in an effective bandwidth of 5 GHz for each scan. The absorption spectra presented in this work used around 50 µbar of methanol (Sigma-Aldrich 99.99%) or ethanol (Sigma-Aldrich 99.9%) in the absorption

cell. Portions of the absorption spectrum of methanol and ethanol were measured at room temperature using seven different LO frequencies (1035 GHz, 1044 GHz, 1073 GHz, 2029 GHz, 2065 GHz, 2822 GHz, and 3374 GHz). The raw spectra have been processed to remove spurious content, and to align the baseline, further details on data treatment can be found in the Supplement 1.

2.3. THz comb measurements

A THz frequency comb was used to demonstrate the possibility of making precise determinations of the frequency of the molecular laser output. The THz frequency comb was produced by focusing the output of a femtosecond laser (MenloSystem C-Fiber 780), emitting at 780 nm, onto a low-temperature-grown GaAs (LTG-GaAs) interdigitated photoconductor integrated with a spiral antenna built at the IEMN [23]. The IR comb produces a photocurrent oscillating at the repetition rate of the femtosecond laser, and its harmonics, inside the biased photomixer ($U = 5.3$ V and $I = 6.6$ µA) which causes the spiral antenna to radiate a THz frequency comb. The repetition rate of the femtosecond laser, which defines the THz comb spacing, was locked to a synthesizer (AnaPico APSIN20G) oscillating at 88.04905 MHz. The THz frequency comb was collimated by a hyperhemispherical silicon lens and overlaid with the molecular laser beam using the same 12 µm Mylar beamsplitter as used to overlay the SR and the molecular laser output in the THz heterodyne spectroscopic measurements.

2.4. FTIR measurements

The spectrum of methanol was also recorded by an FTIR spectrometer for comparison with the new THz heterodyne instrument. The FTIR spectrometer is a commercial Bruker IFS125 instrument, with an optical path difference (OPD) of 8.8 m, resulting in an ultimate resolution of about 0.001 cm^{-1} (or 30 MHz, as defined by Bruker). The absorption spectrum of methanol was recorded in the 50-300 cm^{-1} spectral range using an experimental set-up already described in numerous papers (see e.g. Reference [24]). Briefly, less than 1 µbar of methanol was injected in a room temperature cell equipped with multi pass optics aligned for a 140 m absorption pathlength. The cell was connected to the FTIR spectrometer, also under vacuum, via two 50 µm thick polypropylene film windows. The FTIR was equipped with a 6 µm thick composite-Mylar beamsplitter and a liquid-He cooled Si-bolometer. The acquisition time was 20 h. The FTIR spectrum has been calibrated using residual water transitions in the spectrum, and was up-sampled with a zero padding factor of 2.

3. Results and discussion

Methanol in particular has an intense, yet complex (due to internal rotation of the methyl group with respect to the hydroxyl group) absorption spectrum spanning the THz range, making it a useful molecule for benchmarking THz spectrometers [25–28]. The methanol spectra recorded with the THz heterodyne spectrometer show very good signal-to-noise ratio (SNR) after only 105 seconds of acquisition time (Fig. 2.). These spectra can be directly compared with an absorption spectrum recorded over 20 hours at 30 MHz resolution using the FTIR spectrometer. The FTIR spectrum allows a broadband view of the THz absorption of methanol, revealing thousands of lines over the 3 THz of bandwidth presented in Fig. 2. However, the FTIR apparatus function dominates the spectral profile, preventing the identification of spectral features separated by less than 30 MHz. Because of this, intramolecular dynamics of the internal rotor large amplitude motion of methanol, which leads to fine splitting of each rotational transition, are obscured in the FTIR spectrum yet appear nicely resolved in the heterodyne spectrum. An example of this case is evident in Fig. 2(c). The number of observed transitions for each LO used in the THz heterodyne spectrometer is given in Table 1, along with some average fitting parameters.
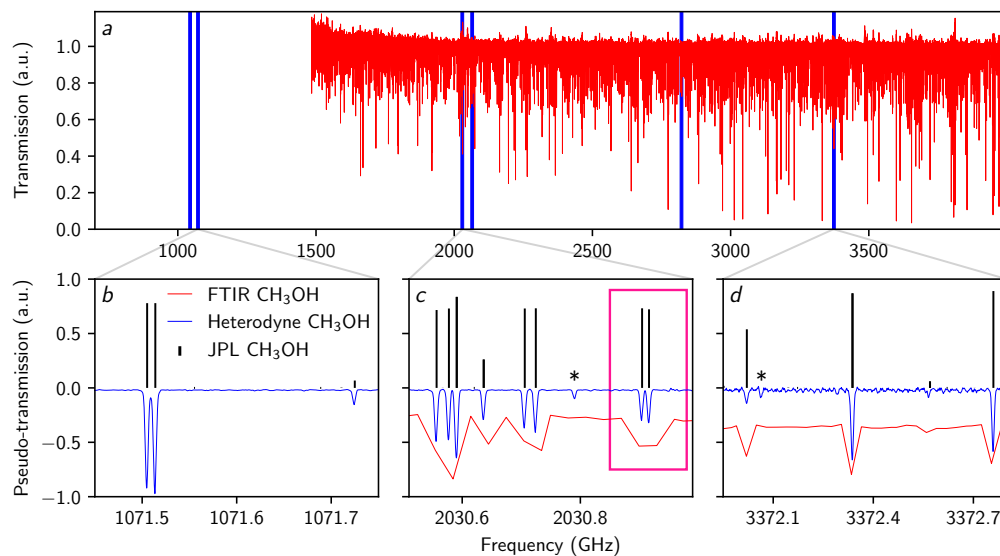
Fig. 2. Comparison of a methanol transmission spectrum recorded by the FTIR spectrometer with methanol pseudo-transmission spectra recorded by the THz heterodyne spectrometer. **a**, The FTIR spectrum below 4 THz (red) with the position of six LO frequencies used in the heterodyne THz spectrometer (blue lines). The broadband FTIR measurement is limited at the low-end to around 1500 GHz by reduced transmission of components in the instrument. **b**, **c**, **d**, Partial portions of spectra recorded by the THz heterodyne spectrometer (blue) at LO frequencies of 1073 GHz (**b**), 2029 GHz (**c**), and 3374 GHz (**d**) along with the FTIR spectrum (red). Peaks originating from the opposing sideband from the one displayed are marked with an asterisk. Transition frequencies of methanol taken from the JPL database are shown as black lines (Ref. [29]). Highlighted in pink in **c** is an example of a torsional fine splitting.

The dual-sideband nature of recordings produced using the heterodyne experiment creates some ambiguity concerning the absolute transition frequencies: since the recorded spectrum includes both the upper sideband (ν_{SR} - ν_{LO}) and lower sideband (ν_{LO} - ν_{SR}) there are two possible original THz frequencies for any peak observed in the IF spectrum. A tunable LO provides a mechanism to assign these recorded peaks to a particular sideband. By making a small change to the mid-IR output frequency of the QCL, the THz output of the molecular laser can be slightly detuned by around 1 MHz [19]. Figure 3(a) shows the shift in IF of the observable transitions caused by this change. The direction of that shift reveals whether the transition originated from the upper sideband or the lower sideband, allowing unambiguous assignments.

An important parameter of the instrument is its ability to measure precise molecular absorption frequencies. Thanks to the high resolution of the heterodyne spectrometer, the absorption lineshapes can be well fit to a Voigt profile, as demonstrated in Fig. 3(a). The measured Gaussian FWHM values across the spectral range match well with the expected room temperature Doppler broadening values (Fig. 3(b)), highlighting the low apparatus function broadening of the heterodyne instrument. The centre frequency of the highest SNR lines in this dataset could be fit with a 95% confidence interval of 10 kHz, more than two orders of magnitude better than the typical precision reachable using an FTIR spectrometer.

Although the peak position can be precisely determined in the IF spectrum, determining an accurate value for the transition frequency in the THz range is more challenging. The frequencies of the upper and lower sidebands recorded in each heterodyne measurement were inferred

Table 1. List of combinations of different LO frequencies (and the associated laser gain molecule) and absorbing molecules. The number of transitions fitted in each spectrum is reported together with the weighted average offsets of the experimentally-determined transition frequencies from their literature values, and the weighted averages of the Gaussian FWHM values of the fit transitions for each LO.

LO transition frequency (GHz)[a]	LO transition uncertainty (MHz)[a]	Molecular laser target molecule	Molecule studied	Number of transitions fit[b]	Weighted average frequency offset of fits from expected value (MHz)[c,d]	Weighted average Gaussian FWHM of fits (MHz)[c]
1035.2013	3 to 30	$^{15}NH_3$	Ethanol	12	2.58(7)	1.83(17)
1044.4973	3 to 30	$^{15}NH_3$	Methanol	2	2.19(3)	2.23(15)
1073.0499	0.3 to 3	$^{14}NH_3$	Methanol	4	-0.41(8)	2.51(22)
2029.2005	0.3 to 3	$^{14}NH_3$	Methanol	26	-0.80(20)	4.64(8)
2064.9399	3 to 30	$^{15}NH_3$	Methanol	4	-0.29(31)	4.60(32)
2822.2564	0.3 to 3	$^{14}NH_3$	Methanol	1	0.35(5)	5.87(17)
3373.6128	0.3 to 3	$^{14}NH_3$	Methanol	7	-1.04(54)	7.54(60)

[a]All ammonia transitions targeted for the output of the molecular laser originate from the $\nu_2 = 1$ state of ammonia. The frequencies and uncertainties were taken from the latest HITRAN database (Ref. [30]). The $^{14}NH_3$ transitions listed in HITRAN are based on work by Yu *et al.* (Reference [31]), whereas the $^{15}NH_3$ transitions are based on work by Canè *et al.* (Ref. [32]).
[b]Doublets with less than 10 kHz splitting were considered as a single transition with identical broadening parameters and an averaged position. Some transitions were not appropriate for fitting due to low signal, overlapping features, or spurious interference. The full list of methanol transitions used in this work is given in Table S1.
[c]Transitions were fit to a Voigt profile with the Lorentzian component fixed to the FWHM pressure-broadening value predicted using the HITRAN self-pressure broadening rate of 12 MHz mbar^{-1} for methanol transitions (Ref. [30]). The validity of the HITRAN pressure-broadening rate is discussed in the Supplement 1. The averages were calculated using individual values weighted to the inverse of their uncertainties. The uncertainty of the weighted averages is the 95% confidence interval (CI) $1.96\ \sigma\ (N)^{-1/2}$ where σ is the (weighted) standard deviation and N the number of data points where $N > 2$. For $N = 1$ the uncertainty is the 95% CI of the fit parameter, whereas the uncertainty for $N = 2$ is 0.5 $(\delta x^2 + \delta y^2)^{1/2}$ where δx and δy are the uncertainties of the two data points.
[d]The fit line positions do not include any treatment of possible pressure shifts although, based on the pressure shift data determined by Slocum *et al.* around 1.49 THz (Ref. [33]), a shift of around ±20 kHz would be present, on average, for the transitions reported here.

assuming an LO frequency equal to the HITRAN literature frequency of the ammonia transition involved in the lasing scheme [30]. These literature values are generally based on empirical fitting of FTIR measurements, and hence have a relatively large typical uncertainty of around 1 MHz for $^{14}NH_3$ and around 10 MHz for $^{15}NH_3$. Tuning the parameters of the molecular laser, namely the mid-IR QCL frequency and THz laser cavity length, to maximize the THz power, provides a THz laser frequency very close to the centre frequency of the targeted transition [19]. However, although the instantaneous linewidth of the molecular laser is small (less than 10 kHz), the instantaneous frequency can vary from the targeted NH_3 transition frequency by 100s of kHz, due to Doppler broadening of the mid-IR pump transition and the free-running nature of the QCL [17,19]. An absolute determination of the LO frequency (and therefore the THz transition frequencies of all molecular lines identified in the heterodyne spectra) is therefore necessary. This could be made by systemically mixing the output of the molecular laser with a THz frequency comb of a precisely defined repetition rate [34–36]. A demonstration of this approach was performed with an LO frequency of 1073 GHz, depicted in Fig. 4. By fitting the predicted beat notes arising from mixing between the THz comb and the LO to the recorded beat spectrum (56 notes in total over the 2.5 GHz bandwidth of the FFTS), it is possible to determine the frequency of the LO to less than 20 kHz uncertainty (95% CI of fit) for a total recording time of 5 seconds.

The possibility to mix the LO with a THz frequency comb has important implications for future versions of the spectrometer. Currently, the low frequency (1-100 Hz) frequency instabilities of
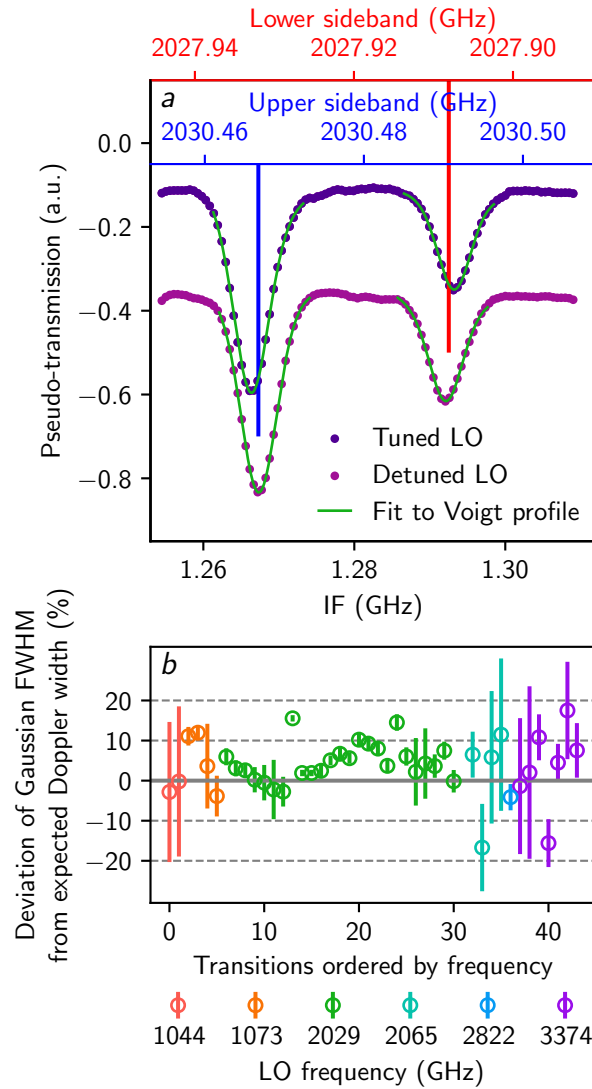
Fig. 3. a, the spectrum of methanol recorded by the heterodyne spectrometer with tuned QCL settings (purple, $\nu_{LO} = 2029$GHz), and the same spectrum recorded after slightly detuning the QCL (magenta). Since the LO frequency is red-shifted after detuning, peaks in the IF that are also red-shifted must originate from the lower sideband. Alternatively, peaks in the IF that are blue-shifted must originate from the upper sideband. The methanol transitions from the JPL database (Ref. [29]) corresponding to the upper sideband (blue) and lower sideband (red) are indicated. Also included is a fit of a Voigt profile to the recorded peaks (green). The data has been smoothed and resampled by a factor of 1/7. **b**, The deviation in percent of the fit Gaussian FWHM value from the expected value (the calculated FWHM Doppler broadening with temperature = 292 K) for each fit methanol transition, coloured by the different LOs.

the free-running QCL (which are divided by about 30 when transferred to the THz laser output [18,19]) limit the effectiveness of averaging beyond 1 minute of acquisition time. Therefore, the sensitivity of the instrument would greatly increase by phase-locking the output of the
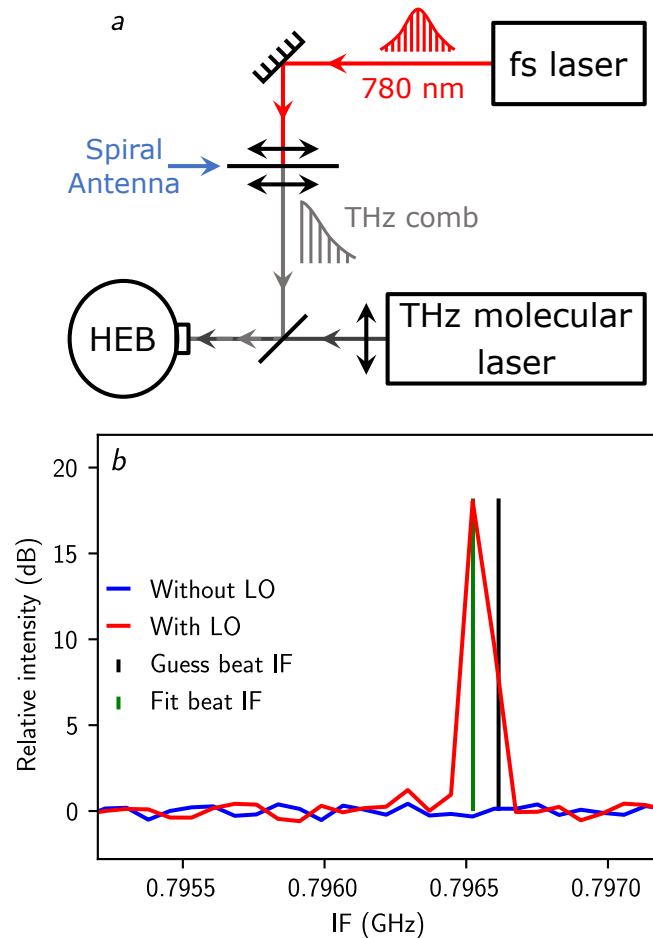
Fig. 4. Example of molecular laser output beating with a THz comb. **a**, schematic of the THz frequency comb generation and its mixing with the output of the molecular laser. **b**, a portion of the recorded spectrum of the THz frequency comb without the LO (blue) and with the LO (red). The observable peak is the beat note arising from mixing between the 12196th mode of the comb, which has a frequency of 1073.84621 GHz (see methods), and the LO (ν_{LO} = 1073 GHz). Also included are the predicted positions of the beat note using either a guess LO frequency which assumes the HITRAN (Ref. [30]) value of the targeted ammonia emission (black), or the value resulting from a fit of the LO frequency to the 56 different beat notes recorded across the 2.5 GHz IF range (green). We find a shift of +90 kHz when comparing the guess LO frequency and the fit LO frequency. The fit assumes mixing between well-determined THz comb frequencies and an uncertain LO frequency. Additional uncertainty on the fit LO frequency introduced by the error in the repetition rate of the femtosecond laser becomes negligible when this error is below 1 ppb, which is achievable with commercial GPS-disciplined reference clocks.

QCL. This is possible by feeding the beat signal of the THz molecular laser with the THz frequency comb standard into a phase-locked loop controlling the QCL current. This approach has been demonstrated to provide excellent frequency and power stability using a molecular laser similar to that used in this study [19], and metrological-grade THz sources have been created using a THz QCL locked to a THz comb [37]. Additionally, a more stable LO would improve

the frequency accuracy of the derived molecular transition frequencies. The THz heterodyne spectrometer presented in this work could determine transition frequencies to within less than 20 kHz uncertainty using a phase-locked LO, which is comparable to the best THz spectroscopic techniques available to date [12].

It is important to note that the spectral coverage of the THz heterodyne spectrometer clearly depends on the library of THz LO frequencies that can be produced by the molecular laser. This library is expanding to the point where it will allow no-gap THz coverage [20,38]. To fully benefit from this catalogue it will be necessary to limit strong atmospheric water vapour absorption, possibly by using an evacuated or purged beam path. Finally, a straightforward gain in sensitivity can be made by using a longer absorption pathlength cell. For instance, coupling the multi-pass absorption cell used for the FTIR spectrometer measurements with the THz heterodyne spectrometer would result in a gain of two orders of magnitude in sensitivity.

4. Conclusion

A new spectrometer based on heterodyne mixing between SR and an EC-QCL-pumped molecular laser has been demonstrated to operate between 1 to 3.3 THz, at 80 kHz resolution with high sensitivity. The instrument can be coupled with a THz frequency comb for precise determinations of transition energies. The range of the instrument is extendable to 5.5 THz, while the frequency accuracy and sensitivity of the instrument can be improved through a range of measures. Even without the implementation of these improvements, based on the high performance of the instrument demonstrated in this work, both in terms of sensitivity and resolution, the synchrotron-based THz heterodyne spectrometer will prove to be a valuable tool for molecular physics studies in the THz domain.

Disclosures. The authors declare no conflicts of interest.

Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

Supplemental document. See Supplement 1 for supporting content.

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