Spectrally resolved thermal emission of atmospheric gases measured by laser heterodyne spectrometry

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Received 22 June 2018; accepted 11 July 2018; posted 12 July 2018 (Doc. ID 335850); published 3 August 2018

The demonstration of thermal infrared quantum cascade laser heterodyne spectrometry to resolve local thermodynamic equilibrium molecular emission lines from earth’s atmospheric constituents is presented. The instrument is described, as well as the early steps towards radiometric calibration. Room temperature ethylene emission line measurements carried out in the laboratory are used to validate the instrument. High-resolution (0.02 cm⁻¹) emission lines from atmospheric carbon dioxide and water vapor are then recorded in a zenith-looking configuration and compared to a radiative transfer model and ideal instrument model expectations.

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OCIS codes: (010.0280) Remote sensing and sensors; (300.2140) Emission; (300.6310) Spectroscopy, heterodyne; (140.5965) Semiconductor lasers, quantum cascade.

https://doi.org/10.1364/OL.43.003810

High spectral resolution remote sounding of infrared molecular emission provides quantitative characterization of distant molecular samples through the extraction of thermo-physical information contained in spectral lineshapes such as temperature, pressure, local thermodynamic equilibrium (LTE), velocity, and electromagnetic field. This is a versatile and highly selective remote analysis method. When applied to fundamental ro-vibrational molecular bands lying in the long wave and far infrared, atmospheric molecules at LTE and ambient temperatures produce small radiance contrasts that often require large, complex, and cooled spectrometers [1] to be spectrally resolved. Relying on pure molecular emission signals for remote sounding, while challenging, does not require solar illumination, which is an important benefit, especially in the long wave infrared (LWIR), where atmospheric scattering is insignificant. For instance, while ground-based high-resolution spectrometers operating in solar occultation mode deliver high signal-to-noise ratios (SNRs) due to the intense solar background, they require active following of the sun and cannot operate under cloudy conditions or at night.

Spectrally resolved infrared emission sensing is operationally carried out with Fourier transform spectrometers (FTSs). This includes space-borne systems operating in the limb emission sounding mode such as the Envisat/MIPAS [2] and Aura/TES [3]. High-resolution FTS instruments are powerful, but large and complex. Alternatively, when high spectral resolution is needed, laser heterodyne spectro-radiometry (LHR) is an attractive technique. As spectral filtering is done in the radio-frequency (RF) domain [4], optical instrumental background radiation is limited, which is a particular advantage for the small radiance contrasts observed in the LWIR.

High-resolution LHR emission spectroscopy in the LWIR has been reported only in the context of planetary atmosphere remote sounding, predominantly for non-LTE molecular emission, where the high spectral resolution and narrow field-of-view of LHR is exploited. For example, early work demonstrated the resolution of the emission lineshape from carbon dioxide (CO₂) at ∼10 μm from which wind velocities in the upper atmosphere of Venus were deduced [5]. CO₂ emission in the Mars atmosphere at ∼10 μm [6], ammonia from the Jupiter atmosphere at ∼11 μm [7], and ethane emission from that of Titan at ∼12 μm [8] were also reported using LHRs.

To the best of our knowledge, high spectral resolution emission spectroscopy of the earth’s atmospheric constituents using LWIR LHR has never been reported, despite the usefulness of this approach for ground-based zenith measurements of greenhouse gases, pollutants, and tracers during day and night, and independently of the sun position. In this Letter, we report on the development, demonstration, and assessment of such an LHR for high-resolution LTE molecular thermal emission spectroscopy, and demonstrate a spectrally resolved atmospheric signal from CO₂ and water vapor (H₂O). First, the implementation of the breadboard instrument is described, as well as the rationale behind the design choices. Secondly, a first iteration of instrumental calibration is sketched out since, in contrast to transmission measurements, emission spectroscopy requires radiometric calibration to infer quantitative information from signals. Thirdly, the instrument demonstrator is
validated by measuring room temperature emission spectra of ethylene ($C_2H_4$) contained in a gas cell. Lastly, the instrument is coupled to a zenith-looking configuration to demonstrate clear sky atmospheric emission spectroscopy of H$_2$O and CO$_2$.

The instrument developed for emission spectroscopy is inherited from a quantum cascade laser (QCL) LHR operating in solar occultation mode, which has been fully described elsewhere [9]. However, it has been modified to meet the demands of LTE atmospheric emission spectroscopy.

The optical layout is shown in Fig. 1. The local oscillator (LO) optical path is depicted in red. The LO is a QCL operating at $\sim 953.1$ cm$^{-1}$, whose optical radiation is collimated (CL), attenuated (ATT), expanded, and re-imaged onto a liquid N$_2$-cooled, fast (1 GHz) HgCdTe photodiode (PD1). PD1 has not been optimized for the specific wavelength used in this demonstration, and its heterodyne efficiency $\eta$ has been estimated to be only $\sim 26\%$. Laser light transmitted through the beam splitter (BS) goes through a 3\° long etalon towards a second photodiode (PD2) for relative LO frequency calibration.

The LO can be continuously tuned from 952 to 956 cm$^{-1}$ by both temperature and current, though in normal operation the laser temperature is kept constant, and the frequency is tuned over $\sim 1$ cm$^{-1}$ by a current ramp applied on top of the fixed injection current. The current tuning also modulates the LO optical power, which needs accounting for in the calibration.

The signal path is depicted in blue. In normal operation, the radiation comes from the atmosphere and is focused onto the plane of a chopper (MOD) and re-imaged onto PD1 to be superimposed onto the LO field.

Compared to the LHR developed for atmospheric transmission spectroscopy in solar occultation, new additions included are depicted in green. A blackbody (B1) provides a cold reference against which the signals are measured. BB1 is a small cavity mounted onto the cold finger of a miniature Stirling cooler (Ricor K508). The temperature is measured by Pt100 platinum resistances to be $T_b \sim 60$–70 K, which ensures negligible radiance emission compared to the instrument noise floor. The image of the BB1 cavity is superimposed to that of the source at the plane of the gold-coated reflective chopper. In this way, the instrument measures the brightness contrast between BB1 and the scene using phase-sensitive detection.

A gas cell path for controlled LTE molecular emission spectroscopy was also added. To simulate a “deep space” background representative of a transparent atmosphere, BB2, identical to BB1, has been added behind the gas cell.

Lastly, the calibration target (BB3) is a further PID-controlled blackbody (Isotech Hyperion R), operated at temperatures spanning 263.15–293.15 K, hence covering a range representative of the lower troposphere.

Throughout the instrument, off-axis paraboloidal and elliptical gold-coated mirrors (OAPM and OAEM) have been used and aligned using the back-propagated LO methodology. The system optical efficiency $\kappa$ from BB2 or BB3 to PD1 is estimated as 67% from the optics specifications.

The RF processing chain after PD1 passes the intermediate frequency (IF) signal through an RF filter (50–350 MHz bandpass), which defines the double sideband bandwidth $B$ and spectral resolution as 600 MHz. The RF power is measured by a Shottky diode, whose output voltage is fed into a lock-in amplifier, which demodulates the heterodyne voltage signal $U_{\text{het}}$.

To inform the instrument calibration, a theoretical model of the LHR was considered [10,11] and adapted to the present case. The IF signal is produced by PD1; it passes through a low-noise pre-amplifier (input impedance $Z = 50$ $\Omega$, gain $G_1 = 36$ dB), followed by a second-stage amplification (gain $G_2 = 35$ dB). The IF signal power is filtered by the passband filter and converted into voltage by the Shottky diode (responsivity of $k_{\text{sd}} \approx 1200$ V/W). The heterodyne voltage measured is expressed by Eq. (1), where $e$ is the elementary charge, $h$ is Planck’s constant, $\nu$ is the photon frequency, and $P_i$ and $P_{\text{LO}}$ are the optical powers contributing to the heterodyne mixing, respectively, coming from the source and the LO:

$$U_{\text{het}} = 2k_{\text{sd}}10^{G_1/10}10^{G_2/10}Z \cdot \left(\frac{\eta e}{h \nu}\right)^2 P_i P_{\text{LO}}. \tag{1}$$

$P_{\text{LO}}$ is indirectly measured by the DC voltage component $U_{\text{dc}}$ from PD1, which has been calibrated using a power meter such that $P_{\text{LO}} = (-4.94 \pm 0.03) \times 10^{-4} \times U_{\text{dc}} - (3.3 \pm 0.2) \times 10^{-5}$. The radiant contrast flux $P_s$ received by the detector is expressed by Eq. (2), where integration over the receiver coherent etendue and bandwidth has been accounted for:

$$P_s = \frac{1}{2} \lambda^2 B \cdot (k_{\text{tgt}} \cdot L_{\nu}(T_{\text{tgt}}) - k_{\text{ref}} \cdot L_{\nu}(T_{\text{ref}})). \tag{2}$$

$L_{\nu}$ is the spectral radiance at frequency $\nu$, $T_{\text{ref}}$ refers to the cavity temperature of BB1, and $T_{\text{tgt}}$ refers to that of the target blackbody in the field-of-view. $k_{\text{tgt}}$ and $k_{\text{ref}}$ refer to the optical efficiencies of the target and reference optical arm, respectively. Here, for all practical purposes, the second term on the RHS of Eq. (2) is negligible.

Equations (1) and (2) indicate that at a given wavelength, $U_{\text{het}}$ is a bilinear function of the source spectral radiance and LO power. Therefore, the effect of the LO power modulation introduced by its continuous frequency tuning also needs to be calibrated.

Radiometric calibration is performed with the dedicated optical arm using BB3 and retaining the ideal physical model.
from Eq. (1). Heterodyne voltages are recorded as a function of $P_{\mathrm{LO}}$ and $P_S$. A subset of the calibration data is shown in Fig. 2, obtained while continuously tuning the LO for four different BB3 temperatures. For each measurement, 10 scans with an integration time per point of 50 ms were recorded, and the in-phase and quadrature components were averaged separately before calculating the signal magnitude. The $\sim 1 \text{ cm}^{-1}$ frequency tuning of the LO does not yield significant spectral radiance variation, so $L_e$ is assumed to be constant across the LO scan.

The linear fits to the experimental data are also shown in Fig. 2. For these, the least reliable data where $P_{\mathrm{LO}} < 90 \mu\text{W}$ have been discarded, since they are hardly discernable from the noise floor, especially at the lowest BB3 temperature. The theoretical ideal SNR can be calculated using equations provided in Ref. [11]. The values are $\sim 5$ and $\sim 9$ at $T_{\text{BB}}$ of 263.15 and 293.15 K, respectively, at the experimental conditions of Fig. 2. Using a hot blackbody (1323.15 K), the instrument was established to operate to within two times the ultimate shot noise limit at optimum $P_{\mathrm{LO}}$ levels ($\sim 200 \mu\text{W}$). The use of magnitude signals from the lock-in amplifier also produces a bias on near-zero signals, as negative signal fluctuations are rendered positive when the magnitude is calculated.

The averaged bilinear proportionality constant between $U_{\text{het}}$ and the product $P_S \times P_{\mathrm{LO}}$ derived from the calibration measurements is found to be $(6.5 \pm 0.3) \times 10^{12} \text{ V/W}^2$. In comparison, the theoretical value calculated from Eq. (1) is found to be $(7.3 \pm 1.3) \times 10^{12} \text{ V/W}^2$. Uncertainties on the calculated value are driven by the large uncertainties on amplifier gains and heterodyne efficiency.

For this first demonstration, the calibration model has been kept ideal. A more sophisticated model informed by further experimental analysis would be needed to fully describe the $U_{\text{het}}$ dependence and improve the calibration accuracy. An updated model would include effects such as background RF power in the signal or residual emission contributions from optics, their variations with LO power, and non-linearities. Evidence of additional effects can be seen in Fig. 2 for low levels of signal power, where data are better represented when adding a constant parameter to the linear dependence (green dashed lines). This is the scope for follow-on detailed investigations.

The ability of the LHR to spectrally resolve LTE molecular emission was first analyzed in the laboratory using gas cell analogs. Through modeling, low pressure $\text{C}_2\text{H}_4$ was found to be the most suitable test molecule within the LO tuning range. A glass cell of 10 cm length was filled with $\text{C}_2\text{H}_4$ at a total pressure of $20.0 \pm 2.0 \text{ mbar}$. The following experiments were conducted:

- The cell was placed in the LO path to record a high SNR absorption spectrum using direct tunable laser absorption spectroscopy (TLAS) for reference. An averaged spectrum is shown in Fig. 3(a).
- The cell was placed as indicated in Fig. 1, and BB2 was set to a high temperature (1323.15 K) to produce a strong background against which heterodyne transmission spectroscopy could be done. This produces good SNR spectra showing the influence of the instrument lineshape of the spectrometer, as shown in Fig. 3(b). Ten spectra acquired over 90 s each were averaged.
- Lastly, BB2 was replaced to provide a cold background (80 K) against which the LTE emission of ethylene at room temperature could be measured. This spectrum appears in Fig. 3(c). Ninety-nine spectra were averaged for a total acquisition time of 149 min.

All spectra were frequency calibrated using the transmission signals from the $3^\prime$ long germanium etalon. The absolute frequency calibration was provided by the ethylene frequency transitions taken from HITRAN 2012. A gas cell transmission model was fitted to the TLAS spectra using optimal estimation inversion. In Fig. 3(a), the model trace is shown in red. The residual from the fit is shown in the lower panel. The total ethylene pressure retrieved was $22.80 \pm 0.05 \text{ mbar}$. The quoted errors on total pressure only account for random instrument noise propagation. However, there is also a clear model error as the model fails to reproduce all the molecular transitions appearing in the experimental spectrum: either ethylene transitions are missing in the HITRAN2012 database or interfering molecules were present in the cylinder mixture.
Given the mixture specifications, the low pressure and short absorption path length, the latter explanation is less likely.

The heterodyne transmission spectrum in Fig. 3(b) was fitted similarly to the TLAS one, but with the addition of the instrument lineshape convolution. The unaccounted for lines create broader mismatch structures in the residual. The returned ethylene total pressure was 25.5 \pm 0.02 \text{ mbar}.

The emission spectrum in Fig. 3(c) was calibrated in spectral radiance and fitted using a simple isothermal radiative transfer model given in Eq. (3):

\[
L_v = L_{v, bb} \cdot e^{-\alpha(\nu)l_{\text{cell}}} + L_{v, \text{cell}} \cdot (1 - e^{-\alpha(\nu)l_{\text{cell}}}), \tag{3}
\]

where \( L_{v, bb} \) is the Planck spectral radiance from BB2 \((T = 80 \text{ K})\), and \( L_{v, \text{cell}} \) is that of the cell \((T_{\text{cell}} \approx 293 \text{ K})\); \( l_{\text{cell}} \) is the cell length; and \( \alpha(\nu) \) is the spectral absorption coefficient derived from HITRAN2012 molecular data. \( A_{bb} \) is an additional broadband absorption term found to be necessary to account for system losses not specifically captured by the model and for an additional baseline bias induced by laser excess noise. When operating in emission mode to capture molecular LTE signals, the contribution from in-quadrature laser excess noise becomes significant against emission signals. As a result, it adds a bias to the demodulated magnitude. This bias was also found to be slowly varying in time and will need to be better characterized and accounted for in subsequent developments of the instrument.

The fitted emission data returned a pressure of 19.5 \pm 0.2 \text{ mbar} and a broadband absorption contribution of 0.208 \pm 0.002. The pressure retrieved is comparable to the experimental value, despite the systematic, slightly varying bias to the baseline.

The emission measurements performed on the C\(_2\)H\(_4\) gas cell analog validated the tunable QCL LHR in the laboratory, as well as the overall approach to signal calibration. Laser noise related background issues were also identified as needing further investigation. The next step was to couple the instrument field-of-view to the clear sky and demonstrate the first measurement of spectrally resolved atmospheric emission lines of CO\(_2\) and H\(_2\)O from the ground, in a zenith viewing configuration.

With the same operating conditions, a set of spectra was collected over almost 1 h in mid-latitude summertime clear sky conditions. Each spectrum was acquired over 90 s, and Fig. 4 shows the averaged set. The heterodyne signal was calibrated into spectral radiance using Eqs. (1) and (2). A significant residual second-order polynomial baseline was subtracted, and the constant offset of the resulting spectrum was adjusted. The experimental data are shown as black crosses, a synthetic observation emulating measurement conditions as a blue line, and the same model with noise four times above the shot noise limit as red crosses. The model was produced using an observing system simulator [9] with a constant CO\(_2\) volume mixing ratio profile of 400 ppmv, and H\(_2\)O, temperature and pressure profiles from the closest available radiosonde station (Larkhill, no 3743, sonde released 23/08/2016 09:00 UTC).

The qualitative agreement between the traces is fair. The varying background observed during laboratory validation measurements [Fig. 3(c)] also shows in the atmospheric measurements. With noise levels \(\sim\)10 times above the shot noise limit, the instrument performs within acceptable limits, especially since the LO was observed to exhibit significant excess noise, compared to other QCL-based LHRs tested and operated in the mid-infrared.

The results demonstrate well the first measurement of spectrally resolved LTE emission from atmospheric constituents using a thermal infrared QCL-based LHR, as well as the first steps in producing calibrated spectral radiance data. These results are not yet sufficiently robust quantitatively to obtain meaningful geophysical data, and more work is required to develop this early proof-of-principle study to operational readiness. In particular, given the long integration times, both instrument and calibration stabilities require improvement.

Vertical sensitivity analysis suggests that such an instrument can provide information on the lower troposphere for CO\(_2\) and H\(_2\)O, and up to two independent pieces of information can be resolved (degrees of freedom for signal). This demonstration opens the path to using thermal infrared LHR for the characterization of earth’s atmosphere when direct sun occultation is not practical, for instance, for night time sounding.

The LHR performance can be further improved through spectral multiplexing, as used in astronomy [12], rather than sequential channel acquisition (LO scanning), as demonstrated with this early prototype. Implementing spatial multiplexing to obviate the limit of the single spatial mode field-of-view is another way to improve the instrument SNR, and both enhancement methods will be considered in the future following this demonstration Letter.

**Funding.** UK Space Agency (RP10G0348B201); Natural Environment Research Council (NERC) (NE/P003230/1).

**REFERENCES**

1. P. F. Bernath, Phys. Chem. Chem. Phys. 96, 177 (2000).
2. H. Fischer, Atmos. Chem. Phys. 8, 2151 (2008).
3. R. Beer, Appl. Opt. 40, 2356 (2001).
4. D. Weidmann, Rev. Sci. Instrum. 78, 073107 (2007).
5. E. C. Betz, Astrophys. J. 208, L141 (1976).
6. M. Mumma, Science 212, 45 (1981).
7. K. Fast, Icarus 156, 485 (2002).
8. T. Kostiuk, Geophys. Res. Lett. 32, L22205 (2005).
9. A. Hoffmann, Atmos. Meas. Tech. 9, 5975 (2016).
10. T. G. Blaney, Space Sci. Rev. 17, 691 (1975).
11. D. J. Wilson, Infrared Phys. 31, 109 (1991).
12. T. Kostiuk, Infrared Phys. Technol. 35, 243 (1994).