Impact of Lock-In Time Constant on Remote Monitoring of Trace Gas in the Atmospheric Column Using Laser Heterodyne Radiometer (LHR)

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Abstract: The time constant selected for lock-in amplification (LIA) has a crucial impact on observed line shapes in laser heterodyne spectroscopy, in particular in the case of ground-based remote monitoring of trace gas in the atmospheric column using laser heterodyne radiometer (LHR). Conventional simulation could not allow validation of LHR spectra measured in a real and complex atmospheric environment exhibiting large temporal and spatial variability (humidity, temperature, pressure, etc) that impact significantly the measured LHR spectra profiles. High-precision spectral measurement is thus crucial to avoid any spectral distortion resulting from the measurement. In this paper, the impact of LIA time constant on spectral line shape is investigated for LHR operating in continuous laser tuning mode, based on analysis of laboratory heterodyne spectra, in terms of signal-to-noise ratio (SNR), line width broadening, absorption depth and line shift. With respect to the given frequency scanning speed in continuous mode and to the halfwidth of the absorption feature to scan, a reasonable scanning time $\Delta T_{\text{scan}}$, the time needed for scanning laser frequency through the halfwidth $\Delta \nu_{\text{HWHM}}$ of the absorption line, equal to or longer than 14 times of the LIA time constant $\tau$ is concluded in order to efficiently reduce the noise while without significant shift and distortion of the line shape. Experimental validation was carried out using a laser heterodyne absorption spectroscopy approach in the laboratory. Four different combinations of time constants $\tau$ and scanning time $\Delta T_{\text{scan}}$ were used to record heterodyne spectra of a CH$_4$ absorption line near 1242.00 cm$^{-1}$ in continuous laser tuning mode. An optimal combination of a scanning time of 137 ms with a time constant of 1 ms was obtained. This optimal combination was used for ground-based measurements of CH$_4$ and N$_2$O in the atmospheric column by LHR. The extracted LHR spectrum is in good agreement with a referenced TCCON (Total Carbon Column Observing Network) FT-IR (Fourier-transform infrared) spectrum.

Keywords: lock-in amplification time constant; laser heterodyne spectrum; continuous tuning of laser frequency; high-precision; line shape; laser heterodyne radiometer

1. Introduction

Since the last decade, there has been a growing development of laser heterodyne radiometers (LHR) [1–5] for ground-based remote sensing of greenhouse gases (GHGs, such as nitrous oxide (N$_2$O), methane (CH$_4$), water vapor (H$_2$O), carbon dioxide (CO$_2$) and ozone (O$_3$) in the atmospheric column. Though the vertical air transport in the troposphere is smaller than in the longitudinal direction [6] but is nonetheless of critical importance for the study of pollutant transport, climate change, global environmental parameters
and anthropogenic effects on atmospheric chemistry [7,8]. Vertical concentration profiles of key atmospheric trace gases are essential in validating chemical transport models, satellite observations, and provide evidence for environmental assessment and policy formulation [9,10]. LHR exhibits its unique advantages in comparison with conventionally used Fourier-transform spectrometer (FTS) for ground-based measurements of vertical concentration distribution, which include high spectral resolution (<10$^{-3}$ cm$^{-1}$, mainly determined by the selected electronic filter bandwidths), high sensitivity (within a factor of ~2 of the quantum noise limit) [2], high spatial resolution owing to a very small field of view (~0.4 mrad, compared to ~2.4 mrad of the conventionally used FTS) and cost-effective compact instrumental dimension.

In an LHR system, a lock-in amplifier (LIA) is usually used to recover weak heterodyne signals buried in noise [11,12] through phase-sensitive detection (PSD) of signals and rejection of noises by a low-pass filter (whose cut-off frequency is determined by the LIA time constant $\tau$) [13]. Meanwhile, the used LIA time constant might significantly impact the line shape of the recorded LHR spectrum [3]. The impact of the LIA time constant on laser heterodyne spectrum measurements was discussed for LHR operating in point-by-point tuning mode of laser frequency, where a time interval (between two sampling points) longer than ~6 times of the LIA time constant $\tau$ should be used to avoid deformation of LHR spectrum line shape [4,5].

In this paper, we report on an investigation on the impact of LIA time constant $\tau$ on LHR spectrum line shape in continuous tuning mode of the laser frequency. Continuous tuning mode is particularly interesting in fast extraction of high-precision line shape of LHR spectrum compared with point-by-point tuning mode [14]. Relationship between scanning time $\Delta T_{\text{scan}}$ (the time needed for scanning laser frequency through the halfwidth $\Delta \nu_{\text{HWHM}}$ of the absorption line, which depends upon the frequency scanning speed $\nu_{\text{sc}}$) and the LIA time constant $\tau$ in continuous tuning mode of laser frequency has been experimentally investigated, which was then validated by laser heterodyne absorption experiment performed on the LHR measurement of the CH$_4$ absorption spectrum.

2. Materials and Methods

2.1. Principle of Laser Heterodyne Radiometer

The principle of LHR is schematically shown in Figure 1. In an LHR, the electromagnetic field of the sunlight $E_S(t) = A_{S0}(\omega_t)\cos(\omega_t t)$ at frequency $\omega_t$ is mixed in a photomixer with an electromagnetic field $E_L(t) = A_{L0}(\omega_L)\cos(\omega_L t)$ at frequency $\omega_L$ from a local oscillator (LO). A beat note at an intermediate frequency ($\vert \omega - \omega_L \vert$), produced from the photomixing, is amplified by a low-noise amplifier and filtered by a band-pass filter. This heterodyne signal is then square-law detected and fed into an LIA, the output of the LIA is sampled by a laptop for further data processing. The heterodyne absorption spectrum of atmospheric species can be recovered by scanning the LO frequency across the absorption line (leading to a change in intensity of the resulting radio frequency (RF) beat signal). The shape of the ground-recovered atmospheric absorption spectrum contains information on the vertical distributions of the target absorbers. It is possible to retrieve trace gas abundances at different altitudes through a retrieval algorithm based on an appropriate inversion model [3–5].
Figure 1. Basic principle of a typical laser heterodyne radiometer (LHR). RF: Radio frequency; IF: Intermediate frequency; LIA: Lock-in amplifier; LO: Local oscillator.

2.2. Analytical Model

In continuous tuning mode, deformation of the LHR spectrum line shape is mainly introduced in the process of signal demodulation of the LIA, in which the whole LHR spectrum passes through a low-pass filter of the LIA, the cut-off frequency and order of the low-pass filter may have different degrees of influence on the LHR spectrum.

The cut-off frequency (fc) of the low-pass (LP) filter is driven by the LIA time constant τ (in [s]) as $f_c = 1/(2\pi\tau)$ [15]. The time constant τ is a very critical parameter for the use of LIA, which impacts noise suppression and the line shape of the measured LHR spectrum. The longer time constant τ can significantly filter out noise, while it also results in a blue-shift of the spectral line center (shifting to the frequency scan direction/decrease in wavelength) and then distorts the line shape (becoming broadened and asymmetric) [15,16].

The frequency shift $\delta \nu$ can be approximately expressed by [17]:

$$\delta \nu = \frac{d\nu}{dt} \tau = \nu_sc \tau$$

(1)

where $d\nu/dt = \nu_sc$ is the frequency scanning speed in [cm$^{-1}$/s]. In continuous periodical scanning, the frequency scanning speed is the ratio of the frequency scanning range $\Delta \nu_{\text{scan}}$ to the scanning period $T$ (in [s]) that is the reciprocal of the scanning frequency.

In order to avoid deformation of the LHR spectrum line shape, the LIA time constant $\tau$ has to be appropriately chosen with respect to the time $\Delta t_{\text{scan}}$. Simulations of the impact of $\tau$ have been performed in order to investigate the optimal $\tau$ with respect to the experimentally applied frequency scanning speed. The effective transfer function of the LP filter (Figure 2) can be expressed by Equation (2).

Figure 2. Scheme of a LP filter. R is the resistor and C is the capacitor.

According to Kirchhoff’s Laws and the definition of capacitance:

$$V_{\text{in}}(t) - V_{\text{out}}(t) = RC \frac{dV_{\text{out}}(t)}{dt}$$

(2)
where R is the resistance and C is the capacitance of the LP filter. For simplicity, assuming that samples of the input and output are taken at evenly spaced points in time separated by $\Delta t$, Equation (2) can be expressed in terms of $V_{out}$ at time $k$, $V_{in}$ at time $k$ and $dV_{out}$ of $V_{out}$ at time $k$ and $k-1$, respectively:

$$V_{in}(k) - V_{out}(k) = RC \cdot \frac{V_{out}(k) - V_{out}(k-1)}{\Delta t}$$

(3)

Rearranging terms in Equation (3) gives a recurrence relation:

$$V_{out}(k) = V_{in}(k) \cdot \left( \frac{\Delta t}{RC + \Delta t} \right) + V_{out}(k-1) \cdot \left( \frac{RC}{RC + \Delta t} \right)$$

(4)

The first term on the right side of Equation (4) is the contribution from the input, and the second term is the inertia from the previous output. This differential model of the LP filter described in Equation (4) provides a way to determine the output data based on the input and the previous output values.

Based on Equation (4), the effect of the LP filter for frequency scan in continuous tuning mode is simulated by using a pseudocode algorithm with the help of Matlab. In the simulation, $V_{in}$ is a Hitran simulation spectrum of CH$_4$ around 1233.45 cm$^{-1}$ with an HWHM line width of 0.014 cm$^{-1}$, and $V_{out}$ is the simulation output resulting from different experimental parameters: scanning period $T$, scanning speed $\nu_{sc}$, scanning time $\Delta T_{scan}$ ($\Delta \nu_{HWHM}/\nu_{sc}$) over a spectral range of $\Delta \nu_{scan} = 1$ cm$^{-1}$, and time constant $\tau$. The simulation results are overviewed in Table 1 and presented in Figure 3.

**Table 1.** Simulation of LP filter effect on absorption line shape with different $\tau$. HWHM: Half Width at Half Maximum.

| Halfwidth $\Delta \nu_{HWHM}$ (cm$^{-1}$) | 0.014 | 0.014 | 0.014 | 0.014 | 0.014 | 0.014 | 0.014 | 0.014 | 0.014 |
|----------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Scanning range $\Delta \nu_{scan}$ (cm$^{-1}$) | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     |
| Scanning period T (s)                  | 0.3   | 0.5   | 1     | 1.5   | 2     | 2.5   | 3     | 5     | 10    |
| Scan frequency $\nu$ (Hz)              | 3.33  | 2     | 1     | 0.67  | 0.5   | 0.4   | 0.33  | 0.2   | 0.1   |
| Scanning speed $\nu_{sc}$ (cm$^{-1}$/s) | 3.33  | 2     | 1     | 0.67  | 0.5   | 0.4   | 0.33  | 0.2   | 0.1   |
| Scanning time $\Delta T_{scan}$ (ms)   | 4.17  | 6.95  | 13.9  | 20.85 | 27.8  | 34.75 | 41.7  | 69.5  | 139   | 417   |
| $\tau$ (ms)                            | 0.1   | 0.1   | 0.1   | 0.1   | 0.3   | 0.3   | 0.3   | 1     | 1     |
|                                        | 0.3   | 0.3   | 0.3   | 0.3   | 1     | 1     | 1     | 3     | 3     |
|                                        | 1     | 1     | 1     | 1     | 3     | 3     | 3     | 10    | 10    |
|                                        | 3     | 3     | 3     | 3     | 10    | 10    | 10    | 30    | 30    |
|                                        | 10    | 10    | 10    | 10    | 30    | 30    | 30    | 100   | 100   |
|                                        | 30    | 30    | 30    | 30    | -     | -     | -     | -     | -     |
|                                        | -     | -     | 100   | -     | -     | -     | -     | -     | -     |

As can be seen in Figure 3, when the scanning time $\Delta T_{scan}$ is 9–23 times of time constant $\tau$, the output spectrum (red) is almost consistent with the input spectrum (black) and the noise can be efficiently rejected without causing obvious shift and distortion of the line shape. The scanning time $\Delta T_{scan}$ (Table 1 in blue bold) as a function of the optimum time constant $\tau$ (Table 1 in red bold) is plotted in Figure 4. The mathematical relationship between the time constant $\tau$ and the scanning time $\Delta T_{scan}$ is obtained from a linear fit ($r^2 = 99.25$):

$$\Delta T_{scan} = \Delta \nu_{HWHM}/\nu_{sc} \geq 14\cdot \tau$$

(5)
Figure 3. Simulation of output spectra from the LP filter using different parameters (see Table 1), in comparison to the Hitran simulation of input spectrum of CH₄ near 1233.45 cm⁻¹.
As can be seen in Figure 3, when the scanning time $\Delta T_{\text{scan}}$ is equal to or longer than 14 times of the LIA time constant $\tau$ in order to efficiently reduce the noise without significant shift and distortion of the line shape. Based on Equation (5), with respect to the given frequency scanning speed in the continuous mode and to the halfwidth of the spectrum to scan, the reasonable scanning time $\Delta T_{\text{scan}}$ should be equal to or longer than 14 times of the LIA time constant $\tau$ in order to efficiently reduce the noise without significant shift and distortion of the line shape.

2.3. Experimental System Description

An experimental investigation has been performed on measurements of heterodyne spectra under different $\tau$ and $\nu_{ac}$ combinations, based on a blackbody simulating sunlight emission.

The developed proof of concept (PoC) LHR prototype operating in the mid-infrared (mid-IR) near 8 $\mu$m is schematically shown in Figure 5. As a typical LHR, it includes a sunlight collection system associated with a sun-tracker, a local oscillator (tunable laser source), a photomixer to generate the beating signal at RF, an RF receiver, a signal modulation and demodulation module, as well as a frequency metrology module (in our case, direct absorption of the target molecule in a 12.5 cm long single-pass reference cell was used). To characterize and optimize the performance of the developed PoC LHR, a stable blackbody (BB) source was used as sunlight. Heterodyne measurements of CH$_4$ absorption spectra were performed in the laboratory using a 12.5 cm single-pass absorption cell.

Radiation from the blackbody (BB, MODELS 67030, Newport Inc. Florida, USA) at 1000 °C was collected and collimated with off-axis parabolic mirror (OAPM) 1 ($f_1 = 120$ mm), then focused and directed by OAPM 2 ($f_2 = 75$ mm) towards a 12.5 cm long single-pass cell (Figure 5a) that was filled with CH$_4$ mixture in air at atmospheric pressure. The BB beam was filtered by an optical filter in germanium in order to let only the transmission of BB (BP) filter (Model 15542, Mini-Circuits®) that was filled with CH$_4$ mixture in air at atmospheric pressure. Heterodyne measurements of CH$_4$ absorption spectra were performed in the laboratory using a 12.5 cm single-pass absorption cell.

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![Figure 4. Plot of $\Delta T_{\text{scan}}$ vs. time constant $\tau$, associated with a linear fit.](image)

Based on Equation (5), with respect to the given frequency scanning speed in the continuous mode and to the halfwidth of the spectrum to scan, the reasonable scanning time $\Delta T_{\text{scan}}$ should be equal to or longer than 14 times of the LIA time constant $\tau$ in order to efficiently reduce the noise without significant shift and distortion of the line shape.

|                           | Value       | Standard Error |
|---------------------------|-------------|----------------|
| Intercept                 | 1.69483     | 3.38353        |
| Slope                     | 13.83824    | 0.36377        |
Springs, CO, USA) for measurement of the RF signal power that is proportional to the square of the input beat signal amplitude. The output signal from the square-law detector was demodulated with a lock-in amplifier (LIA, Model 5110, AMETEK Inc. Berwyn, PA, USA with time constant range: 1 ms–300 s.). A National Instruments data acquisition card (PCI 6251, NI Inc. Austin, TX, USA) was used to digitize the output signal from the LIA via a custom-written LabVIEW program. The data were then transferred to a laptop for further data processing.

Figure 5. (a) Schematic of the developed LHR prototype. BB: Blackbody; EC-QCL: external cavity quantum cascade laser; OAPM: Off-axis parabolic mirror; BS: Beam splitter; BP Filter: Band-pass filter; DAQ: Data acquisition card. (b) Picture of the mid-IR LHR receiver (without sun-tracker part). Red dot line: sunlight beam path; orange dot line: blackbody beam path; yellow dot line: He-Ne laser beam path; blue dot line: EC-QCL beam path; green dot line: combined LO-BB beams to the photomixer.
One part of the EC-QCL beam (transmitted by the BS) is directed to either a 12.5 cm long custom-made Fabry-Pérot etalon (with a free spectral range, FSR = 0.0333 cm$^{-1}$) for relative frequency calibration or to a single-pass cell filled with target gas sample for determination of the EC-QCL absolute frequency.

The LO laser frequency was scanned across an appropriate CH$_4$ absorption line (around 1233.46 cm$^{-1}$) by applying a sine-wave (with an amplitude of +3 V$_{pp}$ and an offset of +1.6 V$_D$ (limited by the EC-QCL structure) from a function generator to the PZT (Piezoelectric ceramic transducer) element of the EC-QCL. Heterodyne spectra of CH$_4$ absorption of the incident BB radiation (Figure 6, black) were recorded using four combinations of different $\tau$ and $\nu_{sc}$ (Table 2) and fitted to a Lorentz profile (Figure 6, blue and red).

Table 2. Used time constants at a given scanning speed of the LO frequency $\nu_{sc}$. (Note: the spectral half width $\Delta\nu_{HWHM}$ of the used CH$_4$ line around 1233.46 cm$^{-1}$ is 0.0538 cm$^{-1}$ [20] at ambient pressure).

| Scanning Frequency (mHz) | 20  | 50  | 100 | 250 |
|--------------------------|-----|-----|-----|-----|
| Scanning period $T$ (s)  | 25  | 10  | 5   | 2   |
| Scanning range $\Delta\nu_{scan}$ (cm$^{-1}$) | 0.787 | 0.787 | 0.787 | 0.787 |
| halfwidth $\Delta\nu_{HWHM}$ (cm$^{-1}$) | 0.0538 | 0.0538 | 0.0538 | 0.0538 |
| Scanning speed $\nu_{sc}$ (cm$^{-1}$/s) = $\Delta\nu_{scan}/T$ | 0.03148 | 0.0787 | 0.1574 | 0.3935 |
| Scanning time $\Delta T_{scan}$ (ms) = $\Delta\nu_{HWHM}/\nu_{sc}$ | 1709 | 684 | 342 | 137 |

| $\tau$ (ms) | 100 | 300 | 1000 |
|-------------|-----|-----|-------|
|             | 30  | 100 | 30    |
|             | 100 | 300 | 30    |
|             | 1000| 300 | -     |
Figure 6. BB-based heterodyne spectra of CH$_4$ absorption at different scanning speed ($\nu_{sc}$) (i.e., different given scanning time $\Delta T_{scan}$) combined with different time constants ($\tau$), respectively. Line shape fits were performed using the Lorentz profile (red or blue).
3. Results
3.1. Experimental Results

Based on the analysis of the heterodyne absorption spectra shown in Figure 6 (black), signal-to-noise ratio (SNR), line width broadening ($\Delta\nu_b$), absorption depth, line shift ($\delta\nu$), and noise level ($1\sigma$) of these spectra were analyzed and summarized in Table 3, the optimal time constants ($\tau$) at given scanning speeds of LO frequency ($\nu_{sc}$) and scanning times ($\Delta T_{scan}$) were obtained from the current work, as shown in Table 3 in bold and Figure 6 in red.

Table 3. Analysis of BB-based heterodyne spectra of CH$_4$ absorption at different scanning speeds of the LO frequency ($\nu_{sc}$) (i.e., different given scanning time $\Delta T_{scan}$) with different time constants ($\tau$).

| $\nu_{sc}$ (cm$^{-1}$/s) | $\Delta T_{scan}$ (ms) | $\tau$ (ms) | SNR | $\Delta\nu_b$ (cm$^{-1}$) | Absorption Depth (cm$^{-1}$) | $\delta\nu$ (cm$^{-1}$) | Fit Residual ($1\sigma$) |
|--------------------------|------------------------|-------------|-----|--------------------------|-------------------------------|--------------------------|--------------------------|
|                           |                        | 100         | 5   | 0.0554                   | 0.0126                       | 0.0032                   | 0.0026                  |
|                           | 300                    | 8           | 0.0656 | 0.0114 | 0.0095                   | 0.0015                  |
|                           | 1000                   | 8           | 0.0711 | 0.0062 | 0.0325                   | 0.0008                  |
|                           | 300                    | 5           | 0.0548 | 0.01258 | 0.0031                   | 0.00230                  |
|                           | 100                    | 6           | 0.0640 | 0.01244 | 0.0081                   | 0.00210                  |
|                           | 300                    | 8           | 0.0722 | 0.01154 | 0.0243                   | 0.00180                  |
|                           | 1000                   | 6           | 0.1222 | 0.00570 | 0.0821                   | 0.00089                  |
|                           | 100                    | 6           | 0.0650 | 0.01251 | 0.0016                   | 0.00230                  |
|                           | 300                    | 6           | 0.0627 | 0.01204 | 0.0048                   | 0.00209                  |
|                           | 1000                   | 7           | 0.0672 | 0.01101 | 0.0181                   | 0.00156                  |
|                           | 300                    | 7           | 0.0812 | 0.00824 | 0.0490                   | 0.00115                  |
|                           | 30                      | 7           | 0.0541 | 0.01261 | 0.0004                   | 0.00174                  |
|                           | 10                      | 9           | 0.0599 | 0.01181 | 0.0041                   | 0.00129                  |
|                           | 30                      | 8           | 0.0733 | 0.00736 | 0.0120                   | 0.00096                  |

As can be seen, the selection of the LIA time constant $\tau$ should be well matched to the scanning speed of the LO frequency as well as the scanning time. When the time constant is too small, the noise could not be efficiently removed. While a longer (than the optimal one) time constant would result in reduced absorption depth, a shift in absorption center frequency and distortion of absorption line shape.

Comparing the above four optimal combinations for heterodyne measurements, it is seen that the combination of the scanning speed of the LO frequency of 0.3935 cm$^{-1}$/s (the scanning time of 137 ms) and the LIA time constant of 1 ms could provide a relatively low noise level and the highest absorption depth without an obvious shift in absorption center frequency and distortion of the line shape. This relatively fast scanning time $\Delta T_{scan}$ of 137 ms makes it easier to acquire a fast extraction of the high-precision line shape of LHR spectrum. This combination was therefore selected for our further LHR measurements.

3.2. Field Measurement

Using the optimal combination of the scanning time of 137 ms and the time constant of 1 ms, the developed LHR instrument was deployed to a field campaign in Dunkerque (51.05°N/2.34°E) for ground-based remote sensing of greenhouse gases in the atmospheric column.

The LO laser frequency was scanned around 1262.00 cm$^{-1}$ to probe absorption lines of N$_2$O (at 1261.9871 cm$^{-1}$) and CH$_4$ (at 1261.6450 and 1262.2249 cm$^{-1}$). An RF filter of 225–270 MHz pass-band was used to remove 1/f noise as well as other extraneous noises.
outside of the bandwidth, and this pass-band resulted in a ~0.003 cm\(^{-1}\) double-sideband spectral resolution for the remote measurements.

The measured CH\(_4\) and N\(_2\)O heterodyne spectrum in the atmospheric column is presented in Figure 7 (blue curve), accompanied by a referenced TCCON (Total Carbon Column Observing Network) FT-IR (Fourier-transform infrared) spectrum (Figure 7 (red curve)) measured using a Bruker IFS 125HR FTS (resolution: 0.02 cm\(^{-1}\)) of the TCCON observation network [21] on the QualAir platform of University of Paris 6. As can be seen, the LHR spectrum, with higher SNR, is in good agreement with the referenced FT-IR spectrum. Due to interference of nearby water vapor absorption that changes with time and space [22], wings on either side of the LHR spectrum are sometimes slightly different from those of the referenced FT-IR spectrum. The overall spectral line shapes of both two spectra are well consistent. In comparison to FTS, LHR is more suitable for field deployment owing to its room-temperature operation capacity, compact size, and lightweight (0.6 \times 0.9 m\(^2\)/25 kg for the present LHR vs. 2 \times 4 m\(^2\)/700 kg for a traditional FTS).

![Figure 7. Atmospheric absorption spectrum of CH\(_4\) and N\(_2\)O recorded with a Bruker IFS 125HR Fourier-transform spectrometer (FTS) in Paris (in red), with our LHR in Dunkerque (in blue).](image)

4. Discussion

Study and experimental investigation of the impact of LIA time constant on observed LHR line shape in continuous tuning laser frequency mode are carried out. Based on the present work, the scanning time \(\Delta T_{\text{scan}}\) of laser frequency across the halfwidth of the absorption line \(\Delta \nu_{\text{HWHM}}\), the scanning speed of the LO laser frequency \(\nu_{\text{sc}}\) and the LIA time constant \(\tau\) should be appropriately matched such that \(\Delta T_{\text{scan}} = \Delta \nu_{\text{HWHM}} / \nu_{\text{sc}} \geq 14\tau\) in order to obtain high-precision heterodyne spectrum (with minimum line shift and line shape distortion). This relationship was validated by laser heterodyne measurements of CH\(_4\) absorption spectra in the laboratory using four combinations of different time constants \(\tau\) and scanning time \(\Delta T_{\text{scan}}\) in continuous tuning mode. The optimal combination of the scanning time of 137 ms and the time constant of 1 ms, which can efficiently reduce the noise without introducing obvious line shift and distortion, was therefore selected for ground-based measurements of CH\(_4\) and N\(_2\)O in the atmospheric column. The extracted LHR spectrum is in good agreement with a referenced TCCON FT-IR spectrum.

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References

1. Lu, X.; Huang, Y.; Wu, P.; Liu, D.; Ma, H.; Wang, G.; Cao, Z. Distributed Feedback Interband Cascade Laser Based Laser Heterodyne Radiometer for Column Density of HD and CH4 Measurements at Dunhuang, Northwest of China. Remote Sens. 2022, 14, 1489. [CrossRef]

2. Shen, F.J.; Wang, G.X.; Wang, J.J.; Tan, T.; Wang, G.S.; Jesek, P.; Té, Y.V.; Gao, X.M.; Chen, W.D. Transportable mid-infrared laser heterodyne radiometer operating in the shot-noise dominated regime. Opt. Lett. 2021, 46, 3171–3174. [CrossRef]

3. Lu, X.J.; Cao, Z.S.; Tan, T.; Huang, Y.B.; Gao, X.M.; Rao, R.Z. Instrument line shape function of laser heterodyne spectrometer. Acta Phys. Sin. 2019, 68, 064208. [CrossRef]

4. Tsai, T.; Rose, R.A.; Weidmann, D.; Wysocki, G. Atmospheric vertical profiles of O3, N2O, CH4, CCl2F2, and H2O retrieved from external-cavity quantum-cascade laser heterodyne radiometer measurements. Appl. Opt. 2012, 51, 8779–8792. [CrossRef][PubMed]

5. Wang, J.J.; Wang, G.S.; Tan, T.; Zhu, G.; Sun, C.Y.; Cao, Z.S.; Chen, W.D.; Gao, X.M. Mid-infrared laser heterodyne radiometer (LHR) based on a 3.53 µm room-temperature interband cascade laser. Opt. Exp. 2019, 27, 9610–9619. [CrossRef][PubMed]

6. Brasseur, G.P.; Jacob, D.J. Modeling of Atmospheric Chemistry; Cambridge University Press: Cambridge, UK, 2017; pp. 84–204.

7. Ehhalt, D.H. Concentrations and distributions of atmospheric trace gases. Ber. Bunsenges. Phys. Chem. 1992, 96, 229–240. [CrossRef]

8. Tsai, T. External cavity quantum cascade lasers for spectroscopic applications. Doctoral Dissertation, Princeton University, Princeton, NJ, USA, 2012.

9. Mahieu, E.; Duchateau, P.; Demoulin, P.; Walker, K.A.; Dupuy, E.; Froidevaux, L.; Randall, C.; Catoire, V.; Strong, K.; Boone, C.D.; et al. Validation of ACE-FTS v2.2 measurements of HCl, HF, CCl3F and CCl2F2 using space-, balloon- and ground-based instrument observations. Atmos. Chem. Phys. 2008, 8, 6199–6221. [CrossRef]

10. Marquart, S.; Ponater, M.; Mager, F.; Sausen, R. Future development of contrail cover, optical depth, and radiative forcing: Impacts of increasing air traffic and climate change. J. Clim. 2003, 16, 2890–2904. [CrossRef]

11. Scofield, J.H. Frequency domain description of a lock-in amplifier. Am. J. Phys. 1994, 62, 129–133. [CrossRef]

12. Wang, G.X.; Rebou, S.; Choque, J.; Fertein, E.; Chen, W.D. Circular regression-based dual-phase lock-in amplifier for coherent recovery of weak signal. Sensors 2017, 17, 2615. [CrossRef][PubMed]

13. SRS. About Lock-in Amplifiers. Available online: http://www.thinksrs.com/downloads/PDFs/ApplicationNotes/AboutLIAs.pdf (accessed on 16 May 2015).

14. Rohart, F.; Mejri, S.; Sow, P.; Tokunaga, S.K.; Chardonnet, C.; Darquié, B.; Dinesan, H.; Fasci, E.; Castrillo, A.; Gianfrani, L. Absorption line shape recovery beyond the detection bandwidth limit: Application to the precision spectroscopic measurement of the Boltzmann constant. Phys. Rev. A Am. Phys. Soc. 2014, 90, 042506–042630. [CrossRef]

15. Pelant, L; Valenta, J. Luminescence Spectroscopy of Semiconductors. Oxford Scholarship Online. 2012. Available online: https://oxford.universitypressscholarship.com/view/10.1093/acprof:oso/9780199588336.001.0001/acprof-9780199588336 (accessed on 1 May 2012).

16. Brodersen, S. Noise filter effects in recording spectroscopes. J. Opt. Soc. Am. 1953, 43, 1216–1220. [CrossRef]

17. Demtroder, W. Laser Spectroscopy: Basic Concepts and Instrumentation; Springer: Berlin/Heidelberg, Germany, 1996.

18. Kostiuk, T.; Mumma, M.J. Remote sensing by IR heterodyne spectroscopy. Appl. Opt. 1983, 22, 2644–2654. [CrossRef][PubMed]

19. Shen, F.J.; Akil, J.; Wang, G.X.; Poupin, C.; Cousin, R.; Siffert, S.; Fertein, E.; Ba, T.; Chen, W.D. Real-time monitoring of NO2 production in a catalytic reaction process using mid-infrared quantum cascade laser. J. Quant. Spectrosc. Radiat. Transf. 2018, 221, 1–7. [CrossRef]

20. Gordon, I.E.; Rothman, L.S.; Hill, C.; Kochanov, R.V.; Tan, Y.; Bernath, P.F.; Birk, M.; Boudon, V.; Campargue, A.; Chance, K.V.; et al. The HITRAN2016 molecular spectroscopic database. J. Quant. Spectrosc. Radiat. Transf. 2017, 203, 3–69. [CrossRef]

21. Té, Y.; Jesek, P.; Franco, B.; Mahieu, E.; Jones, N.P.; Paton-Walsh, C.; Griffith, D.W.T.; Buchholz, R.R.; Hadji-Lazaro, J.; Hurtmans, D.; et al. Seasonal variability of surface and column carbon monoxide over the megacity Paris, high-altitude Jungfraujoch and Southern Hemispheric Wollongong stations. Atmos. Chem. Phys. 2016, 16, 10911–10925. [CrossRef]

22. Kämpfer, N. Monitoring Atmospheric Water Vapour: Ground-Based Remote Sensing and In Situ Methods; Springer: New York, NY, USA, 2013; Volume 13, pp. 1–7.