

Supplementary material:

Mid-infrared multiheterodyne spectroscopy with phase-locked quantum cascade lasers

J. Westberg,^{1,a)} L. A. Sterczewski,^{1,2,a)} and G. Wysocki^{1,b)}

¹ *Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544, USA*

² *Faculty of Electronics, Wrocław University of Science and Technology, Wrocław 50370, Poland*

Derivation of confidence intervals for the measurements in dual-detector multiheterodyne spectroscopy

In the presented dual-detector multiheterodyne (MH) spectroscopic system, the measurement is performed by comparing two subsequent acquisitions, denoted as zero-gas (Z), and sample gas (G). In each acquisition, the MH signal is captured simultaneously from two detectors, denoted as sample (S), and reference (R). The optical transmission T of each mode of the laser interacting with the sample can be calculated as follows

$$T = \frac{\frac{P_{GS}}{P_{GR}}}{\frac{P_{ZS}}{P_{ZR}}} = \left(\frac{V_{GS}}{V_{GR}} \cdot \frac{V_{ZR}}{V_{ZS}} \right)^2, \quad (\text{S1})$$

where P_{ij} is the mean power of the MH beat note in each acquisition $i=\{G,Z\}$ and detector $j=\{S,R\}$, proportional to the mean squared voltage magnitude V_{ij} . Since each variable is obtained with some uncertainty, an error propagation analysis has been performed to determine the confidence interval for each measurement. The transmission function T is expanded into Taylor series:

$$T \approx T_0 + \frac{\partial T}{\partial V_{GS}} V_{GS} + \frac{\partial T}{\partial V_{GR}} V_{GR} + \frac{\partial T}{\partial V_{ZR}} V_{ZR} + \frac{\partial T}{\partial V_{ZS}} V_{ZS}. \quad (\text{S2})$$

The variance of a sum of two random variables X and Y can be expressed as $\sigma_{X+Y}^2 = \sigma_X^2 + \sigma_Y^2 + 2\sigma_{XY}$, where σ_X^2 is the variance of X , σ_Y^2 is the variance of Y and σ_{XY} represents covariance. There is no correlation between the two

^a J. Westberg and L. A. Sterczewski contributed equally to this work.

^b Author to whom correspondence should be addressed. Electronic mail: gwysoki@princeton.edu.

subsequent acquisitions, Z and G , but such correlation exists between the sample and reference channels, S and R , within a single acquisition. Thus we can write:

$$\begin{aligned}
\sigma_T^2 &\approx \left| \frac{\partial T}{\partial V_{GS}} \right|^2 \sigma_{GS}^2 + \left| \frac{\partial T}{\partial V_{GR}} \right|^2 \sigma_{GR}^2 + \left| \frac{\partial T}{\partial V_{ZR}} \right|^2 \sigma_{ZR}^2 + \left| \frac{\partial T}{\partial V_{ZS}} \right|^2 \sigma_{ZS}^2 + 2 \frac{\partial T}{\partial V_{GS}} \frac{\partial T}{\partial V_{GR}} \sigma_{GSGR} + 2 \frac{\partial T}{\partial V_{ZR}} \frac{\partial T}{\partial V_{ZS}} \sigma_{ZRZS} = \\
&= \left| \frac{\partial T}{\partial V_{GS}} \right|^2 \sigma_{GS}^2 + \left| \frac{\partial T}{\partial V_{GR}} \right|^2 \sigma_{GR}^2 + \left| \frac{\partial T}{\partial V_{ZR}} \right|^2 \sigma_{ZR}^2 + \left| \frac{\partial T}{\partial V_{ZS}} \right|^2 \sigma_{ZS}^2 + 2 \frac{\partial T}{\partial V_{GS}} \frac{\partial T}{\partial V_{GR}} \rho_{GSGR} \sigma_{GS} \sigma_{GR} + \\
&\quad + 2 \frac{\partial T}{\partial V_{ZR}} \frac{\partial T}{\partial V_{ZS}} \rho_{ZSZR} \sigma_{ZS} \sigma_{ZR},
\end{aligned} \tag{S3}$$

where σ_{ij} denotes the uncertainty of the beat note's (BN's) voltage estimation, and ρ_{ijj^*} denotes the correlation coefficient of the instantaneous amplitude between both detectors at a given frequency and timescale. The uncertainty of the BN's voltage can be extracted from an Allan deviation plot, whereas the correlation coefficient can be deduced from a time series of the S - and R -BN's voltage with a sampling interval corresponding to the acquisition time. Such a characterization can be performed on-line in a working MH system, or from previously acquired samples.

The partial derivatives of the transmission function T are inserted into Eq. (S3) yielding:

$$\begin{aligned}
\sigma_T^2 &\approx (2V_{GS}\sigma_{GS})^2 \left(\frac{V_{ZR}}{V_{GR}V_{ZS}} \right)^4 + \left(\frac{2\sigma_{GR}}{V_{GR}^3} \right)^2 \left(\frac{V_{GS}V_{ZR}}{V_{ZS}} \right)^4 + (2V_{ZR}\sigma_{ZR})^2 \left(\frac{V_{GS}}{V_{GR}V_{ZS}} \right)^4 + \left(\frac{2\sigma_{ZS}}{V_{ZS}^3} \right)^2 \left(\frac{V_{GS}V_{ZR}}{V_{GR}} \right)^4 + \\
&\quad - 8 \frac{V_{GS}^3}{V_{GR}} \left(\frac{V_{ZR}}{V_{ZS}V_{GR}} \right)^4 \rho_{GSGR} \sigma_{GS} \sigma_{GR} - 8 \frac{V_{ZR}^3}{V_{ZS}} \left(\frac{V_{GS}}{V_{ZS}V_{GR}} \right)^4 \rho_{ZSZR} \sigma_{ZS} \sigma_{ZR}.
\end{aligned} \tag{S4}$$

After dividing both sides of Eq. (S4) by T^2 and taking the square root, the relative error of the transmission function (the upper and lower limits of the error bars) can be calculated as

$$\frac{\sigma_T}{T} \approx \sqrt{\left(2 \frac{\sigma_{GS}}{V_{GS}} \right)^2 + \left(2 \frac{\sigma_{GR}}{V_{GR}} \right)^2 + \left(2 \frac{\sigma_{ZR}}{V_{ZR}} \right)^2 + \left(2 \frac{\sigma_{ZS}}{V_{ZS}} \right)^2 - 8 \rho_{GSGR} \frac{\sigma_{GS} \sigma_{GR}}{V_{GS} V_{GR}} - 8 \rho_{ZSZR} \frac{\sigma_{ZS} \sigma_{ZR}}{V_{ZS} V_{ZR}}}. \tag{S5}$$

Two important conclusions can be drawn from the analysis of this equation. Firstly, the use of the dual-detector scheme is reasonable only if the instantaneous amplitudes of the BNs in both detectors are highly correlated. Otherwise, the uncertainties simply add in quadrature, thereby increasing the total measurement uncertainty. Secondly, even if the correlation coefficient ρ_{ijj^*} is one, the total uncertainty of the measurement, assuming

nonzero σ_{ij} terms, is close to zero only if the signal to noise ratios (SNRs) of the sample and reference detector are the same:

$$\frac{\sigma_{GS}}{V_{GS}} = \frac{\sigma_{GR}}{V_{GR}} \quad \text{and} \quad \frac{\sigma_{ZS}}{V_{ZS}} = \frac{\sigma_{ZR}}{V_{ZR}}. \quad (\text{S6})$$

Intuitively, this implies that a sensitive dual-detector MH system requires closely matched photodetectors.

If only two uncorrelated acquisitions of sample (G) and zero-gas (Z) are taken, using only a sample detector S , Eq. (S5) can be simplified into the well-known variance formula

$$\frac{\sigma_T}{T} \approx \sqrt{\left(2 \frac{\sigma_{GS}}{V_{GS}}\right)^2 + \left(2 \frac{\sigma_{ZS}}{V_{ZS}}\right)^2} \quad (\text{S7})$$

The obtained result is consistent with Villares et al.¹, in which the authors derived the uncertainty of water vapor measurement referenced to dry nitrogen as,

$$\frac{\sigma_T}{T} \approx \sqrt{\left(2 \frac{\sigma_{V_{H_2O}}}{V_{H_2O}}\right)^2 + \left(2 \frac{\sigma_{V_{N_2}}}{V_{N_2}}\right)^2}. \quad (\text{S8})$$

Determination of the bandwidth-normalized noise-equivalent absorption (NEA) value

The noise-equivalent absorption (NEA) is defined as the standard deviation of the absorption baseline normalized to the square root of the acquisition time. The baseline can be obtained either through a measurement without absorber ($Z=G$) or by subtracting a spectroscopic fit from the data (if accurate modeling is feasible).

Assuming N discretely sampled transmission values, \mathbf{T}_i , the baseline, \mathbf{B}_i , can be defined (for the two cases) as,

$$\begin{aligned} B_i^M &= T_i^S - T_i^M \\ B_i^Z &= T_i^{Z_1} - T_i^{Z_2}, \end{aligned} \quad (\text{S9})$$

where T_i^S denotes the measured transmission from the sample at optical mode i , T_i^M the calculated model, and $T_i^{Z_1}$ and $T_i^{Z_2}$ two independent zero-gas measurements. The definition of the corrected sample standard deviation gives,

$$\sigma_{B_{M,Z}} = \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(B_i^{M,Z} - \overline{B_i^{M,Z}} \right)^2}. \quad (\text{S10})$$

Finally, the NEA is defined as the standard deviation of the baseline normalized to the square root of the acquisition time, τ , which yields,

$$\text{NEA} = \sigma_{B_{M,Z}} \sqrt{\tau}, \quad (\text{S11})$$

NEA is expressed in units of $\text{Hz}^{-1/2}$.

References

¹ G. Villares, A. Hugi, S. Blaser, and J. Faist, Nat. Commun. **5**, 5192 (2014).