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Gas equilibration gas modulation refractometry for assessment of pressure with sub-ppm precision

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Gas modulation refractometry (GAMOR) is a methodology that, by performing repeated reference assessments with the measurement cavity being evacuated while the reference cavity is held at a constant pressure, can mitigate drifts in dual Fabry-Perot cavity based refractometry. A novel realization of GAMOR, referred to as gas equilibration GAMOR, that outperforms the original realization of GAMOR, here referred to as single cavity modulated GAMOR (SCM-GAMOR), is presented. In this, the reference measurements are carried out by equalizing the pressures in the two cavities, whereby the time it takes to reach adequate conditions for the reference measurements has been reduced. This implies that a larger fraction of the measurement cycle can be devoted to data acquisition, which reduces white noise and improves on its short-term characteristics. The presented realization also encompasses a new cavity design with improved temperature stabilization and assessment. This has contributed to improved long-term characteristics of the GAMOR methodology. The system was characterized with respect to a dead weight pressure balance. It was found that the system shows a significantly improved precision with respect to SCM-GAMOR for all integration times. For a pressure of 4303 Pa, it can provide a response for short integration times (up to 10 min) of 1.5 mPa (cycle)1/2, while for longer integration times (up to 18 h), it shows an integration time-independent Allan deviation of 1 mPa (corresponding to a precision, defined as twice the Allan deviation, of 0.5 ppm), exceeding the original SCM-GAMOR system by a factor of 2 and 8, respectively. When used for low pressures, it can provide a precision in the sub-mPa region; for the case with an evacuated measurement cavity, the system provided, for up to 40 measurement cycles (ca. 1.5 h), a white noise of 0.7 mPa (cycle)1/2, and a minimum Allan deviation of 0.15 mPa. It shows a purely linear response in the 2.8–10.1 kPa range. This implies that the system can be used for the transfer of calibration over large pressure ranges with exceptional low uncertainty. © 2019 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1116/1.5090860

I. INTRODUCTION

Fabry-Perot cavity (FPC) based refractometry is a sensitive technique for assessment of gas refractivity, density, pressure, and gas flows.1–17 The technique is built on the principle that the frequency of a cavity mode in an FPC is shifted when gas with a given refractivity is let into the cavity.1–3,15 Recent works have indicated that the technique has the potential to replace current pressure standards, in particular, in the 1–100 kPa range.18–24 With the revision of the SI system in May 2019, in which the Boltzmann constant will be defined as a fixed value with any uncertainty, the performance would, in principle, be limited only by the accuracies of quantum calculations of gas parameters and the determination of the gas temperature.

Ordinary FPC refractometry is, in general, limited by the stability of the length of the cavity;17,25–27 a length change of 1 pm of a 30 cm long cavity during a measurement corresponds, for N2, to an uncertainty in the assessment of pressure of 1 mPa. To achieve this degree of precision with FPC-based refractometry, an exceptional mechanical stability is required.

A means to alleviate this is to utilize a dual FP cavity (DFPC) in which two cavities are bored in the same spacer block; in this case, one cavity serves as the measurement cavity (in which gas is let in and pumped out), while the other is the reference cavity.3,13–18,26,27 For each cavity, a laser is locked to one of the cavity modes and the beat frequency of the two lasers is measured. Any change in length of the cavity spacer that is common to the two cavities will then cancel in the beat frequency and not affect the assessment.

Despite this, since the two cavities in a DFPC setup can drift dissimilarly, the highest performance still requires extraordinary stable conditions. As a means to remedy this, gas modulation refractometry (GAMOR) has recently been developed.28,29 By performing repeated reference assessments with the measurement cavity being evacuated (while the reference cavity is held at a constant pressure), the methodology can significantly reduce the influence of the long-term drifts (i.e., eliminating its linear parts) that are mainly caused by length changes of individual cavities. This makes it possible to take advantage of the high precision FPC-based refractometry.
has at short time scales also for long measurement times. It was recently shown that a GAMOR instrumentation with a non-temperature-stabilized cavity spacer, when referenced to a dead weight pressure balance, could reduce the influence of drifts of the cavities 3 orders of magnitude with respect to a DFPC refractometer with conventional (static) detection. This system could demonstrate a (1σ) sub-ppm precision for pressure assessment in the 5 kPa range.28

On short time scales, the assessment of refractivity from a given density of gas by the GAMOR instrumentation realized was limited by white noise. Although, in general, such noise can be averaged down, averaging can only be performed when the gas pressures have become fully equilibrated. Since it takes considerable time for the measurement cavity to reach equilibrium during the emptying stage, the performance of the original GAMOR realization on short time scales was limited by the gas evacuation process.

On long time scales, it was restricted by temperature gradients in the cavity spacer. The differences in temperature between the temperature probes and the walls of the cavities resulted in uncertainties in the assessments of the gas temperature to which the pressure is proportional.

This indicates that there are possibilities to improve on the precision of the GAMOR methodology. Regarding its short-term characteristics, it would be beneficial if the time it takes for the system to reach stable conditions for the reference assessments could be shortened, so that the reference signal could be averaged over a longer time. For the long-term characteristics, the precision could be improved if the signal could be averaged over longer time before being influenced by any drift.

In this work, we present a novel realization of GAMOR, partly based on its original realization,28 with some parts upgraded, but also encompassing a new gas modulation methodology, that together address these concepts. To improve on the short-term characteristics, we have developed and realized a new modulation methodology termed gas equilibration GAMOR (GEq-GAMOR) that shortens the time it takes to reach equilibrium conditions for the reference assessments. In this methodology, instead of evacuating the measurement cavity for the reference measurement, the gas in the measurement cavity is let into the reference cavity, to equalize the pressure in the two cavities. This implies that in GEq-GAMOR, the amount of gas in both cavities is modulated within each measurement cycle. Since gas equilibration at pressures in the viscous flow range is a faster process than evacuation of a cavity filled with gas down to vacuum (in the molecular regime), this allows for assessment (averaging) of the beat frequency during the reference assessment over a longer time. This reduces the noise picked up in an individual measurement cycle, which thereby contributes to an improved white noise characteristics of the system. To improve on the long-term stability, we have implemented a temperature stabilized cavity spacer with an improved temperature measurement capability.

The performance of the novel system in terms of precision is compared to that of the first realization of GAMOR,28 henceforth referred to as single cavity modulated GAMOR (SCM-GAMOR). It is shown that GEq-GAMOR can provide a two times better precision under short-term conditions and that the drifts have been reduced significantly (more than 8 times for integration times for 500 measurement cycles, or 18 h). When used for low pressures, it is demonstrated that it can provide a (2σ) precision in the sub-mPa region; for an evacuated measurement cavity, and for up to ca. 40 measurement cycles (ca. 1.5 h), the system exhibits a white noise of 0.7 mPa (cycle)1/2, and a minimum Allan deviation of 0.15 mPa. Finally, the system is characterized with respect to its linearity by comparison with a dead weight pressure balance over the 2.8–10.1 kPa range. The accuracy of the instrumentation is not addressed in this work but will be scrutinized in a coming publication.

II. THEORY

Since GEq-GAMOR has much in common with SCM-GAMOR, the theoretical description of the former can most conveniently be based on that of the latter, which, in turn, can be assessed from expressions for ordinary (i.e., unmodulated) DFPC-based refractometry. To provide a comprehensive description of GEq-GAMOR, the basis for SCM-GAMOR is therefore reviewed in the supplementary material35 (“Derivation of expressions that relate the change in beat frequency between the two laser fields to the refractivity of the gas in the measurement cavity in SCM-GAMOR and GEq-GAMOR”). Based on this, the defining expressions for GEq-GAMOR are derived and presented. In addition, the last part of the supplementary material35 contains a list of the entities used together with their designation (“Nomenclature”). For both methodologies, it is assumed that, for each measurement cycle, the measurement cavity is filled with gas from an external source to a pressure of \( P_{\text{Ext}} \), whose refractivity, \( n_{\text{Ext}} - 1 \), is to be assessed by refractometry.

A. SCM-GAMOR

An expression that relates the change in beat frequency between the two laser fields to the change in refractivity of the gas in the measurement cavity in SCM-GAMOR is derived as Eq. (SM-18) in the supplementary material.35 It is here of importance to consider the fact that, for practical reasons, the measurement cavity is not evacuated to a pure vacuum during the reference assessment; we will assume that, under this assessment, it contains a minor, remaining amount of gas, henceforth referred to as the residual amount of gas, that has a refractivity of \( n_{\text{Res}} - 1 \). The expression derived shows that, when the measurement cavity is filled with gas with a refractivity of \( n_{\text{Ext}} - 1 \), the refractivity can be assessed from measurements of the change in beat frequency between the two laser fields using the expression28

\[
n_{\text{Ext}} - 1 = \frac{\Delta f_{(0,\text{Res} \rightarrow \text{Ext})} + \Delta n_{m}(\text{Res} \rightarrow \text{Ext})}{1 - \Delta f_{(0,\text{Res} \rightarrow \text{Ext})}/\nu_{m}^{(0)}} + (n_{\text{Res}} - 1),
\]

where \( \Delta f_{(0,\text{Res} \rightarrow \text{Ext})} = \Delta f_{(0,\text{Res} \rightarrow \text{Ext})}/\nu_{m}^{(0)} \), where, in turn, \( \Delta f_{(0,\text{Res} \rightarrow \text{Ext})} \) is the shift in beat frequency when the measurement cavity, after being evacuated to a residual refractivity,
is filled with the gas to be characterized. It is formally given by $f_{(0, Ext)} - f_{(0, Ref)}$ where $f_{(0, Ext)}$, referred to as the filled measurement cavity beat frequency, is the beat frequency between the modes addressed in the reference and the measurement cavities when the reference cavity is empty while the measurement cavity contains the gas to be assessed (with a refractivity of $n_{Ext} - 1$), while $f_{(0, Ref)}$, referred to as the evacuated measurement cavity beat frequency, is the beat frequency when the reference cavity is empty while the measurement cavity is evacuated to a refractivity of $n_{Ref} - 1$. $\nu_m^{(0)}$ is the frequency of the $q_m^{(0)}$th cavity mode addressed in the empty measurement cavity. The assessments of $f_{(0, Ext)}$ and $f_{(0, Ref)}$ are henceforth referred to as the filled measurement cavity assessment and the (evacuated measurement cavity) reference assessment, respectively. $\Delta f_{m}^{(Ref-Ext)}$ represents $\Delta f_{m}^{(Ref-Ext)}/\nu_m^{(0)}$, where $\Delta f_{m}^{(Ref-Ext)}$ is the number of modes the laser jumps when the refractivity of the measurement cavity is changed from the residual refractivity, $n_{Ref} - 1$, to $n_{Ext} - 1$. $\epsilon_m$ is the refractivity-normalized deformation coefficient of the measurement cavity,$^{15}$ defined by $\epsilon_m(n_{Ext} - n_{Ref}) = \Delta L_m^{(Ref-Ext)}/\nu_m^{(0)}$, where $\Delta L_m^{(Ref-Ext)}$ is the change in length of the cavity when it is filled with gas (under the same conditions), which includes effects both from an altered length of the cavity spacer and distortion of the mirrors, while $f_m^{(0)}$ is its length when being empty.

Equation (1) shows that to assess $n_{Ext} - 1$ from a measurement of $\Delta f_{(0, Ref-Ext)}$ requires knowledge about the residual refractivity, $n_{Ref} - 1$. Since the residual pressure is significantly smaller than $P_{Ext}$, it can be assessed with sufficient accuracy by a pressure gauge. From such an assessment, $n_{Ref} - 1$ can be calculated.

As an alternative to use Eq. (1) to assess $n_{Ext} - 1$, it is possible to use the value of $n_{Ref} - 1$ to recalculate the evacuated measurement cavity beat frequency $f_{(0, Ref)}$, to the cavity beat frequency that would have been measured if the measurement cavity would have been completely emptied, henceforth referred to as the empty measurement cavity beat frequency, $f_{(0,0)}$. As is shown by Eq. (SM-19) in the supplementary material,$^{35}$ by this, Eq. (1) can be simplified to

$$n_{Ext} - 1 = \frac{\Delta f_{(0,0-Ext)}^{(Ext)}}{1 - \Delta f_{(0,0-Ext)}^{(Ref-Ext)} + \epsilon_m^{(0)}}, \quad (2)$$

where $\Delta f_{(0,0-Ext)}^{(Ext)}$ is given by $\Delta f_{(0,0-Ext)}/\nu_m^{(0)}$, where, in turn, $\Delta f_{(0,0-Ext)}^{(Ref-Ext)}$ is given by $f_{(0, Ext)} - f_{(0,0)}$.

Preferably, the two beat frequencies, $f_{(0, Ext)}$ and $f_{(0,0)}$ (in practice $f_{(0, Ref)}$), should be assessed at the same time. However, since this is technically not possible, $f_{(0,0)}$ is, in practice, for ordinary (unmodulated) DPPC-based refractometry, measured at some instance either before or after the filled measurement cavity assessment. This introduces drifts into the system.

As has been described in the literature$^{28}$ and as is shortly summarized in the Sec. IV, the soul of the GAMOR methodology consists of a methodology to obtain an adequate estimate of the evacuated measurement cavity beat frequency at the time of the filled measurement cavity assessment. The evacuated measurement cavity beat frequency used for calculation of the shift in beat frequency is estimated by a linear interpolation from two evacuated measurement cavity reference measurements performed just prior to, and directly after, the filled measurement cavity assessment. This entity, which is denoted $\tilde{f}_{(0,0)}$ and referred to as the interpolated empty measurement cavity beat frequency, is given by Eq. (SM-11) in the supplementary material$^{35}$ or Eq. (8), $f_{(0,0)}$, thus, represents what the empty measurement cavity beat frequency would have been at the time of the filled measurement cavity assessment in case the measurement cavity had not been filled with gas. This implies that in GAMOR, $n_{Ext} - 1$ is given by Eq. (2) with $\Delta f_{(0,0-Ext)}^{(Ext)}$ assessed as $\Delta f_{(0,0-Ext)}^{(Ext)}/\nu_m^{(0)}$, where

$$\tilde{\Delta f}_{(0,0-Ext)} = f_{(0,0)} - f_{(0,0)}.$$

B. GEq-GAMOR

In GEq-GAMOR, the filled measurement cavity assessment is performed as in SCM-GAMOR, i.e., with the measurement cavity being filled with gas while the reference cavity is evacuated. For the reference assessment, however, the gas in the measurement cavity is let into the reference cavity to equalize the pressure in the two cavities. The measured change in beat frequency in GEq-GAMOR, $\Delta f_{(Eq-Ref, Eq-Ext)}$, therefore formally represents the difference in beat frequency between the filled measurement cavity assessment, $f_{(Ref, Ext)}$, and the case when both cavities contain gas with the same but a finite refractivity, $n_{Eq}$, denoted $f_{(Eq, Eq)}$ and henceforward referred to as the gas equilibrium beat frequency, i.e., $f_{(Ref, Ext)} - f_{(Eq, Eq)}$. Since $\Delta f_{(Eq-Ref, Eq-Ext)}$ differs from the corresponding entities in SCM-GAMOR, i.e., $\Delta f_{(0, Ref-Ext)}$ or $\Delta f_{(0,0-Ext)}$, neither Eq. (1) nor Eq. (2) can be used for GEq-GAMOR straight off.

There are a few possible remedies to this. The one presented here is to first recalculate $f_{(Ref, Ext)}$ to $f_{(0, Ext)}$ by using the assessment of the residual pressure in the reference cavity (assessed by a pressure gauge), followed by a recalculation of $f_{(Eq, Eq)}$ to the empty measurement cavity beat frequency it would correspond to if both cavities would have been evacuated, denoted $f_{(0,0)}^{(Eq)}$ and referred to as the estimated empty measurement cavity beat frequency.

As is shown in the supplementary material,$^{35}$ the latter entity is given by

$$f_{(0,0)}^{(Eq)} \approx [1 + (n_{Eq} - 1)] f_{(Eq, Eq)} - Q_{Eq} \nu_m^{(0)}$$

$$- \Delta \nu(n_{Eq} - 1) \nu_m^{(0)}, \quad (4)$$

where

$$Q_{Eq} = \Delta f_{m}^{(0-Ext)} - \Delta f_{m}^{(Ref-Ext)} - \Delta f_{r}^{(0-Eq)} / \nu_m^{(0)},$$

and where we have expressed the relative deformations of the two cavities due to the gas under gas equilibrium conditions, $\Delta f_{r}^{(0-Eq)}$ and $\Delta f_{m}^{(0-Eq)}$ (representing the relative deformation of the length of the reference and the measurement cavities when they are filled with gas to a refractivity of
where \( \epsilon_f(n_{eq} - 1) \) and \( \epsilon_m(n_{eq} - 1) \), where, in turn, \( \epsilon_f \) is the refractivity-normalized deformation coefficient of the reference cavity, and where we have used \( \Delta \varepsilon \) as a short hand notation for \( \epsilon_m - \epsilon_f \).

This implies that, for the case with GEq-GAMOR, the refractivity of the gas that has been let into the measurement cavity can be assessed from Eq. (2) in which \( \gamma_{(0,0)} \) is replaced by \( \{f_{(0,Ext)} - \gamma_{(0,Ext)} f_{(0,0)} \} / v_m \cdot f_{(0,Ext)} \) is the residual-gas-corrected value of \( f_{(0,Ext)} \), while \( f_{(0,0)} \) is estimated by linear interpolation [again according to Eq. (SM-11) in the supplementary material or Eq. (8)] from two \( f_{(0,Ext)} \) values, which, in turn, are assessed, by using Eq. (4), from two gas equilibrium reference assessments, i.e., two \( f_{(Ext,Eq)} \) measured just prior to and directly after the filled measurement cavity assessment.

C. Assessment of gas density and pressure

The conversion of a given refractivity, \( n_{eq} - 1 \), to gas density, \( \rho_{Ext} \), is being performed through the extended Lorentz–Lorenz equation, given by Eq. (SM-20) in the supplementary material, \(^{35,36} \) which implies that the density can be assessed from the refractivity by

\[
\rho_{Ext} = \frac{2}{3A_R}(n_{eq} - 1)[1 + \tilde{B}_p(T)\rho_{Ext}],
\]

where \( A_R \) and \( \tilde{B}_p \) are the molar dynamic polarizability and a refractivity virial coefficient, respectively, where the latter is given by \( -\left(1 + 4B_R/A_R^2\right)/6 \), where, in turn, \( B_R \) is the refractivity virial coefficient in the Lorentz–Lorenz equation.\(^{15,30,31} \)

The corresponding pressure, \( P_{Ext} \), can thereafter be obtained from the density as

\[
P_{Ext} = k_B T N_A \rho_{Ext}[1 + B_p(T)\rho_{Ext}],
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature of the gas, \( N_A \) is the Avogadro number, and \( B_p(T) \) is a density virial coefficient.\(^{20,26} \)

III. EXPERIMENTAL SETUP

The setup for GEq-GAMOR, which is illustrated in Fig. 1, is based, to a large degree, on that for SCM-GAMOR.\(^{28} \) Each of the two arms of the refractometer is addressed by light from a narrow linewidth Er-doped fiber laser (NTK, Kohera, Adjutik E15), emitting light within the C34 communication channel, i.e., around 1.55 \( \mu \)m.

For improved locking bandwidth, the light from each laser is sent through a fiber-coupled acousto-optic modulator (AOM, AA Opto-Electronic, MT110-IR25-3FIO). The first order output from this is split by a 90/10 polarization maintaining fiber splitter (Thorlabs, PMC1550-90B-FC), whose high transmission output is connected to an electrooptic modulator (EOM, General Photonics, LPM-001-15) that is modulated at 12.5 MHz for Pound-Drever-Hall (PDH) locking. The output of the EOM is then coupled into free space by a collimator and sent through a mode-matching lens, a polarizing beam splitter (PBS), and a quarter-wave (λ/4) plate, before it enters the cavity. The low power outputs of the 90/10 fiber splitters of the two arms are merged by a 50/50 fiber coupler (Thorlabs, PMC1550-50B-FC) whose output is sent to a beat frequency detecting photodetector (Thorlabs, PDA8GS).

For the locking, both the back reflected and the transmitted light are used. The reflected light is passed through the quarter-wave plate a second time and is deflected by the PBS before it is collected with a fast photodetector (Thorlabs, PDA10CE-EC). The transmitted light is detected by a large area photodetector (Thorlabs, PDA50B-EC).

The outputs from the photodetectors are connected to a commercial digital servo module based on a field programmable gate array (FPGA, Topica, Digilock 110). In this, to produce a PDH error signal for the locking, the reflected signal from each reflection detector is demodulated at 12.5 MHz before it passes through one of two proportional–integral–derivative servos. One provides a slow feedback (with a bandwidth up to 100 Hz), which controls the piezo-electric transducer of the fiber laser, while the other gives a fast feedback (with a bandwidth up to around 100 kHz), which is connected to a voltage controlled oscillator that produces an RF of around 110 MHz for the frequency tuning of the first order output of the AOM. The transmission signal is

![Fig. 1. Schematic illustration of the GEq-GAMOR system (color online). Blue curves (no arrows): optical fibers; red lines (with arrows, through the cavities): free-space light propagation; black lines (with arrows, not through the cavities): wires; EDFL: Er-doped fiber laser; AOM: acousto-optic modulator; VCO: voltage controlled oscillator; 90/10: 90/10 polarization maintaining fiber splitter; 50/50: 50/50 polarization maintaining fiber splitter; EOM: electro-optic modulator; PBS: polarizing beam splitter cube; λ/4: quarter-wave plate; Ref. Detector: reflection detector; Trans. Detector: transmission detector; FPGA: field programmable gate array; and DAQ: data acquisition system. Only the electronics and some parts of the optics of one arm (No. 1) is shown. See Silander et al. for details of the omitted parts (Ref. 28). The left out parts for arm 2 are identical to those of arm 1.](image-url)
High-purity nitrogen gas is supplied from a central gas unit (represented by “Gas in” in the figure) into the gas supply unit. To ensure stable conditions, a mass flow controller (MFC, Bronkhorst, F-201CV) and an electronic pressure controller (EPC Bronkhorst, P-702CV) are used to provide a continuous flow of gas through the gas supply unit (to reduce the risk for gas contamination) at a constant pressure.

When the pressure assessed by pressure gauge C (Oerlikon-Leybold CTR 101N 1000 Torr) is below a set threshold pressure, valve 4 (Oerlikon-Leybold 28444) opens to fill the pressure stabilizing unit, consisting of a dead weight pressure balance (RUSKA 2465A), with gas. When the pressure reaches a second threshold, set to the pressure balance pressure ($P_{Ext}$), valve 4 closes, whereby the piston floats, providing a stabilized pressure. Pressure gauge D (Oerlikon-Leybold CTR 101N 0.1 Torr) is used to monitor the hood pressure of the dead weight pressure balance.

The refractometer comprises the DFPC, three solenoid valves (1 and 2: Oerlikon-Leybold 28444; and 3: Leycon 215006v01), which are used to control the flow of gas in and out of the cavities, and two pressure gauges (A: Oerlikon-Leybold CTR 101N 1000 Torr; and B: Oerlikon-Leybold CTR 101N 0.1 Torr), which are used to monitor the pressure in the two cavities. During certain parts of the measurement cycle (see below), the gas system is evacuated through valve 3 by a turbo vacuum pump.

**IV. METHODOLOGY**

Before any measurement series was initiated, the wavelengths of the lasers addressing the two cavities under evacuated conditions were measured with a wavelength meter (Burleigh, WA-1500) and converted to frequency, $\nu_m^{(0)}$ and $\nu_r^{(0)}$, respectively. The FSR of each cavity was measured as the frequency shift of the corresponding laser when it was exposed to controlled cavity mode jumps. These two assessments provide sufficient information to unambiguously determine the empty cavity mode numbers $q_m^{(0)}$ and $q_r^{(0)}$ that were addressed by the lasers under evacuated conditions.

To assist in the assessment of mode jumps (see below), the lasers were characterized with respect to their frequency-to-voltage responses, i.e., to $V_m = f(V_m)$ and $V_r = f(V_r)$, where $V_m$ and $V_r$ are the voltages sent to the piezoelectric transducers (PZTs) of the two lasers.
A. Valve switching and gas modulation procedure

As for SCM-GAMOR, to achieve gas modulation in the system, GEq-GAMOR is realized by periodically changing the states of the various valves in the system. Figure 3 shows a schematic illustration of the valve states for the three different states that GEq-GAMOR comprises.

In state I, the beat frequency for the filled measurement cavity assessment, i.e., \( f_{(0,0)(Ext)} \), is assessed. State I follows state III of the previous cycle (see below), in which both cavities are evacuated (obtained by having valves 2 and 3 open). As is illustrated in Fig. 3(a), state I is initiated by closing valve 2 and opening valve 1. As is schematically shown in section I of Fig. 4(a), by this, the measurement cavity (\( C_m \)) is filled with gas up to the pressure that is supplied by the dead weight pressure balance, \( P_{Ext} \), while the reference cavity (\( C_r \)) is being evacuated. To assess the residual refractivity in the reference cavity, \( n_{Ref}/C_0 \), pressure gauge A is used to measure the pressure from which the equilibrium beat frequency, \( f_{(0,0)(Eq)} \), can be estimated. [Since the \( n_{Eq} \)-terms in Eq. (4) typically only contribute to the value of \( f_{(0,0)(Eq)} \) on the 10^{-5} level (on a relative scale), it suffices to assess \( n_{Eq}/C_0 \) with two significant digits to assess \( f_{(0,0)(Eq)} \) with sub-ppm accuracy.] As in state I, the pressure readings in combination with \( V_m \) and \( V_r \) are used to determine \( \Delta \alpha_m^{(0-\alpha-Eq)} \) and \( \Delta \alpha_r^{(0-\alpha-Eq)} \). All this provides conditions for the assessment of \( f_{(0,0)}^{(Eq)} \) by using Eqs. (4) and (5) with good accuracy.

This also indicates that there is no need to continuously or actively monitor the number of mode jumps during any gas filling or evacuation process; the status of the system provides, at any time, enough information to deduce any mode jump in any cavity.

In state III, to ensure gas purity (i.e., to reduce the influence from outgassing and gas leaks), as is shown in

Fig. 3. Schematic illustration of the various states of GEq-GAMOR. Panel (a): State I; Panel (b): State II; and Panel (c): State III. The gas lines with the same color have the same pressure. Hence, a valve that has the same color of the gas lines on its two sides is open, while, if the colors are dissimilar, it is closed.

Fig. 4. Schematic illustration of the principle of the GEq-GAMOR methodology displayed over two measurement cycles. Panel (a): the pressures in the measurement cavity, \( P_{m(t)} \) (red upper curve) and in the reference cavity, \( P_{r(t)} \) (blue lower curve), as functions of time. Panel (b): the corresponding frequencies of the measurement and reference lasers, \( v_{m(t)} \) (red, upper) and \( v_{r(t)} \) (blue, lower), respectively, in the absence of mode jumps (offset to a common frequency \( v_0 \)). Panel (c): the corresponding beat frequencies: the measured one, \( f(t) \) (black upper curve), in the legend denoted \( f \), and the interpolated estimated empty measurement cavity beat frequency, \( \tilde{f}_{(0,0)}(t) \) (green lower line), in the legend denoted \( \tilde{f} \), whose slope is greatly exaggerated for display purposes. Panel (d): the cavity-drift-corrected shift in beat frequency, \( \Delta f \), in the legend denoted \( \Delta f \), given by the difference between \( f(t) \) and \( \tilde{f}_{(0,0)}(t) \). The large colored box indicates over which interval the filled measurement cavity beat frequency is evaluated while the smaller box shows the time period over which the data alternatively were evaluated to assess the dependence of the averaging time on the noise (see the text for details).
Fig. 3(c), the state begins by opening valve 3 whereby, as is shown in section III in Fig. 4(a), both cavities are evacuated.

After this, state I of the next cycle starts.

For this particular case, when the pressure to be assessed is provided by a dead weight pressure balance (as is shown by Fig. 2), the filling of the pressure balance (as was described above, controlled by valve 4) takes place during the first part of state I.

Figure 4(b) shows the frequencies of the measurement and reference lasers, \( v_m(t) \) (red curve) and \( v_r(t) \) (blue curve), respectively, for simplicity in the absence of mode jumps, during the various states (for display purposes, both are offset to a common frequency \( \nu_0 \)).

B. GAMOR feature

The beat signal between the two laser fields is in practice measured during the entire measurement cycle. It can, therefore, be seen as a continuous function of time, i.e., \( f(t) \). A schematic representation of a possible \( f(t) \) cycle is given by the black curve in Fig. 4(c). As has been alluded to above, because of drifts of the cavity spacer, this signal will not be a complete replica of the gas pressure [schematically displayed by the red curve in Fig. 4(a)]. To alleviate this, the estimated empty measurement cavity beat frequency, \( f_{\text{Eq}}(t) \), is calculated at all instances of the measurement cycle by using a linear interpolation between two empty measurement cavity frequencies. The first is measured before the filling of cycle \( n + 1 \), \( f_{\text{Eq}}(t_n) \), and the second after the cycle [identical to the one before the filling of cycle \( n + 1 \)], \( f_{\text{Eq}}(t_{n+1}) \), marked by crosses in Fig. 4(c). In practice, in GEq-GAMOR, these assessments, taken as those used in the original SCM-GAMOR work,\(^2\) which, as is described in that work, in turn, are based upon the literature,\(^{14,26,32}\) and where the molecular polarizability additionally has been recalculated for the actual wavelength used.

Since the DFPC has not yet been fully characterized, the two refractivity-normalized deformation coefficients, \( \varepsilon_m \) and \( \varepsilon_r \), have, temporarily in this work, for convenience, been set to zero. Although this will presently not benefit the accuracy of the technique, it will not affect its precision.

Hence, by this gas modulation procedure, the effect of the linear drift of the cavities is efficiently eliminated from the assessment of gas refractivity, density, and pressure.

V. RESULTS AND DISCUSSION

A. Stability and precision

To evaluate the stability and precision of the refractometer, it was compared to a dead weight pressure balance (RUSKA...
set to a pressure of 4303 Pa ($P_{\text{Ext}}$). Figure 5 shows the pressure difference $\Delta P$ between the pressure assessed by the refractometer, denoted $P_R$, and that set of the dead weight pressure balance, $P_{\text{Ext}}$. The data in Fig. 5(a) consist of 720 individual measurements cycles (i.e., 4 days, each lasting 100 s) taken over a period of 20 h assessed with an SCM-GAMOR system (blue markers), while those in Fig. 5(b) comprise 2700 measurements cycles taken over a period of 100 h (each lasting 130 s) for the GEq-GAMOR system (red markers). The integration times for the filled measurement cavity assessments were 30 and 40 s for SCM-GAMOR and GEq-GAMOR, respectively. Since neither the dead weight pressure balance, nor the DFPC, has yet been fully characterized (e.g., the former with respect to the piston weight and area or the assessments of the hood and residual pressures while the latter with respect to the $\epsilon_m$ and $\epsilon_r$), the means of the difference-signals have been subtracted. The dashed horizontal lines represent two standard deviations ($\pm 2\sigma$) of the pressure differences.

The data taken by the GEq-GAMOR system [Fig. 5(b)] show that the combined $2\sigma$ stability of the system (representing the fluctuations between the dead weight pressure balance and the refractometer) over 4 days was within $\pm 5$ mPa (or $\pm 1$ ppm). This is a significant improvement from the original realization of GAMOR [the SCM-GAMOR system, Fig. 5(a)], which showed $\pm 16$ mPa (or $\pm 4$ ppm) over 20 h (data adapted from Silander et al.\textsuperscript{28}). This indicates that the GEq-GAMOR system has a standard deviation measured over 100 h that is more than a factor of 3 smaller than that of the SCM-GAMOR system assessed over 20 h. This improvement is attributed to the upgraded temperature control and assessment.

Figure 6 shows, by the blue and the red markers, i.e., the first and third sets of data counted from above, respectively, the Allan deviation of the data presented in Fig. 5 (the SCM- and the GEq-GAMOR systems, respectively). The plots show that there is a clear improvement in the stability on all time scales. For comparison, the yellow markers (the lowermost curve) represent a measurement series with an evacuated measurement cavity.

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assessment for GEq-GAMOR, respectively). This shows that the white noise during the reference measurement is in the order of 0.6 mPa Hz$^{-1/2}$ for both methodologies.

However, when assessments are performed with finite (nonzero) pressures, the white noise is higher than when the measurement cavity is empty. For example, for a pressure of 4303 Pa, the white noise was found to be around 6 mPa Hz$^{-1/2}$. The additional noise is believed to originate from a combination of fluctuations in pressure from the dead weight pressure balance and temperature (including its assessment).

B. Linearity

Although the system has not yet been fully characterized, it is possible to assess its linearity. To assess this, a series of measurements were performed for a set of pressure balance weights. Figure 7(a) presents, by the individual markers, the measurements were performed for a set of pressure balance weights, $P_R$, as a function of the estimated pressure of the pressure balance, $P_{dw}$, calculated by using Eq. (4) in Silander et al.,$^{28}$ for seven different weights. The data series were taken over a period of 8 days in a nonconsecutive order (2841, 4303, 7225, 10148, 3426, 5764, and 8687 Pa). Figure 7(b) displays the deviations of the averages of the same set of data in relative units. Note that each red marker represents a set of 50 measurement cycles that have a spread that is significantly smaller than the size of the markers. Hence, they appear as single markers in the figure.

Regarding the data in Fig. 7(a), the black curve shows the best second order fit to the data of the type

$$p = a + bP_{dw} + cP_{dw}^2. \tag{9}$$

The fitted function agrees very well with the data. In addition, it provides a value of the $c$ coefficient of $3 \times 10^{-10}$ Pa$^{-1}$. This shows that the GEq-GAMOR system provides a response that has a very small (virtually insignificant) nonlinear component; the value of the nonlinear term is, for each pressure, smaller than the estimated noise level. It can, therefore, be concluded that the GEq-GAMOR system, evaluated by the theory and the evaluation procedure described above, does not exhibit any noticeable systematic nonlinear dependence over the pressure range addressed. Hence, it suffices to evaluate its performance with respect to its linear response.

A corresponding linear fit to the data in Fig. 7(a), visually indistinguishable from the second order fit, shows that the coefficients $a$ and $b$ are $0.108(1)$ Pa and $1.001405(1)$, respectively, where the uncertainties are estimated from the spread in data at each pressure.

This shows that the deviation of the $b$ coefficient from unity ($1.405 \times 10^{-3}$) is systematic. Possible contributions to this deviation are presumed to originate predominantly from the omission of the cavity deformation (represented by the $e_r$ and $e_m$ entities in the expressions previously addressed) in the assessment of refractivity, and thereby pressure, from the data by using the expressions above, but may also emanate to a minor extent, from the molar polarizability, the temperature assessment, and an incorrect characterization of the dead weight pressure balance.

The fit also reveals a nonzero value of the constant term. The cause for this is presently unknown, but possible causes can be an incorrect piston weight or the assessments of the hood and residual pressures.

VI. SUMMARY, CONCLUSIONS, AND OUTLOOK

A novel technique for refractometry, based on Gas Modulation Refractometry (GAMOR), that outperforms the original realization of GAMOR (here referred to as SCM-GAMOR), has been developed, realized, and scrutinized. It is based upon the fact that the reference measurements, which in SCM-GAMOR are performed by evacuating the measurement cavity, instead are carried out by equalizing the pressures in the two cavities. This new methodology is, therefore, referred to as gas equilibration GAMOR (GEq-GAMOR).

By this, the time it takes to reach adequate conditions for the reference measurements has been reduced. This implies that a larger fraction of the measurement cycle time can be devoted to the acquisition of data, in particular, during the reference assessments. In addition, the residual gas pressure assessment, which for GEq-GAMOR is performed during state I, can be averaged significantly longer than what is the case for SCM-GAMOR (in which the same entity had to be measured under nonequilibrium conditions in state II while the system is being pumped down).
Both these features reduce the white noise and improve on the short-term characteristics. Yet another advantage of GEq-GAMOR is that the pressure during the reference measurement (i.e., the equilibration pressure) does not need to be assessed with the same accuracy as the residual pressure in the measurement cavity in SCM-GAMOR.

The system presented also incorporates a new cavity design with improved temperature stabilization and assessment. This has contributed to an improved long-term response of the GAMOR methodology. Characterization of the GEq-GAMOR system, by using a dead weight pressure balance, shows that, for a pressure of 4303 Pa, it can provide a short-term response in which the precision exceeds that of the original SCM-GAMOR system by a factor of 2. For longer integration times (above 10 cycles, ca. 20 min), the system is limited by flicker noise, which, when expressed in terms of an Allan deviation, is 1 mPa, which, in turn, for this pressure, corresponds to 0.25 ppm. This, thus, corresponds to a precision (defined as twice the Allan deviation) of 0.5 ppm. For the longest integration times considered, it was found that the GEq-GAMOR system could reduce long-term drifts with respect to that of the original SCM-GAMOR system significantly, for 18 h, by a factor of 8.

For the case with an evacuated measurement cavity, it was found that the system is white noise limited up to around 40 cycles (ca. 1.5 h), with a white noise of 0.7 mPa (cycle)$^{-1/2}$, and that it exhibits a minimum Allan deviation (for averaging times in the 40–80 cycle range, corresponding to 1.5–3 h) of 0.15 mPa.

The linearity of the system was assessed by a comparison with a dead weight pressure balance. It was found that the GEq-GAMOR system provides a linear response (with respect to the pressure balance) over the entire pressure range investigated (2.8–10.1 kPa), with no evidence of any systematic nonlinearity. Since there are very few types of nonlinear effects that appear in the lower part of a working range, and since, in this case, no such possible cause has been proposed or suggested, it is plausible to assume that the technique, after a proper characterization, can be used for transfer of calibration for pressures well below the range in which it was characterized.

Outgassing and leaks will contaminate the gas over time and affect its refractivity. This will degrade the accuracy of density and pressure measurements. As the GAMOR principle involves periodical evacuation of the cavities, as is discussed in some detail elsewhere, the effect of gas contamination in GAMOR methodologies is assumed to be small. If though still non-negligible, it can be quantified by altering the modulation period and interpolating the modulation period to zero. This provides a system that in practice is not affected by leakages or outgassing.

This work has mainly been focused on improving the precision and long-term stability of GAMOR. The accuracy of the instrumentation has not yet been addressed. In this case, it was found that the system has a finite (systematic) discrepancy with respect to the dead weight pressure balance, with a linear response that shows a deviation of 0.1405% from the ideal response (unity). This discrepancy can be attributed to a number of causes of which one is the uncharacterized DFPC (primarily the deformation of the cavity due to the pressure of the gas, which has not yet been assessed).

In the future, the accuracy of the system can be improved by characterization with respect to both the physical deformation of the cavity, i.e., the value of $e_m$ and $o_\Delta$, and the gas constants, using a fully characterized pressure balance. This can, for example, be done by using two gases assessed under the same conditions, of which one is He, for which the molar refractivity (together with the relevant refractivity and density virial coefficients) is known. Alternatively, the system can be calibrated in terms of the combination of molar refractivity and physical elongation of the cavity by using a pressure standard.

Since it has been shown that it is possible to construct a GAMOR setup from off-the-shelf components with a relatively simple cavity design, together with high accuracy values of the molar polarizability of gases of potential importance for refractometry, as, for example, recently was presented by Gaiser and Fellmuth, this work opens up for a new class of pressure standards, with no moving actuators, that are traceable to the SI system through frequency and temperature. The potential benefits of these standards, in comparison to current mercury manometer and dead weight pressure balances, are substantial, both in reduced maintenances and operating cost.

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As is indicated by Refs. 15–17, as a predecessor to GAMOR, Drift-Free Fabry-Perot-cavity based refractometry was suggested and scrutinized in some detail.

Note that the expression given for $B_\rho$ in Ref. 24 is incorrect. The correct expression is derived in the supplementary material (Ref. 35).

See supplementary material at https://doi.org/10.1116/1.5090860 for derivations of expressions that relate: i) the change in beat frequency between the two laser fields to the refractivity of the gas in the measurement cavity in SCM-GAMOR and $\text{GEq-GAMOR}$, and ii) gas density in terms of refractivity, and nomenclature.