Assessment of gas molar density by gas modulation refractometry: A review of its basic operating principles and extraordinary performance

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ABSTRACT

A technique for high-precision and high-accuracy assessment of both gas molar (and number) density and pressure, Gas Modulation Refractometry (GAMOR), is presented. The technique achieves its properties by assessing refractivity as a shift of a directly measurable beat frequency by use of Fabry-Perot cavity (FPC) based refractometry utilizing the Pound-Drever-Hall laser locking technique. Conventional FPC-based refractometry is, however, often limited by fluctuations and drifts of the FPC. GAMOR remedies this by an additional utilization of a gas modulation methodology, built upon a repeated filling and evacuation of the measurement cavity together with an interpolation of the empty cavity responses. The procedure has demonstrated an ability to reduce the influence of drifts in a non-temperature stabilized dual-FPC (DFPC)-based refractometry system, when assessing pressure, by more than three orders of magnitude. When applied to a DFPC system with active temperature stabilization, it has demonstrated, for assessment of pressure of N₂ at 4304 Pa at room temperature, which corresponds to a gas molar density of 1.7 × 10⁻⁶ mol/cm³, a sub-0.1 ppm precision (i.e. a resolution of 0.34 mPa). It is claimed that the ability to assess gas molar density is at least as good as so far has been demonstrated for pressure (i.e. for the molar density addressed, a resolution of at least 1.2 × 10⁻¹³ mol/cm³). It has recently been argued that the methodology should be capable of providing an accuracy that is in the low ppm range. These levels of precision and accuracy are unprecedented among laser-based techniques for detection of atomic and molecular species. Since the molar polarizability of He can be calculated by ab initio quantum mechanical calculations with sub-ppm accuracy, it can also be used as a primary or semi-primary standard of both gas molar (and number) density and pressure.

1. Introduction

For a large part of the last hundred years, and in particular since the advent of the laser in the sixties, there has been a continuous strive for the development of optical techniques for chemical analysis that predominantly has been focused upon how to improve on sensitivity (in the form of detection limits), selectivity, and dynamic range. Impressive achievements have been obtained with detection limits of atomic species in the low or below the parts-per-trillion (ppt) region and detection sensitivities of molecules in gas phase into the 10⁻¹⁴ cm⁻³ range [1–7]. It has even been suggested that detection can be made down to the single- or few-atom level [8–11].

However, properties such as precision (the closeness of a number of repeated measurements to each other, i.e. repeatability) and accuracy (the closeness of the measurements to the true value), have not yet received as much attention. A few examples when these entities are of highest importance are when minor changes in species concentration (e. g. of atmospheric constituents such as CO₂ or O₃) or isotopologues of such (e.g. ¹²CH₄, CH₃D, and CH₄) [12] are to be assessed, or when spectroscopic data (A-factors or line strengths) are to be measured. This is not a satisfactory situation.

It is clear that it is not possible for any single technique to display the

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highest performance regarding all of its properties. It is therefore plausible that to improve on some, one has to accept a decrease in performance (or even relinquish) of some others. It is even possible that, to improve on concepts such as precision and accuracy, brand new techniques have to be developed. This leads to the question: how should a technique be realized if one strives for highest possible precision and accuracy? The main aim of this paper is to present a technique that is capable of providing sub-ppm (parts-per-million) precision assessments of molar (or number) gas density and has the potential to provide an accuracy in the low-ppm range; Gas Modulation Refractometry (GAMOR).

2. Status of various laser based detection techniques regarding their capabilities to assess atomic or molecular species with high precision and accuracy

2.1. Precision and accuracy of conventional laser based detection techniques

The most common techniques for sensitive trace element or trace species detection are based on lasers. In these, the laser is predominantly used either for ablation/vaporization/atomization of a sample [as is the case with laser induced breakdown spectroscopy (LIBS)], excitation [as for laser-induced fluorescence (LIF)], excitation and ionization [for laser-induced ionization (LII)], rapid heating [for photoacoustic (PA)], or solely as a probe [as is the case for laser absorption spectroscopy (LAS)]. They have all different abilities, and thereby dissimilar capabilities, for assessment of atomic and molecular species under various conditions.

Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectrometry that uses a highly energetic laser pulse as the excitation source to form a plasma, which atomizes and excites samples [13, 14]. The precision of LIBS is primarily given by the repeatability of the ablation/vaporization/atomization processes of the sample under study, which are highly irregular and non-linear; a given laser fluence (or radiant flux) can, even for a given sample, produce highly varying amounts of atomized material and thereby assessments (up to tens of %). The fact that the output power (or the pulse to pulse fluctuations) of lasers used for LIBS also can fluctuate significantly exacerbate the situation further. Although averaging such laser outputs can improve on the situation, its precision is in general poor.

Its accuracy is often given by the availability of standard reference samples. Alternatively, the amount of a given species can be assessed by comparison with the response from a concomitant constituent in the sample whose concentration or amount is assumed to be known. Since the accuracy can never be better than the combined uncertainties of all processes involved, the technique also has a poor accuracy (in the tens of % to the % range). Despite this, this technique has a number of appealing features that justifies its use.

In LIF, LII, or PA, the atoms or molecules under study are excited to a higher energy level by the absorption of laser light. In LIF, the presence of excited atoms or molecules is detected by the light they spontaneously emit [15–17]. In LII, the laser light is also ionizing the species, whereby their presence is detected in terms of an increased number of charges particles (ions or electrons) [10, 16–18]. In PA, the absorbed energy from the light causes local heating, generating a thermal expansion that creates a pressure wave or sound. Hence, the signal is monitored by means of acoustic detection [23, 24]. The precision of all these highly sensitive techniques is often limited by fluctuations of the output power (or pulse energy) of the lasers (or its transmission in the optical system). Continuous-wave lasers can provide output powers that typically fluctuate or drift, on short time scales, in the low % to the % range. Pulsed lasers typically have higher pulse to pulse fluctuations. As for LIBS, averaging can, to a certain extent, improve on the precision of the assessments; although it cannot reduce disturbances in the output power of the light sources on time scales around (or beyond) that of the averaging process. In addition, for the cases when a sample has to be atomized or in any other way prepared by any sample preparation processes, e.g. by flame or electrothermal atomizers, the fluctuations of such processes can add to the finite precision of the system. This implies that, although it is possible, it is non-trivial to provide assessments with sub-% precision utilizing these types of techniques.

The accuracy of these techniques can again be given, when applicable, by the accuracy of available standard reference samples. In the case no such are available or can be used (as, for example, is the case when combustion constituents are addressed), one has to estimate the accuracy based on a model of the detection process and estimates of the accuracy of all pertinent properties (laser power, beam size, A-factors, quenching rates, temperature of the sample, etc.). Although the accuracy can be reasonable in the former case (again in the low % to the % range), it is most often considerably poorer (in the tens of % or % range) in the latter one.

LAS refers to techniques that use lasers to assess the concentration or amount of a species in gas phase by absorption spectrometry [25–27]. When applied to the assessment of species in gaseous samples, e.g. when referred to as tunable diode laser absorption spectrometry (TDLAS), it can often provide somewhat better precision than the aforementioned techniques. The reason is that they rely solely on the absorbed fraction of light, i.e. ΔI/ΔI0 (where ΔI and ΔI0 are the amounts of power absorbed by the species addressed and to which the species are exposed, respectively) and that there is no ablation/vaporization/atomization process present. This implies that, as long as the amount of light to which the species are exposed can be adequately assessed, the system is not markedly affected by the fluctuations and drifts of the laser power that take place on time scales longer than the time between the two assessments. On the other hand, since it relies on a measurement of a small change in power from a high level, any disturbance (noise or fluctuation) that take place on short time scales (e.g. introduced by the light source or the transmission through the optical system) will deteriorate the precision of the technique. For the case with gaseous samples, the precision of the LAS techniques can therefore often be better than that of the aforementioned techniques, limited by a variety of processes ranging from those in the detector or the detection system, via fluctuations of the laser power on time scales similar to that of the detection process and, if present, of the atomization process, to fluctuations in the optical system (e.g. spatial fluctuations of the laser beam on the detector caused by vibrations or turbulence in the environment). For these types of techniques, the precision can be in the low % range. The use of modulation techniques, which encode and detect the analytical signal at a (high) frequency at which there is a low level of disturbance, can improve on the detectability [28, 29], and thereby also the precision, of LAS techniques [29–35]. In this case, the precision can be in the upper part of the sub-% range.

Again, in the case standards can be used and are available, the accuracy can be given by that of those. If such cannot be used, the accuracy is predominantly given by the accuracy of the spectroscopic data about the transitions addressed (either the A-factor or line strengths). Moreover, since the distribution of the thermal population on the state(s) addressed depends on the temperature, the accuracy is also given by the accuracy by which the gas temperature can be assessed. Since fewer experimental parameters need to be assessed when AS is performed than when the aforementioned techniques are used, the accuracy can in some cases be better than when those techniques are used, but are still often in the low % to the % range.

There are though a few techniques that truly have circumvented the limitation of being restricted by the stability of the output power of the laser source. One such technique is cavity ring-down spectroscopy (CRDS). This technique bases the assessments on a comparison of the ring-down (or decay) times of a cavity in the presence and in the absence of the species addressed [36, 37]. It is, in its basic mode of operation, most often affected by drifts of the cavity, primarily those on time scales corresponding to the time between the assessments when the cavity is filled with gas and evacuated, but, to a certain extent, also those on longer time scales. The precision can therefore, for a well-constructed system, often be comparable to that of LAS. Again, the use of
advanced modulation techniques can improve on the detectability, and thereby also the precision, of CRDS techniques [6]. However, since the precision can never be better than the dynamic range, and the latter is, for ordinary CRDS, at best in the \(10^6\) range, the precision is often still in the upper part of the sub-% range.

The accuracy of a CRDS assessment is, as for the AS techniques, either given by the accuracy of standards (if available), by the accuracy of the spectroscopic parameters used, or non-linearities in the detectors. It is again seldom that the accuracy can be significantly better than in the low % to the % range.

All these techniques have in common that they interact with the imaginary part of the complex index of refraction of the sample, which provides absorption of light and/or excitation of species, which, for all techniques except CRDS, requires an assessment of the power of the light in one way or another. A means to circumvent the aforementioned shortcomings is to realize techniques that are based on the dispersive response of the species addressed, i.e. the real part of their complex index of refraction, since then the signal is carried or mediated by the shift of the phase (frequency or wavelength) of the light rather than its power [38].

However, although there are a number of techniques that rely on the dispersive response of the species addressed but that simultaneously are not affected by the stability of the output power of the laser or the transmission in the optical system, e.g. frequency modulation spectrometry [30,32] and dispersion-detecting noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) [39,40], several of them can still not circumvent the aforementioned shortcomings. The reason is that, despite their use of the dispersive response, the detected signal is still proportional to the power of the laser light. This implies that their precision is still affected by the stability of the output power of the laser or the transmission in the optical system.

There are though a few techniques that rely on the dispersive response of the species addressed but that simultaneously are not affected by the stability of the output power of the laser or the transmission in the optical system, e.g. dual-frequency modulation [41], chirped laser dispersion spectroscopy [42], cavity mode-dispersion spectroscopy (CMDS) [43], and refractometry. While the CMDS technique, which relies on pure frequency measurements of cavity mode positions (so as to avoid precision and accuracy limitations typical of most methods with intensity-dependent detection), has demonstrated an impressive dynamic range of \(2 \times 10^5\) and a precision of \(6 \times 10^{-5}\), Fabry-Perot cavity (FPC) based refractometry has the potential to obtain even better performance [44]. This technique is a sensitive technique for assessment of gas refractivity, i.e. \(n - 1\), where \(n\) is the index of refraction. Since all gases have a finite refractivity at all wavelengths, and since the dispersive response does not originate from a particular transition (it has simultaneous contributions from the wings of all possible transition in the species addressed), refractometry can be seen as “transition-less” spectrometry, applicable to all gases. Although it should preferably address a single gas species at a time, it can do so, as is shown below, with an extraordinary ability regarding precision and accuracy.

2.2. Fabry-Perot cavity based refractometry

FPC-based refractometry is built on the fact that the refractive index constitutes the ratio of an optical length in the presence and absence of gas; for the case with a FPC, with and without gas in the cavity, here referred to as \(L\) and \(L_0\) (where \(L = nL_0\)), respectively. As is shown in Fig. 1, this implies that the frequency of a given cavity mode will shift as gas is let into (or out of) the cavity.

In practice, FPC-based refractometry is most often carried out by locking the frequency of a laser to a longitudinal mode of a cavity. By this, the shift of the frequency of the mode that takes place when gas is let in will be transferred to a shift in the frequency of the laser light. A common way to assess such a shift is to mix the frequency of the laser light down to a radio-frequency (RF) by the use of another laser (a reference laser). This can practically be achieved by merging the two laser fields onto a photodiode. By this, the beat frequency between the two can be measured directly from the photodiode response by the use of a frequency counter. This implies that the shift in the frequency of the cavity mode addressed when gas is let into the cavity is converted to a shift in a measured beat frequency. Since frequency is the entity that can be assessed with highest accuracy in our society (up to one part in \(10^{16}\) and potentially even one part in \(10^{18}\) when optical clocks become the basis for the SI-second) [45], it opens for extra ordinary abilities regarding precision and dynamic range. Hence, refractometry is therefore often based on FPCs [44,46–51].

The conventional means of assessing refractivity by the use of FPC-based refractometry is to assess \(L_0\) and \(L\) in two separate assessments. Under ideal conditions, under which no physical parameter of the system changes with time, it is possible to envision a procedure in which first, once and for all, \(L_0\) is assessed with no gas in the cavity, denoted a reference measurement. Based on this, the refractivity can then be assessed by measurements of the optical length of the cavity when gas is present, i.e. \(L\). As is shown below, if the molar polarizability of the gas is known at the wavelength used (and possibly also some associated virial coefficient), the molar (or number) density of the gas can be assessed from the measured refractivity by the use of the Lorentz-Lorenz equation [52–55]. If also the gas temperature is measured, also pressure can be assessed, by the use of an equation of state [51,56]. Since the molar polarizability of a few gases can be calculated by the use of quantum mechanical ab initio calculations – for He with an accuracy in the low or sub-ppm range (depending on wavelength) [53] – this opens up for extraordinary abilities also regarding accuracy.

As was alluded to above, since all gases have a finite refractivity at all wavelengths, FPC-based refractometry can be used for any gas. Note that FPC based refractometry has so far predominantly been developed for assessment of pressure, which can be achieved, once the temperature of the gas has been assessed, by the use of an equation of state. Recent works have indicated that the technique has the potential to replace current pressure standards, in particular in the 1 Pa to 100 kPa range [54]. Such a realization of the Pascal would not depend on any mechanical actuator but instead directly measure the gas density, potentially decreasing uncertainties and shortening calibration chains. With the revision of the SI-system in May 2019, in which the Boltzmann constant was given a fixed value [56], the performance would, in principle, be limited only by the accuracies of quantum calculations of gas parameters, assessments of the deformation of the cavity material, and gas temperature and purity.
though that to provide the highest accuracy, the molar polarizability of the gas addressed (for the wavelength used) needs to be known (calculated or experimentally assessed) with at least the targeted accuracy. Since the technique does not have any species selectivity, it provides the highest accuracy when pure gases, whose molar polarizabilities have been accurately assessed, are addressed. If gas mixtures are to be addressed, their (relative) composition needs to be known and should not change during the course of the assessment. If the molar polarizability of the targeted gas (or any component of a gas mixture) is not accurately known, the technique cannot provide the highest accuracy but it can still provide high precision.

However, since the materials of which the cavity is made (the spacer as well as the mirrors) are subjected to physical deformation due to a number of reasons (e.g. gas pressure, thermal expansion, aging, relaxations, and diffusion of gas into the material) that changes the length of the cavity in an unpredicted manner, it is not trivial, in practice, to perform high-precision or high-accuracy FPC-based refractometry; even the slightest deformation in length of the cavity will significantly affect the performance of the technique. For example, a change in length of a 30 cm long cavity of 1 Å (hence, comparable to the “size” of an atom) corresponds to an error in the assessment of refractivity of $2.7 \times 10^{-10}$, which, for $N_2$, corresponds to a molar density of $4 \times 10^{-11}$ mol/cm$^3$, a number density of $2.4 \times 10^{13}$ cm$^{-3}$, and, at room temperature, an error in pressure of 100 mPa, all representing 1 ppm of their “typical” values under STP (standard temperature and pressure) conditions. This implies that the performance and applicability of FPC-based refractometry are, in practice, often limited by the stability of the cavity length [51,57,58].

There are several means to alleviate this. One is to utilize a dual-Fabry–Perot cavity (DFPC) in which two cavities, bored in the same cavity spacer, one serving as the measurement cavity and one as the reference cavity, are simultaneously addressed by two laser fields [46,50,51,59–63]. In this case, the signal can directly be measured as the beat signal between the two laser fields. An advantage of this is that any change in length of the cavity spacer that affects the two cavities equally does not affect the refractivity assessment. However, since the lengths of two cavities bored in the same spacer also can fluctuate or drift dissimilarly over time, DFPC-based refractometry will still pick up some disturbances from cavity deformation, although often to a significantly lesser extent than when a single FPC is used.

Other means to alleviate the limitations are to construct the DFPC of low thermal expansion glass, e.g. ultra-low expansion glass (ULE®) [51,62] or Zerodur® [44,50,58,59,64–71], place it in a highly temperature stabilized environment (combined gas and vacuum chamber) [51], and let the system relax and equilibrate for long time periods after each gas filling/emptying [51]. However, this is a cumbersome effort that increases the complexity of the systems as well as limits the use of the technology outside well-controlled laboratories.

2.3. Gas modulation refractometry - GAMOR

Following the success of various modulation methodologies to improve on the performance of laser-based absorption spectrometry by encoding and detecting the signal at high frequencies at which there is less technical noise [28,29] (e.g. wavelength and frequency modulation [29–35]), we decided to develop a methodology, likewise based on modulation, that could improve also on the limiting situation of FPC-based refractometry (primarily reduce the influence of fluctuations and drifts of the length of the cavity on the assessments). The methodology, which is built on a regular alteration of the amount of gas in the measurement cavity, is referred to as Gas Modulation Refractometry (GAMOR) [55,72–74]. The methodology has so far predominantly been developed with the aim of assessing gas pressure of nitrogen, but is also fully capable of assessing both pressure and molar density of a variety of gases.

2.3.1. Principles

As previously has been explicated [55,72,75,76], and as is illustrated in some detail below, the GAMOR methodology is built upon two principles, here referred to as two cornerstones; viz.

(i) the refractivity of the gas in the measurement cavity is assessed by a frequent referencing of filled measurement cavity beat frequencies to evacuated cavity beat frequencies, and

(ii) the evacuated measurement cavity beat frequency at the time of the assessment of the filled measurement cavity beat frequency is estimated by use of an interpolation between two evacuated measurement cavity beat frequency assessments, one performed before and one after the filled cavity assessments.

Each of these cornerstones has its own features and they jointly provide the GAMOR methodology with its unique properties.

2.3.2. Precision

It has been explicated in a pair of detailed scrutinies that the GAMOR methodology can significantly reduce the influence of both fluctuations [74] and drifts [77]. Experimentally, it has been shown that, when GAMOR was implemented in a Zerodur®-based DFPC system for assessment of pressure with no active temperature stabilization, it could significantly reduce fluctuations and drifts; for assessment of $N_2$ at 4303 Pa, the standard deviation could be reduced more than three orders of magnitude, from 6.4 Pa to 3.5 mPa [72]. When applied to a system with active temperature stabilization, it has demonstrated a sub-mPa stability for low pressures and a sub-ppm precision for assessment of 4304 Pa of $N_2$ [55].

The extraordinary properties of the methodology have also opened up for the use of non-conventional cavity-spacer materials that previously were regarded improper for refractometry (since some of their properties previously were considered unsuitable, primarily their thermal expansion) but that instead have other advantageous properties (e.g. a high thermal conductivity, which is of importance for accurate...
Fig. 2. An illustration of the principles of GAMOR implemented on an experimental system exposed to campaign-persistent drifts, displayed over two full modulation cycles. Panel (a) displays, as functions of time, the pressures in the measurement cavity, $P_m(t)$ (the upper red curve) and in the reference cavity, $P_r(t)$ (the upper blue curve). Panel (b) shows the corresponding frequencies of the measurement and reference lasers, $v_m(t)$ (the lower red curve) and $v_r(t)$ (the upper blue curve), respectively, in the presence of drifts (for display purposes, in the absence of mode jumps and offset to a common frequency $v_0$). Panel (c) illustrates the corresponding beat frequencies: by the upper black curve, the measured one in the presence of the gas modulation, $f(t)$, and, by the lower green line, the estimated evacuated measurement cavity beat frequency, $f_{0,0}(t_{n-1}, t_{n+1} \rightarrow t_n)$, which, according to Eq. (5), has been constructed as a linear interpolation between two evacuated measurement cavity assessments (taken at the positions of the cross). Panel (d), finally, displays, by the black curve, the drift-corrected shift in beat frequency, $\Delta f(t)$, at each time instance given by the difference between the beat frequency measured with gas in the measurement cavity, $f(t)$, and the interpolated evacuated measurement cavity beat frequency, $f_{0,0}(t_{n-1}, t_{n+1} \rightarrow t_n)$, The circles in the two lowermost panels illustrate the parts of the data that are used for evaluation of the gas refractivity; the red and the green circles in panel (c) represent $f_{0,0}(t_n)$ and $f_{0,0}(t_{n-1}, t_{n+1} \rightarrow t_n)$, respectively, while the red circle in panel (d) corresponds to their difference, i.e. $\Delta f(t_n)$. The drifts and the slope of the interpolated evacuated measurement cavity beat frequency have been greatly exaggerate for display purposes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3.3. Accuracy

When high accuracy assessments are to be made by FPC-based refractometry, the limiting factor is often the finite deformation of the cavity when gas is let in. To remedy this, a novel procedure for assessment of cavity deformation has recently been developed [76]. It is based on scrutinizing the difference between two pressures, one assessed by the uncharacterized refractometer and the other provided by a pressure reference system, at a series of set pressures, for two gases with dissimilar refractivity (here He and N$_2$). It was shown that, by fitting linear functions to the responses and utilizing the slopes of the fits, the novel procedure and the high precision of the GAMOR instrumentation jointly allowed for an assessment of cavity deformation to such a high accuracy that, when high purity gases are used, the uncertainty in the deformation contributes to the uncertainty in the assessment of molar (and number) density and pressure of N$_2$ with solely a fraction (13%) of the uncertainty of its molar polarizability, presently to a level of a few ppm. This implies, in practice, that, when molar (or number) density or pressure of N$_2$ is targeted, cavity deformation is no longer a limiting factor in GAMOR implemented FPC-based refractometer assessments. This allows for assessments of these entities with an accuracy practically given by the accuracy by which the molecular polarizability is known. Since the molecular polarizability of nitrogen at the wavelength used (1.55 $\mu$m) is known to an accuracy of 8 or 31 ppm (for assessments traceable to a thermodynamic or a mechanical standard, respectively [51,62,76,79]) this indicates that the GAMOR methodology is capable to assess molar (or number) density of nitrogen with a similar accuracy [76]. Since rapid gas exchange can introduce thermodynamic processes that potentially can affect the assessments of molar density and pressure when gas modulation methodologies are used, it is of importance to assess the conditions under which such processes can (and will) affect an assessment. Since such effects are affected by a number of processes, including such caused by the instrumentation used (e.g. the lengths and diameters of gas tubing and temperature conditions), the gases used (their thermodynamic properties), and the mode of operation of the system (the modulation cycle times), such a scrutiny is non-trivial to perform in detail. Work addressing these concepts in some detail is presently being pursued. Preliminary investigations indicate that under the conditions the system so far has been operated (i.e. when nitrogen is assessed at pressures up to some tens of kPa) no such influences have been found. Since the magnitude of such effects are assumed to depend on the gas pressure (i.e. equilibration processes becomes slower the higher the pressure is), it is possible though that longer gas modulation cycle times need to be used when higher pressures are addressed.

5 Since the detection process allows for continuous detection of the beat frequency (the beat frequency is assessed by a rate of 4 Hz, given by the time it takes from the frequency counter to appropriately assess a beat frequency), it is possible to assess (and thereby follow in some detail) gas exchange processes and any possible associated thermodynamic processes associated with those in “real” time. When nitrogen is assessed at pressures up to some tens of kPa, it has been experimentally that the assessed beat frequency changes with time for the first parts of a hundred seconds long the filling cycle. However, and more importantly, it levels off on time scales of a few tenths of seconds. After this leveling off, there are no detectable residual “drift” in the assessed beat frequency. We also do not see any correlated drift in temperature of the cavity spacer. This indicates that the gas exchange processes have reached an equilibrium at these time scales and that no residual thermodynamic processes affect the temperature or gas molar density in the measurement cavity; any remaining change in temperature would, for a constant pressure, as set by our pressure balance, affect the molar density, and thereby the measured beat frequency. This implies that for the pressures so far addressed (up to 16 kPa), and with gas modulation cycle times of 100 s, it is assumed that the gas exchange and thermodynamic processes do not influence the assessments of molar density or pressure.
3.3.4. Other properties

The GAMOR methodology has also a number of other important properties. One is that, since the measurement principle is based on assessing a change in frequency, there is no fundamental limit of the dynamic working range of the technique (there is no physical entity, e.g. sensor response or voltage, that can be “saturated”). In practice, its lower limit is given by the stability at low molar density/pressure assessments, while the upper limit is set by the mechanical properties of the cavity and the vacuum system [55,80]. So far, the GAMOR methodology has demonstrated, with no alteration of any instrumental settings, assessments of pressure in the range from 0.03 mPa to 16 kPa [73]. Hence, it has so far proven a dynamic range in the order of 10^8.

Another important property is that, due to the high accuracy of frequency measurements, and the fact that no moving parts are needed (except for the opening and closing of gas valves), the assessments can be done swiftly without any manual oversight. The fact that GAMOR-based FPC-based refractometry can work in an unattended mode of operation with high precision over such a large dynamic range, which is unprecedented when gas molar (or number) density or pressure is assessed, makes it both unique and versatile.

3. Theory

The GAMOR methodology is based on the same fundamental principle as ordinary (unmodulated) refractometry; it measures the change in refractive index of two situations; one with gas in the measurement cavity and another without. This implies that it is governed by the same basic equations as unmodulated FPC-techniques.

3.1. Assessment of gas refractivity from a measured shift in beat frequency

FPC-based refractometry is based on the fact that, when gas with an index of refraction \( n \) is let into an evacuated (measurement) cavity, the frequency of a given longitudinal cavity mode, \( \nu_1 \), will shift from \( \nu_1 \) to \( \nu_f \), which are given by\(^6\)

\[
\begin{align*}
\nu_1 & = \frac{q_0 c}{2L_1} \\
\nu_f & = \frac{q_o c}{2n(L_0 + \delta L)} = \frac{\nu_1}{n(1 + \delta L)} 
\end{align*}
\]

where \( q_0 \) is the number of the longitudinal mode addressed by the laser when the cavity is evacuated, \( c \) is the speed of light, \( \delta L \) represents the physical deformation (elongation or contraction) of the cavity due to the gas, and \( \delta L / L_0 \) denotes the corresponding relative entity, given by \( \delta L / L_0 \). For the case when DFPC refractometry is performed, most often the second cavity is considered to be a reference cavity whose conditions are not changed, whereby the frequency of an addressed cavity mode in that cavity, \( \nu_2 \), is fixed. This implies that the beat frequency between the two laser fields for the case with filled and empty measurement cavity, denoted \( \Delta f_{0g} \) and \( \Delta f_{00} \), will be given by \( \nu_f - \nu_2 \) and \( \nu_f - \nu_0 \), respectively. As is illustrated in Fig. 1, this implies, in turn, that the shift in the beat frequency, \( \Delta f \), which is defined as \( \Delta f_{0g} - \Delta f_{00} \), in practice, is given by the difference between the two expressions given in Eq. (1).

When GAMOR is utilized, based upon the Eq. (1), it has been found convenient to express the refractivity of the gas under scrutiny, \( n - 1 \), as a function of the shift of the beat frequency between the two laser fields probing the two cavities, \( \Delta f \), as \([55,73,74,76]\).

\[
n - 1 = \frac{\Delta f}{\delta f_0} + \epsilon_m
\]

where \( \Delta f \) is the relative shift of the beat frequency given by \( \Delta f_{0g} \) and \( \epsilon_m \) is a refractivity-normalized relative cavity deformation, defined as \( (\delta L / L_0)(n - 1) \). We have here also allowed for the fact that, as gas is let into (or out of) the cavity, the laser addressing the measurement cavity might need to make (controlled) mode jumps, from one mode to a neighboring one. Hence, \( \delta f_0 \) is a shorthand notation for \( \Delta f_{0g} / q_0 \), where \( \Delta f_{0g} \) is the shift in mode number of the mode addressed in the measurement cavity.

This expression shows that, for each given cavity, \( \epsilon_m \) is the only parameter that needs to be assessed by a characterization process.\(^7\) As was alluded to above, a process for efficient assessment of this has recently been developed [76].

3.2. Assessment of gas molar density and pressure from the gas refractivity

The conversion of refractivity, \( n - 1 \), to gas molar density, \( \rho \), is performed through the extended Lorentz-Lorenz equation, given by Eq. (SM-20) in the supplementary material of Ref. [55]. It is shown in that work that the density can be assessed from the measured refractivity by

\[
\rho = \frac{2}{3A_R} (n - 1)(n + 1/2 - 1/2n) 
\]

where \( A_R \) and \( b_{n-1} \) are the dynamic molar polarizability and a series expansion coefficient, respectively, where the latter is given by \(-1 + A_R b_{n-1} / 6\), where, in turn, \( A_R \) is the second refractivity virial coefficient in the Lorentz-Lorenz equation for the type of gas addressed [52,53,55,78].

In the case pressure is addressed, it can be obtained from the density as

\[
P(T) = RT[1 + B_2(T)\rho]\]

where \( R \) is the molar gas constant, \( T \) is the temperature of the gas, and \( B_2(T) \) is the second density virial coefficient [51].\(^8\)

3.3. The GAMOR methodology – Interpolated modulated refractometry – Principles

As was alluded to above, GAMOR is based on two cornerstones, viz. (i) the refractivity of the gas in the measurement cavity is assessed by frequent referencing of filled to evacuated measurement cavity beat frequencies, and (ii) the evacuated measurement cavity beat frequency at the time of the assessment of the filled measurement cavity beat frequency is estimated by use of an interpolation between two evacuated

\(^6\) Neglecting any possible influence of a finite but minute penetration depth of light into the mirrors [76].

\(^7\) It is of importance to note that Eq. (2) shows that, opposed to some persistent claims of the opposite, the refractivity (and thereby the molar density and pressure) can be assessed without any explicit assessment or monitoring of the length of the measurement cavity, i.e. \( L_0 \). The reason for this is that the change in cavity mode frequency when the measurement cavity is evacuated (or filled with gas) is measured as a relative frequency shift of a cavity mode, \( \Delta f \). There is neither any need to explicitly assess the FSR. The reason for this is that \( \Delta f_{0g} \) is not expressed in terms of the FSR but instead in the mode number of the mode addressed, \( q_0 \), which is an integer that can be assessed uniquely (i.e. with no uncertainty) by ensuring that the assessed refractivity is a continuous function when the measurement laser is making a (controlled) mode jump. An alternative means to assess \( q_0 \) is as the closest integer to the ratio of the frequency of the laser addressing the evacuated measurement cavity, \( \nu_0 \), and the FSR of the cavity. It should be noticed that the former of these means does not require assessment of any physical entity.

\(^8\) If large densities (or high pressures) of gas are to be assessed, additional higher order terms need to be added in the Eqs (3) and (4).
measurement cavity beat frequency assessments, one performed before and one after the filled cavity assessments. Its principles are schematically illustrated in Fig. 2 for the case when the methodology is implemented on an experimental system exposed to campaign-persistent drifts (i.e. drifts that affect the cavity mode frequencies persistently and continuously during the entire measurement campaign).

Fig. 2(a) illustrates, by the upper red curve, the pressure in the measurement cavity, which, according to cornerstone (i), is alternately evacuated and filled with gas, while the reference cavity, indicated by the lower blue curve, is held at a constant pressure (in this case for simplicity chosen to be at vacuum). Campaign-persistent drifts will affect the frequencies of both the measurement and the reference lasers [although possibly to dissimilar extent, as shown in panel (b)] and thereby the assessed beat frequency (the upper black curve in panel (c)). The figure indicates, first of all, that the influence of drifts can be reduced by shortening the modulation cycle period (for a given drift rate, the shorter the gas modulation period is, the less will the assessed beat frequency be affected by drifts).9

In addition, according to cornerstone (ii), the evacuated measurement cavity beat frequency is, for each modulation cycle, not assessed by a single measurement; it is instead estimated by the use of a linear interpolation between two evacuated measurement cavity beat frequency assessments performed in rapid succession — one performed directly prior to when the measurement cavity is filled with gas (for cycle $n$, at a time $t_0$, denoted $f_{0,0}(t_0)$), and another directly after the cavity has been evacuated (at a time $t_{n+1}$, denoted $f_{0,0}(t_{n+1})$), both marked by crosses in Fig. 2(c). By this, the evacuated measurement cavity beat frequency can be estimated at all times $t$ during a modulation cycle. For cycle $n$, for which $t_0 \leq t \leq t_{n+1}$, it is estimated as

$$
\tilde{f}(0,0)(t; t_0, t_{n+1}) = f_{0,0}(t_0) + \frac{f_{0,0}(t_{n+1}) - f_{0,0}(t_0)}{t_{n+1} - t_0}(t - t_0)
$$

(5)

For the case with campaign-persistent drifts, this interpolated value is represented by the green line in Fig. 2(c). The value of the estimated evacuated measurement cavity beat frequency at the time when the filled measurement cavity assessment is performed (assumed to take place at $t_f$), denoted $\tilde{f}(0,0)(t_f; t_0, t_{n+1})$, is marked by a green circle in Fig. 2(c).

By subtracting the estimated (interpolated) evacuated measurement cavity beat frequency ($\tilde{f}(0,0)(t_f; t_0, t_{n+1})$, the green line) from the measured (drift-influenced) beat frequency during gas filling ($f(t)$, the black curve), both in panel (c), a campaign-persistent-drift-corrected net cavity beat frequency, represented by the black curve in panel (d), results. The value of this curve at $t_f$ represents the $\Delta f$ to be used in Eq. (2) when GAMOR is performed.10

9 Although GAMOR most often has been performed by the use of evacuated-measurement cavity reference measurements, it is possible to utilize alternative modes of modulations, e.g. as in gas equilibration GAMOR (GEQ-GAMOR) in which the measurement cavity is not evacuated but instead its gas is let into the reference cavity for a swifter gas equilibration [55].

10 A short gas modulation cycle time also allows for, within a given campaign time, a large number of repeated measurements, which, in turn, allows for both a reduction of the influence of fluctuations [74] and an averaging of a large number of individual assessments that will reduce disturbances (noise) of white type [77].

4. Experimental set-up

4.1. An overview of GAMOR instrumentation developed over the years

Over the years, a variety of GAMOR instrumentation have been developed. While the first versions utilized a simplistic design and were constructed to carry out proof-of-principle demonstrations [58,71,72], the later realizations have been gradually upgraded to improve on their performance, firstly regarding precision [55,73] and lately concerning accuracy [76,81]. Fig. 3 displays three such systems. Common for all systems is that they have been based on DFPC systems with FSRs of around 1 GHz, and finesse values of $10^4$, firstly with cavities bored in Zerodur (the panels (a) and (b)) and lately in Invar (panel (c)). For easy tunability and handling, the cavities are probed by Er-doped fiber lasers (EDFLs) emitting light within the C34 communication channel, i.e., around 1.55 μm.

To be able to assess relevant properties of the various instruments, they have been connected to a dead-weight pressure balance (RUSKA 2465A) that provides a well-defined and stable pressure. The refractometer systems have therefore, so far, mostly been developed for assessment of pressure. Since the measured refractivity swiftly can be connected to molar density (by Eq. (31)), and pressure does not only depend on the molar density but also on temperature (Eq. (4)), also the temperature of the cavity block has been assessed. This has most often been done by the use of Pt-100 sensors placed in holes drilled into the cavity spacer.12

4.2. State-of-the art GAMOR instrumentation

The assessments of pressure (and thereby gas molar density) presented in this work were made either on an early Zerodur®-based DFPC-refractometer (displayed in Fig. 3a) [72] or a more recent Invar-based system [73]. Regarding the latter, which has shown the best performance, the spacer block has a length of 150 mm. The two cavities are made up by 6 mm diameter thoroughgoing holes that have been drilled from the short end sides of the spacer. Each cavity is made up by two highly reflective 12.6 mm diameter concave cavity mirrors (with a radius of curvature of 500 mm) that are placed in machined inlets in the spacer so as to provide cavities with finesse values of $10^4$. To provide vacuum tight seals, the mirrors are pressed, via O-rings, into the spacer material by the use of plates. This allows for easy removal and cleaning or replacement of the mirrors. Each cavity is also connected to a gas handling system by a vacuum tube through which gas either can be supplied or evacuated. The Invar cavity assembly, before being equipped with temperature probes and mounted inside the aluminum enclosure (oven) that is shown in Fig. 3c, is displayed in Fig. 4.

As is shown in the schematic illustration of the set-up in Fig. 5, each cavity is probed by a laser whose frequency is locked to a longitudinal mode in the cavity. After being produced by EDFL, the light in each arm is coupled into an acousto-optic modulator (AOM). The first order output of the this is, in turn, coupled into a 90/10 fiber splitter, whose 90% output is sent to an electro-optic modulator (EOM) that is modulated at 12.5 MHz for Pound-Drever-Hall (PDH) locking [82]. The output of the EOM is sent through an optical circulator to a collimator whose output (10 mW) is mode matched to the TEM₀₀ mode of the FPC. The intracavity power in the cavity is ca. 30 W. The back reflected light, used for locking, is picked-up by the collimator and routed through the circulator onto the a fast photo detector. To provide information for the mode relocking process (see below), also the light transmitted through the cavity is detected, this time by a large area photo detector. The outputs from the photo detectors are connected to a field programmable

12 Lately also by the use of thermocouples that are referred to a gallium fixed-point cell whose temperature is based upon the well-defined melting point of gallium [81].
In the FPGA, the signals from the reflection detectors are demodulated at 12.5 MHz to produce the PDH error signals for the locking process while the signals from the transmission detectors are used to control the feedback when a laser is making a mode hop. The slow components of the feedback (<100 Hz) are sent to the laser while the fast ones (>100 Hz) are routed to a voltage-controlled oscillator (VCO) that produces an RF voltage that drives the AOM at around 110 MHz.

To detect the beat frequency between the two arms, the remaining light fields from the two fiber splitters (i.e., their 10% outputs) are combined in a 50/50 fiber coupler and sent to a fiber coupled photo detector (denoted Beat Detector) whose RF output in turn is routed to a frequency counter.

The temperature of the cavity spacer is monitored by three calibrated Pt-100 sensors that are placed in holes drilled into the cavity spacer. Both the long-term (temporal) stability and the (spatial) gradients in temperature of the cavity were estimated to be below 5 mK [74]. The performance on the shorter time scales was assumed to be better than this.

The PDH locking procedure provides a locking of the frequency of the laser to that of the cavity mode to within a fraction of a % of the full-width-half-maximum (FWHM) of the cavity mode. Since the latter is ~100 kHz (given by the ratio of the FSR and the finesse), this implies that the laser has a frequency stability (versus the cavity mode) that is in the sub-kHz level.

The DFPC spacer is connected to a gas and vacuum system whose details are given elsewhere [73]. High-purity nitrogen is supplied from a central gas unit. The residual amount of gas in the system was monitored by a pressure gauge.
To produce frequencies that provide a beat frequency that is in the center of the working range of the frequency counter the lasers are initially (i.e. before the measurement series) tuned by temperature to suitable cavity modes. After this manual (coarse) setting, to allow for automated assessments, an automatic re-locking routine is engaged, which keeps the beat frequency within the dynamic range of the frequency counter (between 2 and 6 GHz) under all measurement conditions.

A measurement campaign starts by assessment of the frequencies of the two lasers when locked to evacuated cavities, i.e. $\nu_0$ and $\nu_r$, which can be assessed with a relative uncertainty of $2 \times 10^{-7}$ by the use of a wavelength meter, and the mode numbers addressed for the measurement cavity, i.e. $N_2$, which can be assessed uniquely (i.e. with no uncertainty) from the fact that $n - 1$, as given by Eq. (2), should be a continuous function when one of the lasers is making a mode hop. $\nu_0$ was in this case assessed to 190,995.

Moreover, the cavity module has recently been preliminary characterized with respect to its pressure induced cavity deformation by use of a novel two-gas method, using helium and nitrogen. As is further discussed in detail in that work, it was found that the relative elongation per Pa of the cavity being used, $\overline{\delta \varepsilon} / \overline{P}$, is $5.258 \times 10^{-12}$ Pa$^{-1}$, which implies that, when $N_2$ is being detected at the wavelength used, $\varepsilon_n$ is $1.9630(4) \times 10^{-12}$ [76].

5. Results

Although the main aim of this work is to illustrate the performance of GAMOR instrumentation to assess gas molar (or number) density, because of a lack of reference systems for this physical entity, the performance of the system has been assessed by its ability to assess pressure.

5.1. The ability of GAMOR to eliminate the influence of drifts

As was alluded to above, it was early demonstrated, as a proof-of-principle, by use of the instrumentation shown in the uppermost panel in Fig. 3, that the GAMOR methodology, when applied to a DFPC refractometry instrumentation utilizing a non-temperature-stabilized cavity spacer made of Zerodur® could, when assessing pressure, reduce the influence of drifts three orders of magnitude [with respect to when the refractometer utilized conventional (unmodulated) detection] [72]. This is illustrated in Fig. 6. The upper blue curve in panel (a) (right axis) shows the temperature drift over 24 h while the lower red curve (left axis) shows the corresponding drift of a conventional non-temperature-stabilized DFPC refractometry signal (expressed in units of pressure of N$_2$) from an evacuated cavity. The horizontal black line is not, as it might appear, the time axis; it is, in fact, the actual corresponding GAMOR signal. Panel (b) shows an enlargement of a part of this data. Note the more than three orders of magnitude differences in scales. This illustrates the extraordinary ability of the GAMOR methodology to significantly reduce (in practice eliminate) the drifts that could, when assessing pressure, often limit conventional DFPC-based refractometry.

5.2. Estimate of its precision

Utilizing the Invar-based GAMOR instrumentation described in some detail above, together with a dead weight piston balance to provide a reference pressure, we have demonstrated that this system can outperform earlier systems based on Zerodur® and provide assessments with sub-ppm precision, which is, as was alluded to above, several orders of magnitude better than most other laser-based detection techniques [72].

To illustrate the exceptional precision of the methodology, Fig. 7 displays, as a function of time, the GAMOR signal from 4303 Pa of N$_2$ (which corresponds to a gas molar density of $1.7 \times 10^{-6}$ mol/cm$^3$) measured from a series of measurements taken over 24 h of uninterrupted assessments. The seven panels, (a) – (g), display the response of the refractometer with successively enlarged scales of the y-axis. While panel (a) displays the signal with a y-scale ranging over 8 kPa (corresponding to a gas molar density of $3.2 \times 10^{-12}$ mol/cm$^3$), the subsequent panels (b) – (g) display the same data with successively one order of magnitude lesser range of the y-axis: i.e., 800 Pa, 80 Pa, 8 Pa, 0.8 Pa, 0.08 Pa and 0.008 Pa, respectively (where the latter range represents $3.2 \times 10^{-13}$ mol/cm$^3$). Each red data point represents an individual GAMOR cycle, while the black, dashed curves represent moving averages of 10 cycles.

The panels (a) to (e) show that the data has such high reproducibility and precision that, despite an enlargement of the y-axis by 4 orders of magnitude, there is no noticeable noise or drift in the data. Panel (f), which illustrates the data with an enlargement of 5 orders of magnitude, indicates that, only on this scale (i.e., on the 1:10$^8$ level), some noise and drift start to be visible. These are more clearly illustrated in the last panel, panel (g), which shows the magnitude and the form of the noise and drifts, which are on the 1:10$^9$ level.

Treating the same data by an Allan deviation analysis, Fig. 8 shows by the lowermost (blue) curve that the system could, for an empty cavity, demonstrate a white noise response up to $10^4$ s with a minimum Allan deviation of 0.03 mPa (which corresponds to a gas molar density of $1.2 \times 10^{-14}$ mol/cm$^3$). When set to assess pressure at 4303 Pa, the system could provide, by the middle (red) curve (for measurement times of $10^3$ s, representing 10 measurement cycles), a minimum Allan deviation of 0.34 mPa (a gas molar density of $1.4 \times 10^{-13}$ mol/cm$^3$), which corresponds to a relative deviation, i.e. a precision, of 0.08 ppm [73]. For comparison, the uppermost curve (green in colour) represents a comparable curve taken at the same pressure by an earlier Zerodur-based system [55].

The extraordinary performance of this system, with a minimum Allan deviation of 0.03 mPa and a precision of 0.08 ppm when assessing a pressure of 4303 Pa, should be seen as an upper limit for the ability of the refractometer to assess gas molar density. The reason for this is, first of all, that the data in Fig. 8 represent the combined noise, fluctuations and drifts from the pressure balance and the refractometer. This implies that the aforementioned precision is an upper limit of the actual precision of the refractometer when pressure is assessed.
Moreover, since also fluctuations of the assessed gas temperature contribute to the data shown in Fig. 8, it can be concluded that the precision of the refractometer for assessment of pressure, in turn, is an upper limit for its ability to assess gas molar density. This implies that it is possible to conclude that the system has an ability to assess gas molar density with a precision below 0.08 ppm. This implies, in turn, that the system is capable of assessing molar density of $1.7 \times 10^{-6}$ mol/cm$^3$ with at least a resolution of at least $1.4 \times 10^{-13}$ mol/cm$^3$, possibly even better than this. Since the precision is not affected by any systematic uncertainties in any system- or gas-parameters, this limit should be accessible for virtually all gases.

5.3. Estimate of its accuracy

As can be concluded from an inspection of the Eqs. (2) and (3) and their preconditions, the accuracy of an assessment of molar density is affected by only a few experimental parameters, predominantly the penetration depth of the mirrors, the accuracies of the frequency counter, the cavity deformation, the molar polarizability, and the second refractivity virial coefficient of the gas addressed.

It can first of all be concluded that the penetration depth of low dispersion mirrors can be so small so they contribute to an assessment of the in the low (or even sub-) ppm range [76]. Secondly, the accuracy of a frequency assessment by a modern frequency counter, run under the pertinent conditions, is significantly below the standard deviation (and precision) of the assessments. Hence, it can be surmised that the accuracy of the frequency counter will not play any significant role in the assessment of gas molar density. Thirdly, it can be concluded, from gas properties, that the uncertainty of the second refractivity virial term (which, for $N_2$, is 0.007 [62,76]) will influence an assessment of $N_2$ on the 2 ppm level when pressures or gas molar densities under STP conditions are addressed (and thus to a lower degree when lower pressures and smaller molar densities are assessed). Fourthly, it has been concluded that the recently developed procedure for assessment of cavity deformation allows for assessment of cavity deformation to such a level that, when high-purity gases are used, it will affect an assessment of pressure or gas molar density solely with a fraction (typically 13%) of the uncertainty of the molar polarizability of nitrogen [76]. Fifthly, it can be concluded from literature data that the $(k = 2)$ uncertainty of the molar polarizability of nitrogen has been assessed to 8 ppm by the use of mechanical pressure standard [51,62,76]. This implies that the accuracy of an assessment of molar (or number) density when nitrogen is addressed presently is dominated by the latter.

Since the molar polarizability of $He$ can be assessed by ab initio quantum mechanical calculations with sub-ppm accuracy [53], and, if the molar polarizability of other gases are either related to this by experimental assessments or like-wise calculated by similar types of calculations, it can also be used as a primary or semi-primary standard for both molar density and pressure [54]. The $(k = 2)$ uncertainty of the molar polarizability of $N_2$ calculated by a thermodynamic standard is presently 31 ppm [76,79] but is assumed to be improved in the future.

Since there are some gases whose molar polarizability has been assessed with $(k = 2)$ uncertainties in the low tens of ppm range (e.g., Ne, Ar, Xe, CO$_2$, and N$_2$O to 32 ppm) [79], it is possible to conclude that the GAMOR methodology should be capable of producing assessments of gas molar density with an accuracy in the low tens of ppm range for a range of gases (at least those given above). For gases whose molar polarizabilities have not yet been assessed with similarly high accuracy, the accuracy of gas molar density assessments will not reside in the same low ranges until their polarizabilities have been assessed with improved accuracy.

6. Conclusions

A technique for high-precision and high-accuracy assessment of gas molar (and number) density (and pressure) has been presented. The technique achieves this by a combination of properties. First of all, it makes use of the extraordinary ability of Fabry-Perot cavity (FPC) based refractometry to, by use of the dispersive response of light-matter-interaction, in combination of established laser locking technology (the PDH technique), assess refractivity as a shift of a directly
Gas Modulation Refractometry (GAMOR). The GAMOR technique is FPC-based refractometry with a gas modulation methodology, yielding more than three orders of magnitude; reducing the standard deviation built upon a repeated filling and evacuation of the measurement cavity - capable of reducing the influence of drifts in a non-temperature stabilized measurement setting [73]. It has been demonstrated that, when the N2 is addressed, it should be able to achieve an accuracy that is below 10 ppm [76]. It is claimed that the ability to assess gas molar density is at least as good as so far has been demonstrated for pressure.

Since the GAMOR methodology has demonstrated assessments of pressure from 0.03 mPa to 16 kPa with no alteration of any instrumental setting [73], it can be concluded that it has a dynamic range that is at least 8 orders of magnitude. An explanation to the extraordinary sub-ppm precision and high dynamic range of the GAMOR methodology can be obtained by considering the fact that a pressure of N2 of 16 kPa provides, for NIR light in the 1.5 μm range, a shift of the cavity modes in the measurement cavity of 10 GHz, which is more than seven orders of magnitude larger than the frequency stability of the lasers in the cavity modes on the time scale of a single modulation cycle, which is in the sub-kHz level. By averaging over several gas modulation cycles, which improves on the frequency stability of the lasers in the cavity modes to below the 100 Hz level, a dynamic range of eight orders of magnitude can be expected, which is in agreement with the experimental findings and a prerequisite for a sub-0.1 ppm precision.

The methodology achieves a high accuracy by the use of quantum mechanical ab initio calculations of the molar polarizability (so far of N2), which is in agreement with the experimental findings and a prerequisite for a sub-0.1 ppm precision.

Since this technique has a number of appealing properties, in the case it is not directly suitable for all types of applications, it is our hope that it can inspire potential users to the development of new techniques that can fulfill their requirements. It should be clear that it can serve as a base for development of other techniques, or can be used in combination with other techniques that are used for assessment of a number of physical phenomena. One such example is that it can serve as a technique for assessment of gas molar (and number) density when molecular gas parameters (e.g. A-factors and line strengths) are to be assessed.

Declaration of Competing Interest

The authors declare no conflicts of interest.

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