Experimental determination of molar polarizability of nitrogen by a multi-reflection inteferometric technique

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EXPERIMENTAL DETERMINATION OF MOLAR POLARIZABILITY OF NITROGEN BY A MULTI-REFLECTION INTEFEROMETRIC TECHNIQUE

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Abstract:
A novel optical pressure standard, based on a multi-reflection interferometric technique, has been recently developed. It is based on the measurement of the refractive index of a gas through an unbalanced homodyne interferometer (UINT) and is able to measure pressure with a relative standard uncertainty of 10 ppm at 100 kPa [1]. In this work, the interferometer was used to measure the molar polarizability of nitrogen, which resulted in agreement with recent previous determinations, paving the way for using photonic pressure standards as accurate and fast transfer standards of the pascal.

Keywords: molar polarizability; nitrogen; laser interferometry; optical pressure standard

1. INTRODUCTION

In the new SI, the uncertainty of the Boltzmann constant k_B was eliminated, making advantageous to realise the pascal through number density measurements via optical methods, resulting in significant progress achieved in recent years at various metrological institutes and universities all around the world [1-14]. In this contest, a novel optical pressure standard, named UINT and alternative to Fabry-Perot cavity-based realizations, has recently developed [1]. The performance of UINT system, as well as the novel generation of photon-based pressure standards, in long term, would be mainly limited by the accuracies of determination of relevant gas parameters and the temperature assessment. In particular, among the various gas parameters, the molar polarizability A_R is largely the dominant term. From a purely metrological point of view, such standards can operate as primary standard, only in case A_R can be determined from ab-initio calculations. At present, the best accuracy can be obtained using helium, whose polarizability can be determined by quantum-based calculations with sub-ppm uncertainty.

Beside helium, other gases of interest are under study, to estimate their gas properties by ab-initio calculations, in particular argon [15].

An alternative and interesting path, is represented by the experimental determination of the molar polarizability A_R, considering common gases whose properties, at moment, cannot be accurately calculated by first principles and using the optical pressure standards as accurate and fast transfer standards of the pascal. In the present work, nitrogen has been considered as fundamental case study due to its extensive use in pressure metrology: the UINT system was connected to a pressure balance, which was used to accurately measure the pressure by an independent method, allowing an experimental measurement of the molar polarizability at 633 nm, which can be compared to other results in literature.

2. DESCRIPTION OF THE WORK

The UINT optical pressure standard is based on the measurement of the refractive index of a gas through an unbalanced homodyne interferometer with fixed arms. The interferometer was designed to have the measurement arm formed by a multi reflection double mirror assembly to establish an unbalance length L between the two arms larger than 6 m in a compact set-up.

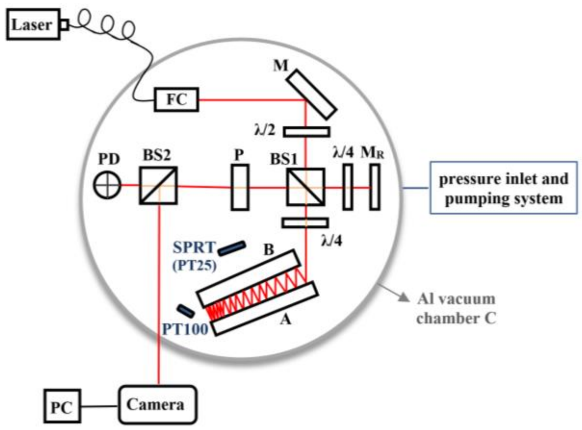

Figure 1: Schematic of the UINT optical pressure standard with laser interferometer placed inside aluminium vacuum chamber C; FC: collimator; MR: reference mirror; P: polarizer; BS1 and BS2: beam splitters, PD: photodiode.

The figure 1 shows the schematic of the system, currently able to work up to 120 kPa and to fulfill the main goal of measuring pressure through a multi-reflection interferometric technique with a relative standard uncertainty of 10 ppm at pressure above 10 kPa.

The fundamental part of the optical system is the double mirror multiplication setup, where the beam is reflected several times between two quasi-parallel mirrors A and B, which are bonded to a custom spacer.

All the optical components of the interferometer are fixed on a circular plate of 210 mm diameter, placed in an aluminium vacuum temperature-controlled chamber C, where the standard pressure p is generated. To minimize deformations due to eventual temperature variations and gradients, the double mirror assembly of dimension (90 × 60 × 27) mm and the circular plate are made both of ZERODUR® glass ceramic, whose nominal mean coefficient of thermal expansion, within the temperature range of 0 °C to 50 °C, is equal to $(0 \pm 0.050\times10^{-6})$/K.

The realization of an accurate optical-based pressure standard requires an assessment of temperature with an uncertainty at millikelvin level. To meet this requirement, the UINT system was equipped with a double-stage temperature control.

Details about the most important steps concerning the realization of the UINT pressure standard are described in [1].

A picture of the system is shown in the figure 2.

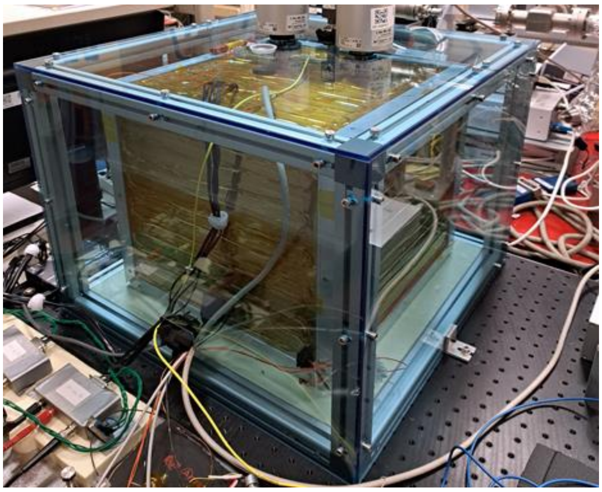

Figure 2: UINT optical pressure standard.

In this work, the gas pressure is measured by a pressure balance, while the UINT interferometer is used to determine the molar polarizability of nitrogen, starting from the measurement of the refractive index of nitrogen and applying the Lorentz-Lorenz equation.

The interferometer substantially operates as a refractometer which determines the refractive index n of the gas at generated pressure p, through the relationship [1]:

$$n = n_{vac} + \frac{\varphi\lambda}{L} \quad (1)$$

where n_{vac} is the refractive index in vacuum condition, at residual pressure p_{res}, φ is the number of interference fringes occurred between p_{res} and p, λ is the laser wavelength and L is the total unbalance of the interferometer under vacuum, i.e. the optical path difference between reference and measurement arm of the interferometer, considering the forward and backward optical path.

The density of the gas can be calculated from the measurement of the pressure p by means of a pressure balance connected to the UINT system, according to the formula [1, 5]:

$$p = \rho RT(1 + B\rho + C\rho^2 + \cdots) \quad (2)$$

in which R is the molar gas constant, B and C are respectively the second and third order density virial coefficients.

At last, A_R can be deduced from the Lorentz-Lorenz equation [1, 5, 13]:

$$\frac{n^2-1}{n^2+2} = \rho(A_R + B_R\rho + C_R\rho^2 + \cdots) \quad (3)$$

where B_R and C_R are respectively the second and third order refractivity virial coefficients, whose values are based on ref. [16].

The nitrogen pressure was measured by the INRiM pressure balance DHI-FLUKE PG7601, whose standard uncertainty is 0.04 Pa + $1\times10^{-5}p$, where p is expressed in pascal. All the measurements were carried out in a range around 100 kPa, where both the standards (UINT and the pressure balance) work at their optimal operational conditions, i.e. at lower level of uncertainty (10 ppm).

The molar polarizability was determined at 633 nm, at mean value of temperature equal to (296.7134 ± 0.0014) K.

The figure 3 shows the results of 20 measurements performed in the period November 2022 - April 2023.

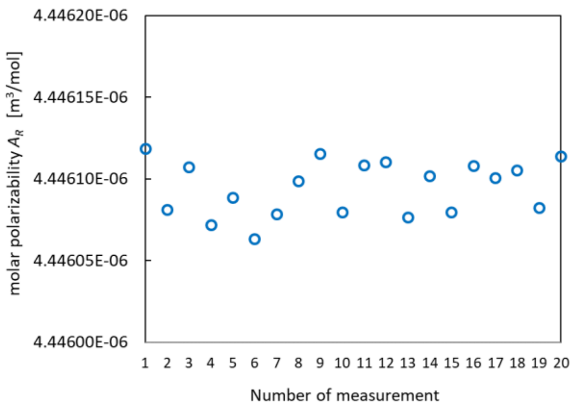

Figure 3: experimental measurements of molar polarizability of nitrogen by means of the UINT optical pressure standard.

The mean value of A_R for nitrogen resulted equal to ($4.446095{\times}10^{-6} \pm 6.3{\times}10^{-11}$) m^3/mol, where the uncertainty has been evaluated according to equations (1-3), and taking into account the repeatability of the measurements (standard deviation over 20 measurements equal to $1.7{\times}10^{-11}$ m^3/mol). Details about the uncertainty budget associated to the UINT system can be found in [1].

The result of this work can be compared with previous results in literature, selected according to their uncertainty level: the table 1 presents the available determinations of molar polarizability of nitrogen at 633 nm, having uncertainty lower than 10^{-9} m^3/mol.

Table 1: determinations of molar polarizability of nitrogen with standard uncertainty lower than 10^{-9} m^3/mol available in literature.

$A_R\times10^{-6}$ [m^3/mol]	$u(A_R)\times10^{-6}$ [m^3/mol]	Reference
4.4454	0.0005	Montixi et al. [17], 1983 (T = 298.15 K)
4.4457	0.0003	Birch [18], 1991 (T = 292.68 K)
4.4464	0.0005	Achtermann et al. [16], 1991 (T = 323 K)
4.4455	0.0006	Hou and Thalmann [19], 1994 (T = 293.45 K)
4.446139	0.000016	Egan et al. [20], 2016 (T_{NIST1} = 302.92 K)
4.446107	0.000068	Egan et al. [21], 2019 (T_{NIST2} = 293.15 K)
4.446095	0.000063	this work, 2023 (T_{INR} = 296.71 K)

It should be noted that the value reported in [22] has not been included in table 1, as the authors in [21] considered their results to supersede those of 2011.

The figure 4 shows the most recent results with lower uncertainties obtained at INRiM (this work) and NIST, where the NIST values, cited in the table 1 and obtained at different temperature, have been normalized at INRiM temperature (T_{INR} = 296.71 K), according to the method reported in [23]:

$$A_R(T_{INR}) = A_R(T_{NIST})[1 + b(T_{INR} - T_{NIST})] \qquad (4)$$

in which the parameter b was taken from [24].

The values of A_R for nitrogen presented in the figure 4 are in agreement within their standard uncertainties (k=1): the most recent determination at INRiM described in this work confirms the two previous values obtained at NIST. Furthermore, these results have a further point in their favour, i.e. they have obtained with different experimental apparatus, making more "robust" their agreement.

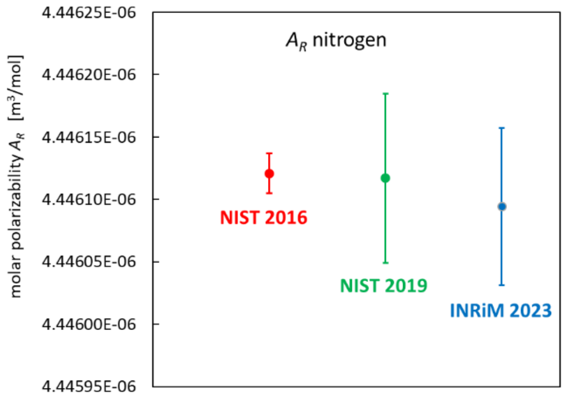

Figure 4: recent determinations of molar polarizability of nitrogen at INRiM and NIST.

3. SUMMARY

The novel UINT optical pressure standard is able to measure pressure with a relative uncertainty of 10 ppm at 100 kPa. It is based on the measurement of the refractive index of a gas through an unbalanced homodyne interferometer, which, in this work, has been used to measure the molar polarizability of nitrogen, representing one the most important gas in pressure and vacuum metrology. The obtained value, equal to ($4.446095{\times}10^{-6} \pm 6.3{\times}10^{-11}$) m^3 / mol, was compared to previous determinations available in literature: in particular, it resulted in agreement at k=1 level with the results with comparable uncertainty, obtained with two different experiments at NIST.

These recent advances in the experimental determination of molar polarizability of nitrogen represent an important step towards the development of photonic-based devices as accurate and fast transfer standards of the pascal.

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