Rayleigh scattering for pressure measurement

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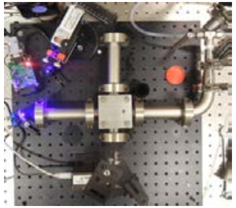

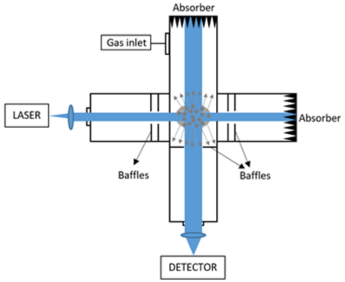

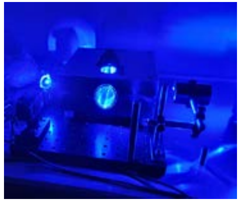

The principle of light scattering

In physics, **scattering** refers to the description of a wide range of physical processes where particles or radiations (for example light) passing through a medium, are deflected away from their original trajectory, due to localized non-uniformities (including the presence of particles and radiation).

The phenomenon of light scattering is a typical manifestation of **light-matter interaction** and strongly depends on frequency of light.

In particular, **the frequency dependence of scattering accounts for the blue color of the sky**

J. W. Strutt (Lord Rayleigh), "On the light from the sky, its polarization and colour", *Philos. Mag. Ser.* 4, 41, pp. 107–120, 1871.

Tyndall scattering in opalescent glass: the transmitted light is orange, but the scattered light is blue...

(https://en.wikipedia.org/wiki/Tyndall_effect)

A crucial contribution to the study of the scattering phenomenon was provided between the second half of the 19th century and the beginning of the following century, allowing to answer ancient questions regarding the origin of the colour of the sky and the sunset

(Abhyankar K D 1996 Hundred and twenty-five years of Rayleigh scattering in the study of the planetary atmospheres *Q. J. R. Astron. Soc.* **37** 281)

1908. № 3.

ANNALEN DER PHYSIK.

VIERTE FOLGE. BAND 25.

1. ***Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen; von Gustav Mie.***

1. Die mannigfachen Färbungen der Metalle im kolloidalen Zustand haben im Laufe der Zeiten recht verschiedenartige Deutungen erfahren. Früher neigte man sehr zu der Meinung, daß die betreffenden Metalle (besonders das Silber) in mehreren verschieden gefärbten Modifikationen aufträten. Später ist die Meinung aufgekommen, daß die Farben auf optischer Resonanz beruhten. Diese Meinung ist besonders eingehend von F. Ehrenhaft[1]) begründet worden. Endlich hat neuerdings J. C. Maxwell-Garnett[2]) nachgewiesen, daß sich die Farben von kolloidalen Metallen, wenn die suspendierten Partikelchen des Metalles sehr klein sind, aus der Theorie, die L. Lorenz[3]) für optisch inhomogene Medien entwickelt hat, einwandsfrei erklären lassen. Die Theorie ergibt für eine feine Metallsuspension, in denen die Dimensionen der Teilchen im Vergleich zur Wellenlänge und außerdem zu ihren gegenseitigen Entfernungen sehr klein sind, eine ganz bestimmte Absorptionskurve, die sich aus den optischen Konstanten des Metalles vorher berechnen läßt und demnach, obwohl sie durchaus verschieden von der Absorptionskurve des soliden Metalles verläuft, doch gar nichts mit Resonanz in dem Sinne, in dem dieses Wort von Ehrenhaft, Wood u. a. gebraucht wird, zu tun hat. So konnte Maxwell-Garnett unter anderem die rote Farbe vieler Goldlösungen, die Ehrenhaft als Resonanz-

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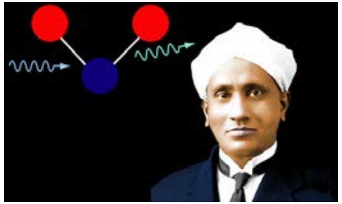
1) F. Ehrenhaft, Wiener Sitzungsber. IIa. **112.** p. 181. 1903; **114.** p. 1115. 1905.

2) J. C. Maxwell-Garnett, Phil. Trans. **203.** p. 385. 1904; **205.** p. 237. 1906. Für den Brechungsexponenten von Gelatine-Silberemulsionen wies auch F. Kirchner in seiner Leipziger Dissertation die Gültigkeit der Lorenzschen Formel nach (Ann. d. Phys. **13.** p. 239. 1904).

3) L. Lorenz, Wied. Ann. **11.** p. 70. 1880.

Annalen der Physik. IV. Folge. 25. 25

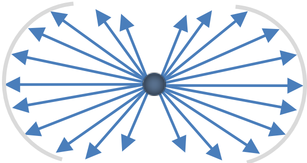
G. Mie, “Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen”, Ann. Phys. 330 (3), 377-445, 1908.



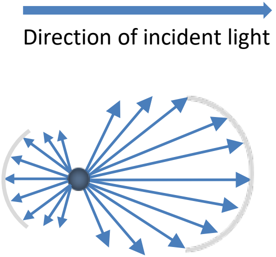
Famousscientists.org

C. V. Raman, “A new radiation” Indian Journal of Physics 2, pp. 387-398, 1928.

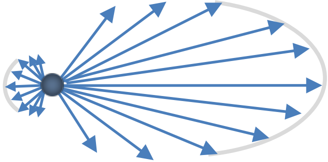
<u>Rayleigh scattering</u>, as well as the <u>Mie scattering</u> for molecules of similar size to the wavelength, can be considered an elastic processes in which the total kinetic energy is conserved and the wavelength and the frequency of the radiation don't change



Rayleigh scattering



Mie scattering



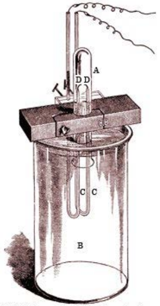
Mie scattering large molecules

The Rayleigh scattering, in particular, refers to elastic scattering of light from particle having small diameter comparing to the wavelength of the incident light.

it is named after the scientist John William Strutt (Lord Rayleigh), who gave a huge contribution to the advancements of physics in different fields and received the Nobel Prize for Physics in 1904 *“for his investigations of the densities of the most important gases and for his discovery of argon in connection with these studies*".

The Nobel Prize in Physics 1904. NobelPrize.org. Nobel Prize Outreach AB 2021. Sun. 10 Oct 2021
https://www.nobelprize.org/prizes/physics/1904/summary/

Lockwood D.J. (2015) Rayleigh and Mie Scattering. In: Luo R. (eds) Encyclopedia of Color Science and Technology. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-27851-8_218-1



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https://www.britannica.com/biography/John-William-Strutt-3rd-Baron-Rayleigh/images-videos#/media/1/492464/109082

Theory of Rayleigh scattering

The classical description of Rayleigh scattering concerns with the effect of the incident radiation on a small particle: the electrons of the atoms/molecules are induced to oscillate by the applied electromagnetic field, behaving like dipole antennas; the irradiated energy, at the same frequency of the incident light, is the Rayleigh scattering.

This simple model provides an excellent explanation for spherical/isotropic molecules such as argon and helium, for which the induced dipole moment vector q is in the same direction of the polarization of incident light, i.e. is linearly proportional to the incident electrical field E_I :

$$q = konst \cdot E_I$$

depends on polarizability α and refractive index n…

For anisotropic molecules, q is not aligned in E_I direction and depends on the orientation of the molecules

In a gas medium , due to the motion of the molecules, microscopic density fluctuations occur, which randomize the phase of light scattered by individual molecules. As consequence, with the exception of the forward direction, the intensity of scattering light can be obtained as the sum of the intensities from the individual molecules, i.e. it is proportional to the number of scattering centres (atoms, molecules…)

The ideal gas low provides a direct link between pressure *p* and number of gas molecules:

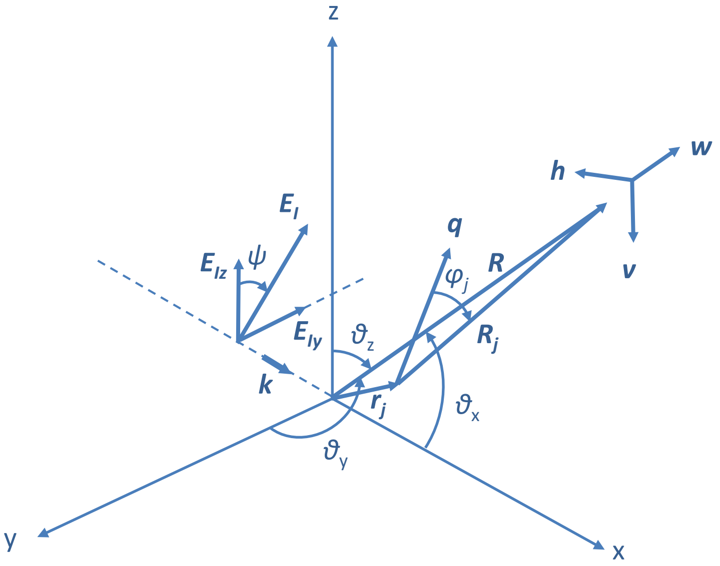
$$p = NkT$$

Where:

- *N* is the number density (ratio between number of gas molecules and volume)
- *K* is the Boltzmann constant
- *T* is the temperature

The intensity of scattering light is proportional to pressure

The figure shows the Rayleigh scattering geometry for a pure gas. The notation and the shown geometry are substantially patterned after Wynn L. Eberhard(1) and Miles et al(2).



The incident light (monochromatic and plane-parallel) propagates along x-axis (E_l electrical vector)

The gas is assumed to be non-polar

ψ is the angle associated to the polarization

Each gas molecule is induced to oscillate by the incident light. The figure shows the j_{th} molecule of a pure gas at a distance r_j from the origin of the x,y,z axes

Vector q is the induced dipole moment vector

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(1) Wynn L. Eberhard, "Correct equations and common approximations for calculating Rayleigh scatter in pure gases and mixtures and evaluation of differences," Appl. Opt. **49**, 1116-1130 (2010)

(2) R. B. Miles, W. R. Lempert and J. N. Forkey, “Laser Rayleigh scattering”, Meas. Sci. Technol. 12, R33-R51 (2001)

Warning: the effective electric field useful for Rayleigh scattering calculation is not the E_I electrical vector

Lorentz(3) calculate the effective electric field “observed” by each molecule, the so-called Lorenz field E_L:

$$\boxed{E_L = LE_I = \frac{n^2+2}{3}E_I}$$

$$L = \frac{n^2+2}{3}$$ is the Lorentz factor (*n* is the refractive index of the pure gas)

Lorentz factor is always >1…

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(3) H. A. Lorentz, “Ueber die Beziehung zwischen der Fortpflanzungsgeschwindigkeit des Lichtes und der Körperdichte” Ann. Phys. 245, 641–664 (1880)

The <u>link</u> between the refractive index *n* and the polarizability is the <u>Lorentz-Lorenz equation</u>:

$$\alpha = \frac{3\varepsilon_0}{N}\frac{n^2-1}{n^2+2}$$

where ε_0 is the vacuum permittivity and N the number density

The polarizability is a propriety of the gas which doesn't directly depend by the number density, so <u>the density of the gas varies with refractive index,</u> following the equation:

$$N = const\frac{n^2-1}{n^2+2}$$

<u>And the number density depends on pressure…</u>

Considering the j_{th} molecule of a pure gas at a distance r_j from the origin, the dipole moment vector is related to polarizability according to:

$$\boxed{q_j = \alpha_j E_L}$$

where α_j in general, is the polarizability 3×3 tensor

Following Miles et al$^{(2)}$, in case of incident light propagating along x-axis, the polarizability tensor simplifies to a 2×3 tensor, as the incident electric vector E_l (and accordingly also E_L) can be described by two components along y and z axes:

$$\alpha_j = \begin{bmatrix} \alpha_{xyj} & \alpha_{xzj} \\ \alpha_{yyj} & \alpha_{yzj} \\ \alpha_{zyj} & \alpha_{zzj} \end{bmatrix}$$

For isotropic molecules having a spherical symmetry (helium, argon…), the induced dipole moment vector q is in the same direction of the polarization of incident light, i.e. the polarizability α is a scalar coefficient.

For gas molecules which are randomly positioned (no correlation between the phases of scattered light from each molecules), the intensity of scattered light can be calculated summing over all the gas molecules, according to :

$$I_s = \frac{1}{2}\sqrt{\frac{\varepsilon}{\mu}}\sum_j \left|E_j\right|^2$$

where

$$E_j = \frac{\omega^2}{4\pi\varepsilon_0 c^2}\frac{1}{R}\left|q\times(q_j\times w)\right|$$

Introducing the differential volumetric scattering cross section $\frac{\partial\beta}{\partial\Omega}$ such that:

$$\frac{\partial\beta}{\partial\Omega} = R^2\frac{I_s}{I_I}$$

$$I_s = \frac{\partial\beta}{\partial\Omega}\frac{1}{R^2}I_I$$

Intensity of incident light $\boxed{I_I = \frac{1}{2}\sqrt{\frac{\varepsilon}{\mu}}\left|E_I\right|^2}$

For randomly positioned and anisotropic molecules, $\frac{\partial\beta}{\partial\Omega}$ can be written in terms of polarizability α and anisotropy factor γ :

$$\frac{\partial\beta}{\partial\Omega} = \frac{\pi^2}{\varepsilon_0\lambda^4} L N \alpha^2 \left[\left(1+\frac{7\gamma^2}{45\alpha^2}\right) - \left(1+\frac{\gamma^2}{45\alpha^2}\right)\times\left(\sin\varphi\cos\vartheta_y + \cos\varphi\cos\vartheta_z\right)\right]$$

Some considerations about the differential volumetric scattering cross section $\frac{\partial\beta}{\partial\Omega}$:

- It is proportional to $\frac{1}{\lambda^4}$ → **blue sky…**
- It is rigorously proportional to α^2 only for isotropic molecules having spherical symmetry
- Depends on the Lorentz factor L
- It is proportional to number density N **(and the number density depends on pressure…)**

Rayleigh scattering for pressure assessment

As repeatedly emphasized above, the Rayleigh scattered light is proportional to gas pressure

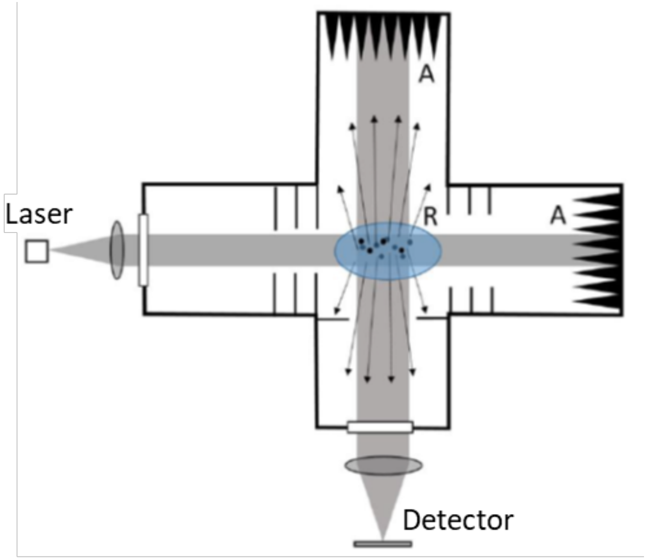
↓

First realization of a Rayleigh scattering-based system for pressure measurement at INRiM*, according to the patent:

> M. Pisani, System for determining the characteristics of a gas and related method for measuring such characteristics, *patent EP3394595 B1*, proprietor: INRiM, granted 11 March 2020

*Istituto Nazionale di Ricerca Metrologica (Italy's National Metrology Institute)

Scheme of the experimental set-up

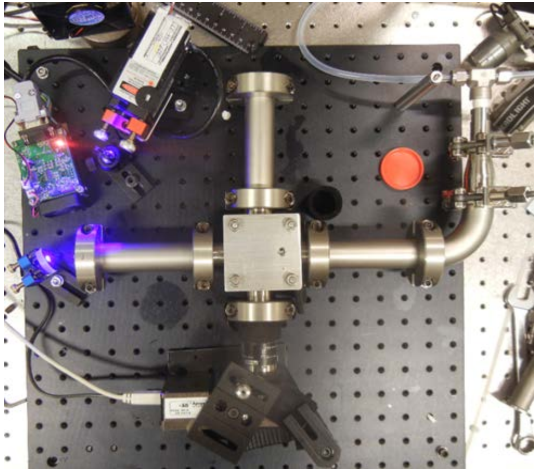


A: absorbers

R: interaction zone

The detector is placed perpendicularly to the direction of propagation of laser light

First practical realization



The first realization is composed by a stainless steel cross-shaped chamber equipped with two optical viewports, respectively for the entrance of laser light and the exit of scattered light towards the detector.

The light source is a blue laser at 460 nm, having a power of 500 mW.

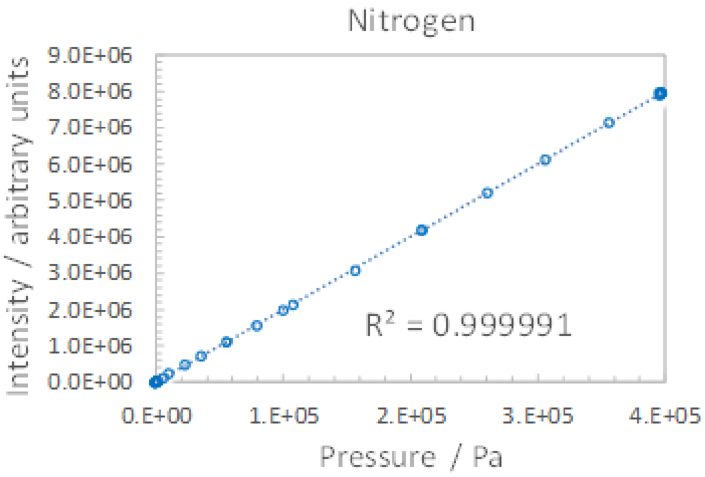
A series of baffles and absorbers have been used to reduce the effect of spurious light on the signal collected by the detector.

The scattered light is collected by a cooled, 16 bit, CCD camera.

In the opposite side of the laser entrance, a 90° pipe bend system has been added to limit backwards reflection of light and to connect the gas inlet system and the oil-free vacuum pump system.

D. Mari, M. Pisani, C. Francese, “ Rayleigh scattering for pressure assessment, Measurement: Sensors 18 (2021) 100253

*First results**



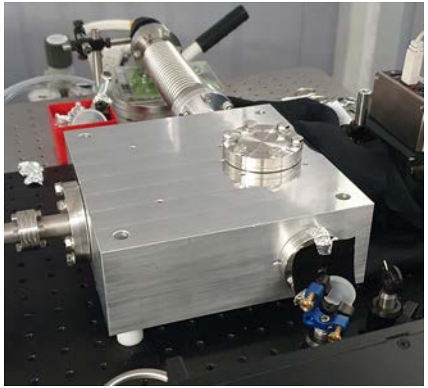
The system has been tested up to 400 kPa

The realized preliminary set-up has evidenced promising results, showing an excellent linearity of the system

The first achievements opened the way to a new improved realization of a Rayleigh scattering-based device for gas pressure measurement

*D. Mari, M. Pisani, C. Francese, " Rayleigh scattering for pressure assessment, Measurement: Sensors 18 (2021) 100253

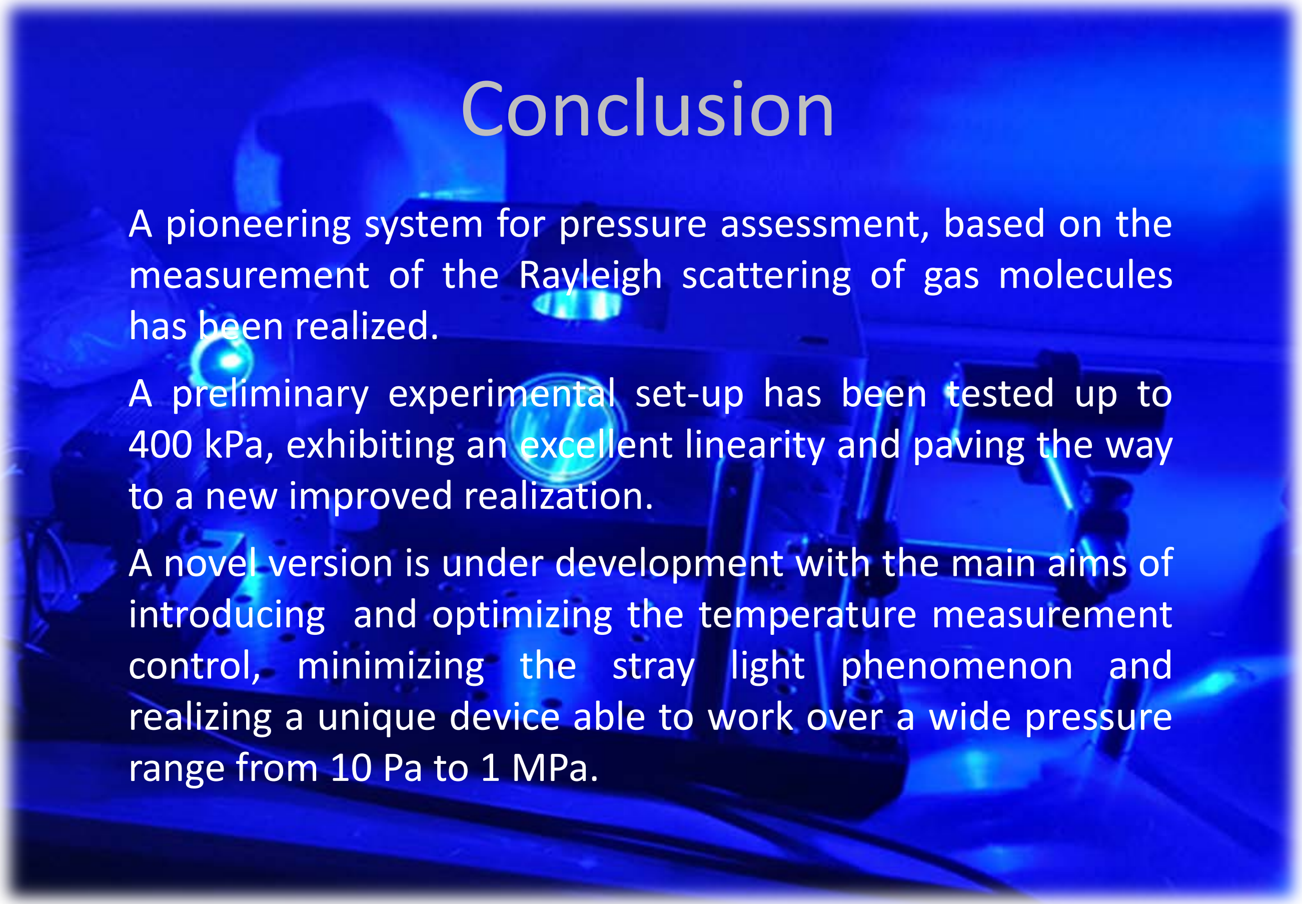
*Novel realization (**RAY**)*



A novel version, named RAY, is under development within the 18SIB04 QuantumPascal EMPIR Project.
In the new layout, the vacuum chamber is equipped with five ConFlat® ports, to connect up to four optical custom viewports and a gas inlet and pumping system.

The custom viewports have been designed and realized to work up to an over-pressure of 2.5 MPa (the expected upper limit of RAY is 1 MPa).

The chamber may host until six temperature sensors to implement the temperature measurement and control and equipped with special absorbers, able to decrease the stray light effect of a factor 10^{-5}.



Conclusion

A pioneering system for pressure assessment, based on the measurement of the Rayleigh scattering of gas molecules has been realized.

A preliminary experimental set-up has been tested up to 400 kPa, exhibiting an excellent linearity and paving the way to a new improved realization.

A novel version is under development with the main aims of introducing and optimizing the temperature measurement control, minimizing the stray light phenomenon and realizing a unique device able to work over a wide pressure range from 10 Pa to 1 MPa.

Thank you