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Rayleigh scattering cross-section measurements of nitrogen, argon, oxygen and air

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ARTICLE INFO

ABSTRACT

Knowledge about Rayleigh scattering cross sections is relevant to predictions about radiative transfer in the atmosphere, and needed to calibrate the reflectivity of mirrors that are used in high-finesse optical cavities to measure atmospheric trace gases and aerosols. In this work we have measured the absolute Rayleigh scattering cross-section of nitrogen at 405.8 and 532.2 nm using cavity ring-down spectroscopy (CRDS). Further, multi-spectral measurements of the scattering cross-sections of argon, oxygen and air are presented relative to that of nitrogen from 350 to 660 nm using Broadband Cavity Enhanced Spectroscopy (BBCES). The reported measurements agree with refractive index based theory within $0.2 \pm 0.4\%$, and have an absolute accuracy of better than 1.3%. Our measurements expand the spectral range over which Rayleigh scattering cross section measurements of argon, oxygen and air are available at near-ultraviolet wavelengths. The expressions used to represent the Rayleigh scattering cross-section in the literature are evaluated to assess how uncertainties affect quantities measured by cavity enhanced absorption spectroscopic (CEAS) techniques. We conclude that Rayleigh scattering cross sections calculated from theory provide accurate data within very low error bounds, and are suited well to calibrate CEAS measurements of atmospheric trace gases and aerosols.

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1. Introduction

The theory and measurements of the scattering of light by gases has been studied for well over a century [1] and is vital to our understanding of radiative transfer in the Earth and other planetary atmospheres. The interaction of light (electromagnetic fields) with a wavelength much larger than the size of a molecule gives rise to the scattering of light. This effect known as Rayleigh scattering, accounts for scattering, local field effects (Lorentz–Lorenz) [2] as well as depolarization from the non-sphericity of particles (King correction factor) [3,4].

The cross-section, σ, for Rayleigh scattering can be calculated based on the refractive index of the gas as follows [5]:

$$\sigma(\nu) = \frac{24\pi^3\nu^4}{N^2}\left(\frac{n_\nu^2-1}{n_\nu^2+2}\right)^2 F_k(\nu), \qquad (1)$$

where ν is the wavenumber of light (cm^{-1}), N is the number density of the gas, n_ν is the wavenumber dependent real refractive index and F_k is the King correction factor which accounts for the depolarization. Detailed derivation and explanation of the different influences on the scattering can be found elsewhere in the literature [5–9].

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While measurements of the different components of scattering (correction factors, refractive index) have been performed for the better part of a century [2,10–13], there are surprisingly few laboratory measurements of Rayleigh scattering cross-sections [5,9,14–16]. In particular there is little data in the near-UV (300–420 nm) and what is available has large uncertainty.

Rayleigh scattering cross-section measurements in the literature have been carried out in two ways: (1) nephelometry [16]; and (2) cavity-ring down spectroscopy (CRDS) [5,9,14,15]. The pioneering nephelometry measurements of Shardanand and Rao [16] are the only work of its kind and consist of the direct measurement of scattered light at discrete angles and then the integration of these signals over all angles. They set a baseline for calculations of Rayleigh scattering cross-sections from theory, but the reported values in the ultra-violet spectral region deviate from theory and have a high uncertainty ($\pm$11%). CRDS measurements [5,9,14,15] leverage the sensitivity of high finesse cavities to retrieve the scattering cross-section at pressures of 1–100% of ambient pressure by measurements of the change in extinction by the decay of pulsed light in a high-finesse optical cavity. The CRDS measurements agreed very well with refractive index based theoretical calculations (within 1%) over the range investigated (479–650 nm [5,9]) and within 10% in the UV (197–270 nm [14,15]). There have been no measurements of the scattering cross-section by CRDS in the near UV.

With the advent of cavity-enhanced absorption spectroscopy (CEAS) in recent years, the Rayleigh scattering of pure gases has found an application as a calibration standard for high finesse optical cavity instruments. CEAS relies on the absolute scattering cross-sections of gases to calibrate the reflectivity of the mirrors forming the high-finesse cavity. These calibrations in particular use the scattering of helium and nitrogen [17,18]. Recent work by Washenfelder et al. [19] used exponential empirical expressions to represent the scattering cross-section by fitting to the experimental data of Shardanand and Rao [16] and Sneep and Ubachs [5]. With the limited number of data points available in the literature, interpolation of the cross-section between points in the range of 350–480 nm can lead to systematic bias and large uncertainty.

In this work we use cavity ring-down spectroscopy to derive *absolute* Rayleigh scattering cross-section of nitrogen at 532 and 405 nm. We then establish the use of broad-band cavity enhanced spectroscopy for the measurement of *relative* Rayleigh scattering cross-sections of argon, oxygen and air with wavelength coverage from 350 to 700 nm, and calibrate our relative cross-section measurements at a large number of other wavelengths using the CRDS data.

2. Experimental

2.1. Calculations of refractive index based Rayleigh scattering

The scattering cross-sections of the gases investigated (He, N_2, O_2, Ar and air) were calculated with Eq. (1) based on the data for refractive index available in the literature which follow the generalized expression:

$$(n-1) \times 10^8 = A + \frac{B}{C - \nu^2} \tag{2}$$

with terms and their values as described in Table 1, along with the corresponding King correction factor (F_k) equations. The F_k values are taken as unity for mono-atomic gases (He, Ar); for diatomic gases (O_2, N_2) the values are taken from *ab initio* calculations as described in Bates [6], and are estimated to have an uncertainty of $< 1\%$. For He, data from references [11–13] are fitted by an expression matching Eq. (2). The Rayleigh scattering cross-section of air was calculated from the expressions given in Bodhaine et al. [7] at 288.15 K and 1013.25 mbar from the refractive index and mixing ratio weighted King correction factors for N_2, O_2, Ar and CO_2.

2.2. Measurements of N_2 Rayleigh scattering by CRDS

The Rayleigh scattering cross-section of N_2 was measured by CRDS using a similar method as that described by Naus and Ubachs [9] and Sneep and Ubachs [5], though the measurements were made at distinct wavelengths of 405.8 nm and 532.2 nm (see Fig. 1). The instrument design has been described previously (Fuchs et al. [20] for 405 nm and references therein; Pettersson et al. [21] for 532 and references therein) and only a brief description of the operation is provided here. A pulse of light is injected into

Table 1
Terms for use in Eq. (2) for the refractive index and for the King correction factor.

Gas	A	B	C	King correction factor	Ref.
He[a,b]	2283	1.8102×10^{13}	1.5342×10^{10}	$F_k(\nu) = 1$	[11–13]
N_2[a,c]	5677.465	318.81874×10^{12}	14.4×10^9	$F_k(\nu) = 1.034 + 3.17 \times 10^{-12} \nu$	[5,9]
N_2[a,d]	6498.2	307.4335×10^{13}	14.4×10^9	$F_k(\nu) = 1.034 + 3.17 \times 10^{-12} \nu$	[5,9]
Ar[a,e]	6432.135	286.06021×10^{12}	14.4×10^9	$F_k(\nu) = 1$	[5,8]
O_2[f,g]	20,564.8	2.480899×10^{13}	4.09×10^9	$F_k(\nu) = 1.09 + 1.385 \times 10^{-11} \nu^2 + 1.448 \times 10^{-20} \nu^4$	[5]

[a] Use $N = 2.546899 \times 10^{19}$ molecules cm^{-3} in Eq. (1).
[b] $14,285 < \nu < 33,333$ cm^{-1}.
[c] $21,360 < \nu < 39,370$ cm^{-1}.
[d] $4860 < \nu < 21,360$ cm^{-1}.
[e] $5000 < \nu < 33,000$ cm^{-1}.
[f] Use $N = 2.68678 \times 10^{19}$ molecules cm^{-3} in Eq. (1).
[g] $18,315 < \nu < 34,722$ cm^{-1}.