# Refractivity of nitrogen gas in the vacuum ultraviolet

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We have measured the refractivity of nitrogen gas in the ultraviolet and the vacuum ultraviolet, using a Fourier-transform spectrometer. A new two-term Sellmeier formula for the standard refractivity between 145 and 270 nm is derived. © 1999 Optical Society of America

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Nitrogen gas near room temperature and atmospheric pressure is transparent at wavelengths longer than 145 nm. This property makes it an attractive candidate for the purge gas used in optical instrumentation for photolithography at 157 nm. Since the optical design of photolithography systems must take into account the refractive index of the purge gas, it must be known accurately.

The refractivity of nitrogen from 164.9 to 204.2 nm was measured by Wilkinson.[1] Later, Abjean *et al.*[2] carried out interferometric measurements of the refractive index of nitrogen at six wavelengths from 180 to 254 nm and noted good agreement with the earlier results of Wilkinson where both measurements overlap. Similar interferometric measurements at 164.1 and 170.2 nm were subsequently made by Bideau-Mehu *et al.*[3] We know of no previous measurement of the refractivity of nitrogen in the vacuum ultraviolet that extends to the onset of the absorption spectrum of nitrogen at 145 nm, the 0–0 band of the Lyman–Birge–Hopfield system.[4]

We used the FT700 vacuum-ultraviolet Fourier-transform spectrometer at the National Institute of Standards and Technology (NIST) to measure the refractive index of nitrogen from 150 to 270 nm. The FT700 spectrometer is a scanning Mach–Zehnder interferometer that is mounted upon an optical bench inside a vacuum chamber. The chamber also contains a reference interferometer with a stabilized helium–neon laser to measure the optical path difference in the main interferometer. The spectrometer is equipped with calcium fluoride optics and thus permits measurements at wavelengths as low as 140 nm. To obtain the refractive index of nitrogen we measured the emission spectrum of a high-current iron–neon hollow-cathode lamp twice, first with an evacuated interferometer tank and again after the interferometer tank was filled with ultrahigh-purity nitrogen. For 31 strong spectral lines from 150 to 270 nm the refractive index of nitrogen was determined from the wave-number shifts of the spectral lines measured in vacuum and in the gas. The refractive index is defined as the ratio of the speed of light in vacuum and in the gas:

$$n(\sigma) = \frac{c_{\mathrm{vac}}}{c_{\mathrm{gas}}} = \frac{\nu\lambda_{\mathrm{vac}}}{\nu\lambda_{\mathrm{gas}}} = \frac{\sigma_{\mathrm{gas}}}{\sigma_{\mathrm{vac}}} = \frac{\sigma_{\mathrm{gas}}^{\mathrm{rel}}}{\sigma_{\mathrm{vac}}}\, n(\sigma_{\mathrm{HeNe}}), \quad (1)$$

where $\lambda$ is the wavelength and $\sigma$ is the wave number of the light in vacuum and gas. $n(\sigma_{\mathrm{HeNe}})$ is the refractive index of nitrogen at the wave number of the helium–neon reference laser, $\sigma_{\mathrm{HeNe}}$, which is accurately known.[5] The last equality in Eq. (1) takes into account that the wave number of the interferometer's reference laser changes to $\sigma_{\mathrm{HeNe}} n(\sigma_{\mathrm{HeNe}})$ when the spectrometer chamber is filled with nitrogen. The wave numbers observed relative to $\sigma_{\mathrm{HeNe}}$, $\sigma_{\mathrm{gas}}^{\mathrm{rel}}$, thus have to be scaled by the same factor to yield $\sigma_{\mathrm{gas}}$. The uncertainty of $n(\sigma)$ is determined by the uncertainty of the spectral line wave number measurements and the uncertainty of $n(\sigma_{\mathrm{HeNe}})$. The combined standard uncertainty was found to be $0.2 \times 10^{-6}$.

The iron–neon hollow-cathode lamp emits a dense line spectrum with strong lines near 200 and 150 nm. For our measurements the lamp was operated at a discharge current of 800 mA and with neon carrier gas at a pressure of approximately 200 Pa. Two different photomultiplier tubes with cesium–tellurium and cesium–iodine photocathodes were used on the two output ports of the interferometer to cover the entire wavelength range from 300 to 150 nm in one observation. The amplified detector signals were subtracted and processed as a single interferogram. The resolving power of the spectrometer was set to $1.3 \times 10^6$ at 150 nm. The temperature of the nitrogen in the spectrometer tank was measured with two silicon diodes with NIST traceable temperature calibration. One of the diodes remained in thermal contact with the optical bench of the interferometer. We used the second diode to measure the gas temperature. That diode was affixed to a small copper sheet, which we mounted upon a block of PTFE [polytetrafluorethylene (Teflon)] to thermally isolate it from the optical bench. After flooding the spectrometer tank with nitrogen to a pressure of approximately 103 kPa we waited until the spectrometer temperature, as measured with the first

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diode, was within 0.03 °C of the gas temperature before measuring the hollow-cathode lamp spectra. The pressure in the spectrometer tank was measured in two ways: We used the known refractive index of nitrogen in the ultraviolet[2] and the accurately known wave numbers of spectral lines of iron in the ultraviolet[6] to carry out an optical pressure measurement, using the observed line shifts. A second, less accurate, pressure measurement with a capacitance manometer that had a relative standard uncertainty of 0.15% was made as a consistency check. The residual oxygen content of the ultrahigh-purity nitrogen used in our experiment was measured with an oxygen sensor and was found to be less than 10 parts in $10^6$ by volume. No attenuation of the signal level at the spectrometer outputs was observed when the spectrometer was filled with nitrogen.

To convert the raw refractive-index data from Eq. (1) to standard conditions [273.15 K (0 °C) and 101,325 Pa] we used the Lorentz–Lorenz formula (see, e.g., Ref. 7)

$$(n^2 - 1)/(n^2 + 2) = R\rho \qquad (2)$$

($R$ is the specific refractivity of the gas and $\rho$ is its density). For gases with refractive indices close to 1, the left-hand side of Eq. (2) can be approximated by a quadratic expansion in $(n - 1)$, and a formula that relates refractivities at any two conditions of temperature and pressure can be derived (see Refs. 5 and 8 for more details):

$$\frac{n_1 - 1}{n_2 - 1} = \frac{P_1 T_2}{P_2 T_1}\frac{Z_2}{Z_1}\left[1 + \frac{n_1 - 1}{6}\left(1 - \frac{P_2 T_1}{P_1 T_2}\right)\right], \qquad (3)$$

where $Z$ is the compressibility of nitrogen. Peck and Khanna[5] provide a simple equation for $Z$ that is based on the compressibility data compilation of Hilsenrath *et al.*[9]:

$$Z = 1 - \frac{P(317.6 - T) \times 10^{-5}}{101325}. \qquad (4)$$

This formula requires pressure $P$ to be in pascals and the temperature $T$ to be in degrees Kelvin. In our case, the second term in brackets in Eq. (3) is negligibly small and the refractivities at different conditions differ by a simple factor. The refractivity of nitrogen, measured at the wavelengths of the 31 spectral lines and converted to standard conditions [273.15 K (0 °C) and 101,325 Pa (760 Torr)] is listed in Table 1.

The refractive dispersion of a gas is commonly expressed with an empirical Sellmeier formula. We fitted a two-term Sellmeier formula to our refractivities after normalizing them to 273.15 K (0 °C) and 101,325 Pa (760 Torr). The resultant formula for the standard refractivity of nitrogen gas,

$$10^6 \times (n - 1)|_{273.15\ \mathrm{K},\ 101{,}325\ \mathrm{Pa}} = \frac{1.9662731 \times 10^6}{22086.66 - \sigma^2} + \frac{2.7450825 \times 10^4}{133.85688 - \sigma^2}, \qquad (5)$$

is valid from 150 to 270 nm. $\sigma$ is the wave number and must be in units of inverse micrometers. The largest deviation of any data point from the fitted Sellmeier formula is smaller than the standard uncertainty of $0.2 \times 10^{-6}$ of the refractivity data.

Our results are illustrated in Fig. 1. The earlier result of Wilkinson[2] in the vacuum ultraviolet diverges

**Table 1. Refractivity of Nitrogen Gas at 273.15 K (0 °C) and 101,325 Pa Measured for 31 Spectral Lines of the Iron–Neon Hollow-Cathode Lamp**

| Vacuum Wavelength (nm) | Wave Number ($\mu m^{-1}$) | Refractivity ($\times 10^6$) |
|---|---|---|
| 278.8107 | 3.586663 | 315.9 |
| 271.9029 | 3.677784 | 317.3 |
| 267.9063 | 3.732648 | 317.9 |
| 261.1875 | 3.828667 | 319.4 |
| 259.9397 | 3.847046 | 319.6 |
| 258.4538 | 3.869163 | 320.1 |
| 252.2851 | 3.963770 | 321.4 |
| 249.0646 | 4.015023 | 322.4 |
| 248.8144 | 4.019060 | 322.3 |
| 239.5627 | 4.174273 | 324.8 |
| 238.2039 | 4.198084 | 325.2 |
| 234.3496 | 4.267129 | 326.6 |
| 229.8170 | 4.351288 | 328.0 |
| 225.9511 | 4.425736 | 329.1 |
| 217.8082 | 4.591195 | 332.3 |
| 216.6774 | 4.615156 | 332.7 |
| 209.6108 | 4.770747 | 336.2 |
| 192.9399 | 5.182961 | 345.5 |
| 191.5449 | 5.220708 | 346.6 |
| 184.2571 | 5.427199 | 352.2 |
| 178.4656 | 5.603321 | 357.1 |
| 174.2108 | 5.740172 | 361.2 |
| 170.1414 | 5.877464 | 365.5 |
| 168.7717 | 5.925164 | 367.2 |
| 165.6338 | 6.037415 | 370.7 |
| 162.8387 | 6.141046 | 374.8 |
| 162.0831 | 6.169675 | 375.7 |
| 160.6853 | 6.223345 | 377.6 |
| 156.1004 | 6.406133 | 384.8 |
| 149.4169 | 6.692683 | 396.9 |
| 149.2119 | 6.701878 | 398.0 |

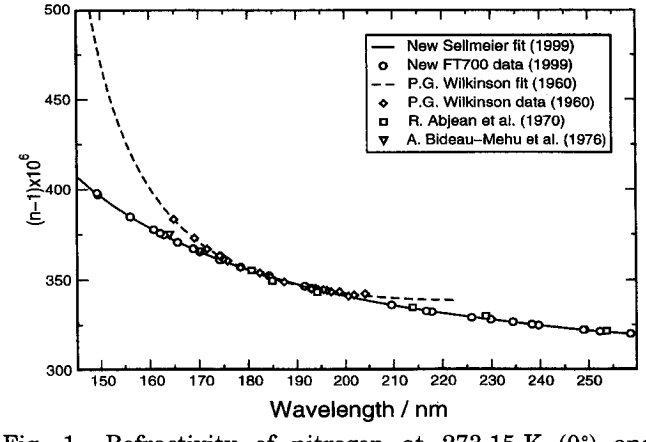


Fig. 1. Refractivity of nitrogen at 273.15 K (0°) and 101,325 Pa in the ultraviolet and in the vacuum ultraviolet.

from our new data below 180 nm. This, and the conspicuous scatter of Wilkinson's data near 200 nm, makes it appear likely that the oxygen content of the nitrogen used by Wilkinson was underestimated. The Sellmeier formula for the standard refractivity of nitrogen that was proposed by Wilkinson[1] yields correct results only in the narrow wavelength range from 180 to 200 nm. Our new Sellmeier formula, Eq. (5), is valid between the onset of nitrogen absorption in the vacuum ultraviolet, near 145 nm, and 270 nm in the ultraviolet.

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