

Brief Communication

Absorption of NO laser-induced fluorescence by hot O₂ and CO₂

K. Verbiezen*, A.P. van Vliet, W.L. Meerts, N.J. Dam, J.J. ter Meulen

Applied Molecular Physics, Institute of Molecules and Materials, Radboud University Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

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1. Introduction

Laser-induced fluorescence (LIF) is frequently used as a diagnostic tool in combustion research, offering high spatial and temporal resolution, high species selectivity, and low intrusion. In many cases, absorption of laser light and/or fluorescence needs to be corrected for. UV-LIF measurements of nitric oxide (NO) can be significantly affected by CO₂ absorption [1,2]; additional absorption can be caused by aromatic fuel compounds, soot, and—especially at high temperatures—O₂. In this Brief Communication, we parameterize the UV absorption spectrum of O₂, and demonstrate the effect of O₂ and CO₂ absorption on NO LIF measurements in a diesel engine.

2. O₂ absorption spectra

Fig. 1 shows O₂ absorption cross sections for a number of temperatures, simulated with LIFSim [3]. Unlike the smooth, structureless CO₂ absorption spectrum [1], the O₂ spectrum consists of many closely spaced rovibronic lines, belonging to the Schumann–Runge ($X^3\Sigma_g^- - B^3\Sigma_u^-$) system that extends from 175 to 535 nm [4]. The actual absorption of an NO (vibronic) fluorescence band depends on the intensities and relative positions of NO emis-

sion and O₂ absorption lines. As this is a numerically expensive calculation for a fitting procedure, we approximate the O₂ absorption cross section by a simplified curve analogous to the CO₂ absorption function [1]. This expression was fitted to simulated absorption spectra (LIFSim) over a range of temperatures (500 < T < 3000 K) and wavelengths (200 < λ < 300 nm), yielding

$$\bar{\sigma}_{\text{O}_2}(\lambda, T) = \exp[a(T) + b(T)\lambda], \quad (1)$$

$$a(T) = -45.25 + 1.34T + 33.66/T, \quad (2)$$

$$b(T) = 1.916 - 0.593T - 19.36/T, \quad (3)$$

with σ in cm², λ in units of 100 nm, and T in units of 1000 K. Some typical curves are shown in Fig. 1. Equation (1) represents an *average* O₂ absorption cross section. At high pressures, the strong variations in O₂ transmission are (to some extent) averaged out by the broad NO emission bands. Although $\exp(\bar{\sigma}_{\text{O}_2}nL) \neq \exp(\overline{\sigma_{\text{O}_2}}nL)$, which may cause significant errors for large O₂ column densities, in our experiments Eq. (1) leads to acceptable deviations of ~5% of the transmission of the detected NO fluorescence (see below) compared to high-resolution calculations. For both CO₂ and O₂, the (average) absorption increases with increasing temperature and with decreasing wavelength.

3. Experiment

NO fluorescence was induced by a 226.035-nm laser beam directed into the measurement cylinder

* Corresponding author. Fax: +31 (0) 24 3653311.
E-mail address: k.verbiezen@science.ru.nl
(K. Verbiezen).

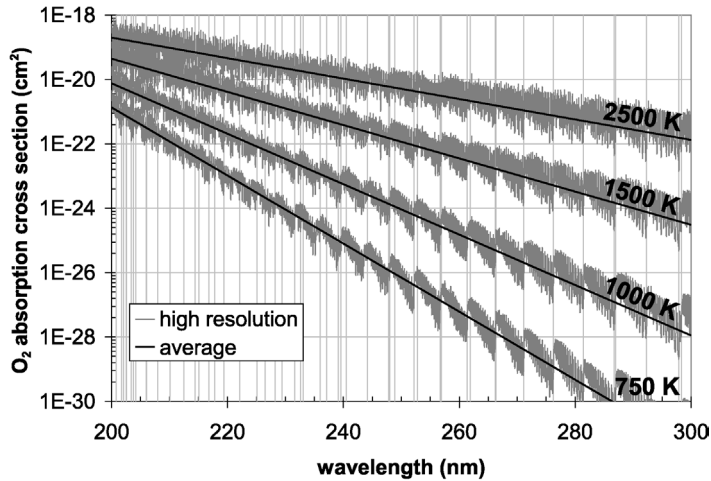


Fig. 1. O_2 absorption cross section vs wavelength, based on LIFSim [3]. The straight lines are fits using Eqs. (1)–(3). Vertical gridlines indicate the band origins, values from Krupenie [4].

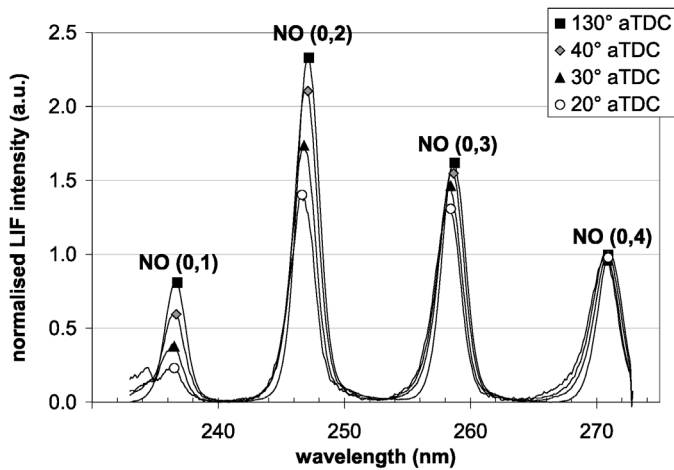


Fig. 2. NO emission spectra (15-shot averages) at various crank angles, all normalized at 271 nm. The spectrum at 130° aTDC is used as a reference spectrum (see text).

of a diesel engine (60 mg fuel injected, gIMEP of 411 kPa); an iCCD camera–spectrograph system recorded the $A-X(0,1)–(0,4)$ vibronic fluorescence bands of NO. Rotational structure is not resolved. The probe volume is 37 mm away from the detection window. Further details can be found in Refs. [5,6].

The relative intensities of the NO fluorescence bands are governed by (constant) Franck–Condon factors; any observed deviations from these intensity ratios are attributed to (wavelength-dependent) absorption of the fluorescence. Some measured spectra are shown in Fig. 2, clearly showing varying relative intensities during the stroke. Transmission spectra are obtained after dividing the fluorescence by a reference spectrum (recorded at the end of the combustion

stroke, 130° aTDC, when temperatures of ~ 800 K are too low to cause significant CO_2 and O_2 absorption), and normalizing these ratios at 271 nm. By taking ratios, the wavelength-dependent detector response is automatically corrected for. Subsequently, these spectra are fitted by simulated O_2 and CO_2 transmission spectra (also normalized at 271 nm). Additionally, wavelength-independent absorption (e.g., by soot) cannot be measured with this technique, being equal for all NO fluorescence wavelengths.

In order to limit the number of free parameters, the O_2 number density was not treated as a variable, but instead calculated from Raman scattering by O_2 and N_2 [6], revealing that only $50 \pm 10\%$ of the O_2 in the probe volume is consumed. The remaining pa-

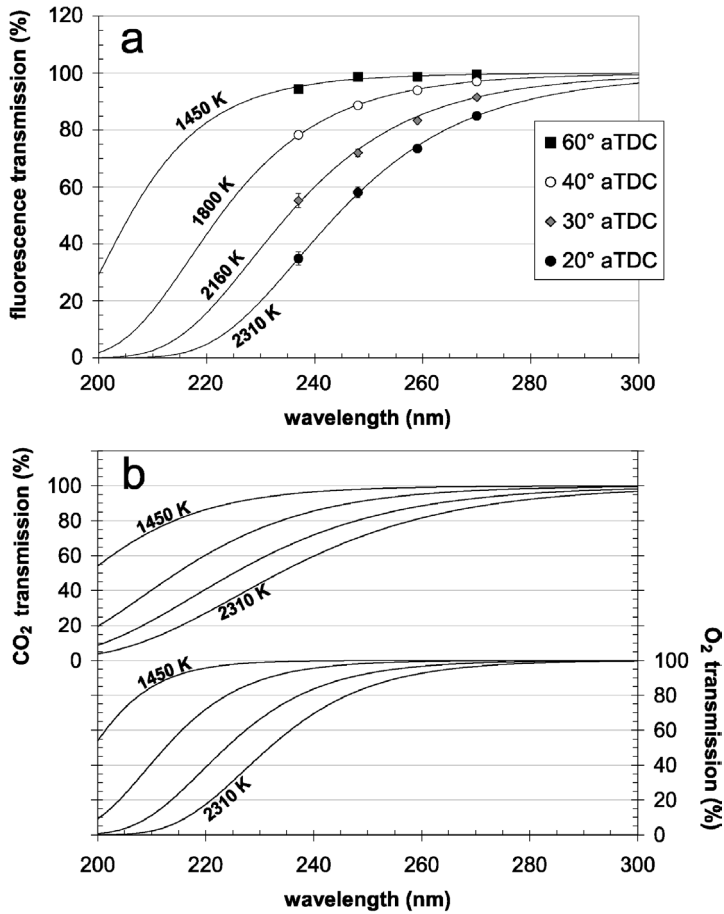


Fig. 3. (a) Experimental data (symbols) and fitted transmission spectra (solid lines), based on absorption by CO_2 and O_2 . (b) The same transmission spectra, split into the individual contributions by CO_2 and O_2 .

rameters, CO_2 density and temperature, follow from the fit.

4. Results and discussion

Fig. 3a displays the transmission of four NO fluorescence bands for a number of crank angles, together with fitted O_2 and CO_2 transmission spectra. In Fig. 3b these fits are split into contributions by CO_2 and O_2 . It is clear that O_2 causes considerable UV absorption, especially at shorter wavelengths and at lower crank angles (i.e., higher temperatures) when O_2 and CO_2 contribute almost equally to the total absorption. Although O_2 absorption has a more pronounced temperature and wavelength dependence, the general shape of the CO_2 and O_2 absorption spectra is similar. Misleadingly, the data in Fig. 2 can be fitted equally well with only CO_2 as an absorber, but this overestimates the CO_2 density by typically 60%. Apparently, this ambiguity can only be resolved with

independent measurements of either O_2 or CO_2 densities.

Acknowledgments

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