

A Fast and Quantitative Technique to Measure NO in the Cylinder of Internal Combustion Engines. Experimental Determination of NO absorption Cross Sections in the $g(0,0)$, $g(1,0)$ and $g(2,0)$ bands at hard temperature and pressure conditions

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Abstract

The various concepts to reduce NO_x emission in Internal Combustion Engines are becoming increasingly unsuited, mostly that pollutant emissions regulations are more and more drastic. The after-treatment of NO_x by catalytic converters is efficient only under certain operating modes of the engine (such as the stoichiometric fuel/air ratio), whereas the exhaust gas recirculation or the lean-burn operating mode affects the stability of the combustion and may thus lead to the inverse effect (more pollutant emissions, mainly unburned HC).

Investigation concerning the NO_x formation inside the combustion chamber is, hence, needed. Various optical techniques have, thus, been implemented for this purpose. The most common one is the Planar Laser Induced Fluorescence (PLIF), which provides concentration fields with a rather significant spatial resolution. However, it is expensive and complex to set up because of severe problems such as the "quenching" with other molecules and the strong dependence of NO fluorescence with the temperature. Moreover, it is not possible to get temporal evolution of concentration fields considering the low pulsing frequencies of the commonly used lasers. Only mean measurements are achievable giving only a global idea on the in-situ formation of NO_x.

To overcome these drawbacks, the direct absorption spectroscopy technique has been chosen. It allows temporal data to be obtained and to depend on the detection system rather than the light source. The present work is a first step for the implementation of a new quantitative technique to detect the temporal evolution of the NO formation inside the combustion chamber of a gasoline engine equipped with optical accesses. The ability of the technique to measure NO concentrations in very hard thermodynamical conditions has been proven.

This technique has widely been used since 1950's, for the measurement of minority species concentrations or the determination of their spectrophysical properties, given the simplicity of its setting up. However, the spectroscopic data published in the literature till nowadays, related to the nitric oxide absorption in the UV region, appear to be disparate and cover only very limited ranges of wavelengths, temperature and pressure. The analysis of previous works from the literature shows that the deviation of the Beer-Lambert's law does not allow to use the values of the nitric oxide absorption cross-sections in the $g(0,0)$, $g(1,0)$ and $g(2,0)$ bands, published up to now. A measurement of this cross-section and a correction of the absorption

law are needed in each particular case, where the instrumental resolution and the pressure and/or temperature conditions in the absorbing gas are different from those already published.

This study aims to develop and optimize UV absorption spectroscopy technique for detecting NO in the combustion chamber of a gasoline engine. A set-up of this technique is presented in Figure 1. Corrections of the Beer-Lambert's law for the NO $g(0,0)$, $g(1,0)$ and $g(2,0)$ absorption bands, first, performed for total pressures up to 30 bar are presented using the modified form of the law proposed by Donovan et al¹. This new formulation is proved to be appropriate for absorption measurements in total column ranging between $0.5 \cdot 10^{18}$ and $3 \cdot 10^{18} \text{ cm}^{-2}$ since correlation coefficients are found higher than 0.99 for all tested pressures (Figure 2). Beyond the higher limit of this interval, a more complicated expression for the corrected Beer-Lambert's law is found, with correlation coefficients higher than 0.999. Using the first correction, absorption cross sections (s_{eff}) of the three NO g bands were determined. In the second part of this work, experiments have been performed in the combustion chamber of a special gasoline engine. Two operating modes have been tested : $1/1$ (ignition every cycle) and $1/n$ (ignition 1 cycle of n) modes. These measurements demonstrated the ability of this technique to detect NO in very hard thermodynamical conditions such as met in internal combustion engines. Quantities of NO were, first, introduced at the intake pipe (the lowest concentration is 1000 ppm), the absorption in the three studied γ bands is clearly distinguishable. Secondly, with classical operating mode (1/1), a continuum absorption, due to the presence of CO_2 , H_2O and O_2 , was observed at the beginning of the ignition of the methane-air mixture, not allowing the detection of NO because of its very low concentration level (about 300 ppm). But from 50 Crank Angle Degrees After the Top Dead Centre, the absorption of NO becomes clear allowing to be assured on this technique.

Measurements of temperature dependence of NO absorption have been recently achieved in a shock tube of the CNRS (Centre National pour la recherche scientifique) of Orleans. The acquired spectra show a good agreement with the computed ones at the $g(0,0)$ as well as at the $g(1,0)$ band up to 1500 K. One of the acquired spectra is shown on figure 3.

Key Words : Gasoline engine, NO emissions, UV absorption spectroscopy, absorption cross sections, NO γ absorption bands.

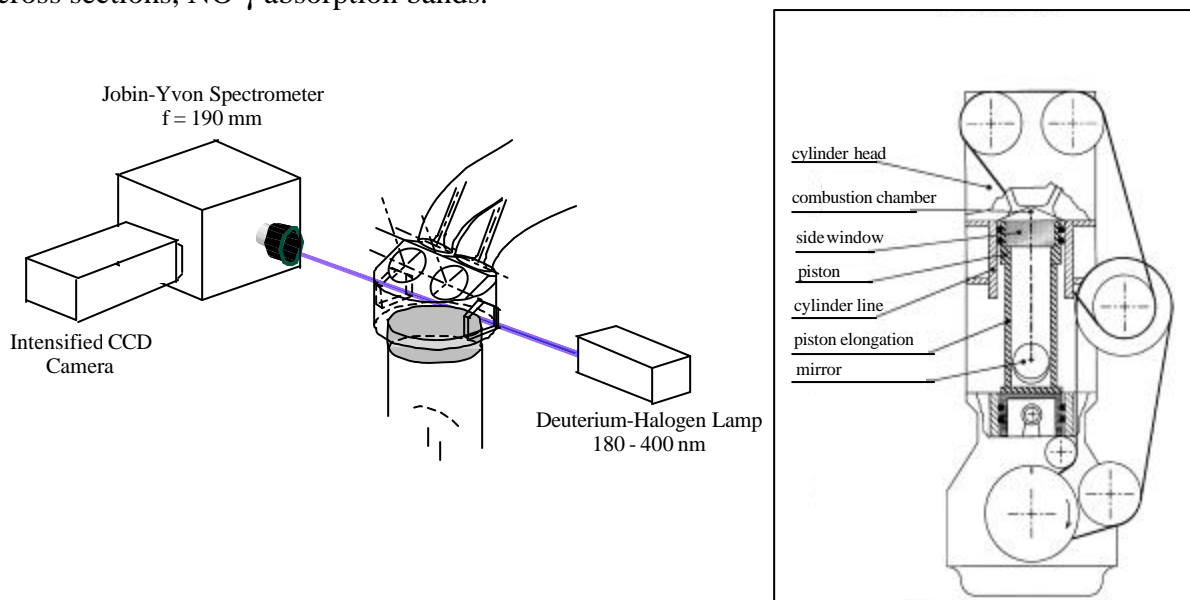


Figure 1. The set-up for the in-cylinder absorption spectroscopy measurements.

¹ R. J. Donovan, D. Husain and L. J. Kirsch, Trans. Faraday Soc., Vol. 66, pp. 2551-2559, 1970.

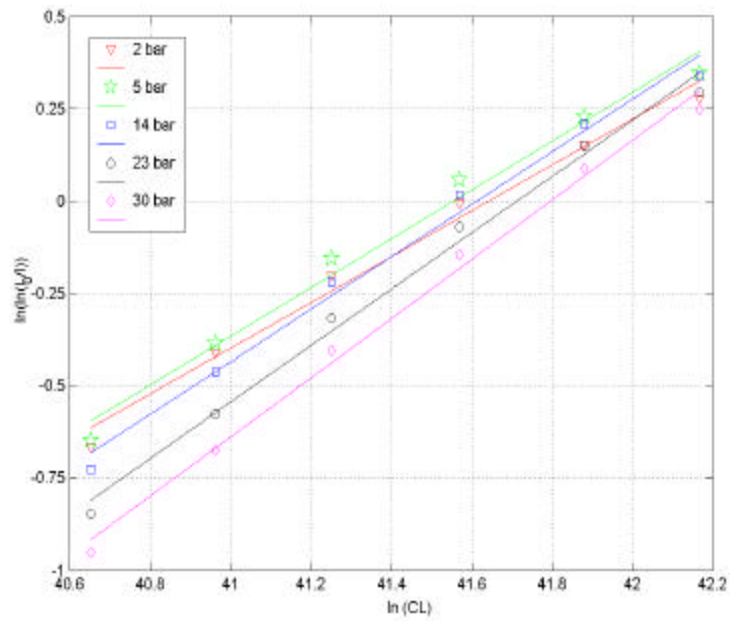


Figure 2. Action curves for the Beer-Lambert's law correction at the peak of the $\gamma(0,0)$ band (226.28 nm), for pressure from 2 to 30 bar, $T = 300$ K.

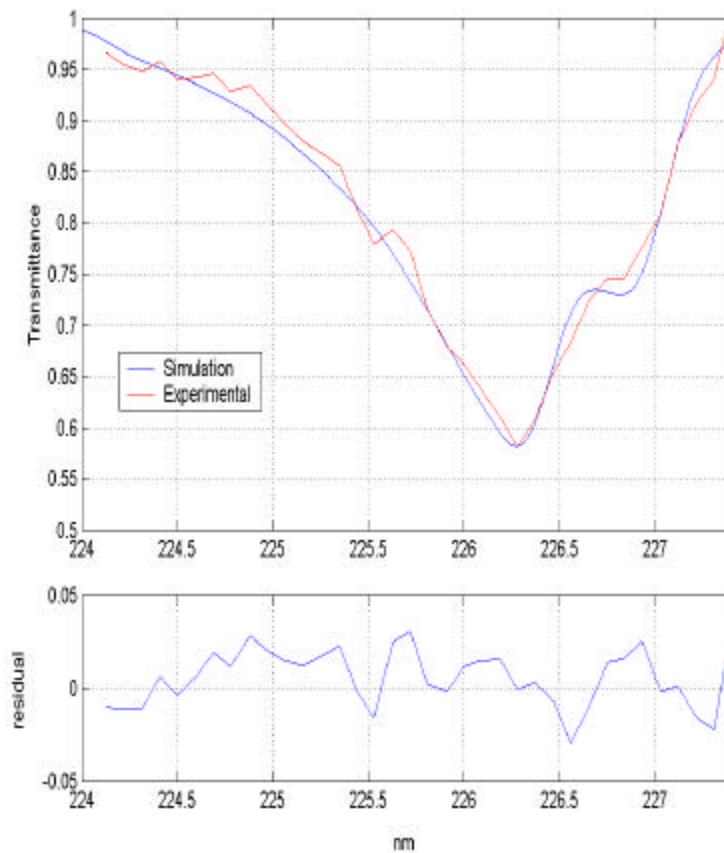


Figure 3. Simulated and acquired spectra (in shock tube) of NO $\gamma(0,0)$ band.
 $T = 985.59$ K, $P = 3.47$ bar, $[NO] = 0.42$ mol / m³