# Emission spectroscopy of nitric oxide in laser-induced plasma

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**Abstract.** In this paper, we investigate the laser-induced breakdown spectra of nitric oxide. Nitric oxide spectra are studied from laser-induced plasma emissions from plasma initiated both in laboratory air. Temperatures are inferred from the spectroscopic emissions using two methods. Spectra are fit to theoretical calculations of the diatomic spectra using the method of diatomic line strengths. For a time delay of 25 $\mu$s the temperature is found to be 6800 Kelvin. Comparisons are also provided to previously determined temperatures using a non-equilibrium air radiation fitting (NEQAIR) program.

## 1. Introduction

Analysis of spectra from laser-induced plasma is of interest in many fields of study and is commonly employed with the use of laser-induced breakdown spectroscopy (LIBS) which has become a popular experimental technique given its ease, low costs, and minimal sample preparation. One of the many applications of LIBS is use in diagnostic studies, such as combustion studies where quantitative analysis is applied to both atomic and molecular spectra [1]. In such works diatomic species of interest were CN, $N_2$, and NH [2, 3]. Of particular interest to combustion are quantitative calculations and analysis of nitric oxide (NO) spectra for studies of nitrogen containing flames and exhaust plumes of rockets. Considered is the near UV emission of the NO $\gamma$-band in the 140-340 nm range [4].

In order to quantitatively study the emission of diatomic molecules, a proper comparison to theory is required. We chose to employ the diatomic line strength method for calculations of theoretical NO spectra. The line strength is a popular method for calculating diatomic, molecular spectra due to its symmetric nature [5]. The formal definition of the line strength is the total sum of degenerate states that produce the same spectral line

$$S_{ul} = \sum_u \sum_l |< u \mid T_k^{(q)} \mid l >|^2 \tag{1}$$

where $u$ and $l$ represent the upper and lower states and $T_k^{(q)}$ is the $k^{th}$ component of the irreducible tensor operator of rank $q$ that gives rise to the spectral transition. This operator is the electric dipole operator and the line strength may be expressed as

$$S_{ul} = S(n'v', nv)S(J', J) \tag{2}$$

where $S(n'v', nv)$ is the electronic-vibration transition strength and $S(J', J)$ is the Hönl-London factor. Expressing the line strength as in Equ. 2 allows for a direct analytical calculation of the line strength, and in turn, the intensity of a diatomic emission spectra which may be expressed as

$$I_{ul} = \frac{16\pi^3 c(a_0 e)^2 C_{abs} N_0}{3\epsilon_0 Q} C_\nu \tilde{v_{ul}}^4 S_{ul} e^{-hF_u/kT} \tag{3}$$

where $a_0$ is the Bohr radius, $e$ is the electron charge, $c$ is the speed of light, $Q$ is the partition function, $N_0$ is the total population of the species, $C_{abs}$ and $C_\nu$ are the absolute and relative calibration factors, $h$ is Planck's constant, $F_u$ is the upper term value, $k$ is Boltzmann's constant, and $T$ is the temperature. A simple, yet rigorous selection rule results from the expression in Equ. 2. Given the relative ease in analytically calculating the Hönl-London factor and the ability for the Hönl-London factor to be analytically zero, allowed transitions are those with a non-vanishing line strength. In this study we apply this method to infer the emission temperature of the NO emission spectra from measurements made in the nominal 230-240 nm range.

## 2. Experimental Details

To study the laser-induced breakdown spectra of nitric oxide, laser-induced plasma were initiated in laboratory air. Optical breakdown is initiated by tightly focussing 1064 nm, 12 nanosecond pulsed laser radiation from a Q-switch, Nd:YAG laser operating in its fundamental mode with an average energy per pulse of 190 mJ. Light from the plasma emission is dispersed by a 0.64 meter Jobin-Yvon czerny turner spectrometer installed with 3600 grooves/mm grating. Spectra are recorded with an intensified, linear diode array coupled to an optical multichannel analyzer. Time synchronization for the laser pulse firing rate and the measurement rate of the linear diode array is achieved with the use of waveform, pulse, and delay generators. Exact details on the timing apparatus used in this experiment and in other, similar laser-induced plasma studies involving atomic and diatomic spectra is provided in reference [6]. Prior to analysis, all spectra were properly calibrated for the detector background and sensitivity response.

## 3. Results

The NO spectra are fit to theoretical calculations tabulated from the line strength method. Comparisons between experiment and theory are made using a Nelder-Mead algorithm, which is used for its ability to use fit multiple parameters simultaneously, including a variable baseline offset. The Nelder-Mead minimizes parameters by iteratively reducing the size of a geometric simplex where the number of vertices in the simplex is one more than the number of parameters to be fit [7, 8]. The parameters considered while fitting were the temperature, spectral resolution, and offset. The spectral resolution parameter is held constant for each fit and is determined from the physical limitations of the experimental apparatus. Given the wavelength region and the high groove density of the grating used, the spectral resolution of the experimental spectra was 0.056 nm which also accounts for slit width effects. The constant offset parameter was allowed to vary. NO spectra were collected and analyzed for 25, 50, and 75 $\mu$s time delays for air breakdown experiments and the inferred temperatures were found to be 6800, 6100, and 5800 Kelvin for 25, 50, and 75 $\mu$s time delays, respectively. The fitting results are depicted in Figure 1.

The temperature results from using the diatomic line strength are in accordance with previously completed NO LIBS experiments in which breakdown was initiated in a 1:1 mixture of $N_2$ and $O_2$ gas near atmospheric pressure. The spectra from that work were analyzed with the use of the non-equilibrium air radiation NASA Gordon-McBride program NEQAIR and the temperatures were found to be 6700 and 6000 Kelvin for 25 and 50 $\mu$s time delays, respectively [2, 9, 10]. It is important to note, however, that the approximate 1 nm spectral resolution of the previous study was significantly lower than that of the presented results. As can be seen in

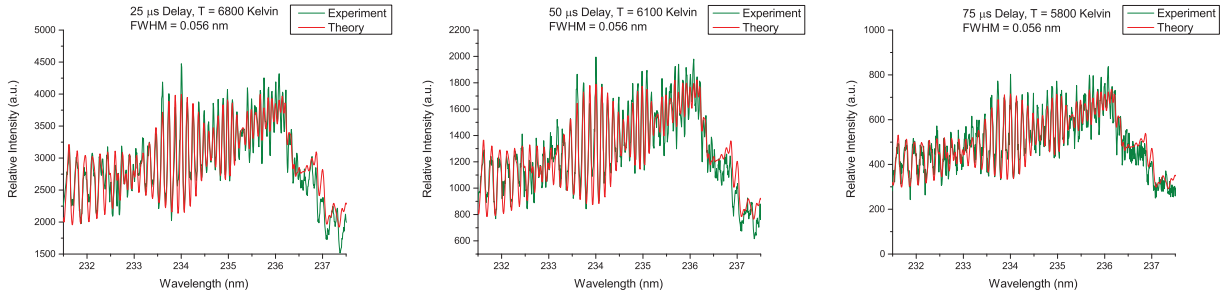


**Figure 1.** Fits to NO laser-induced plasma spectra at 25, 50, and 75 $\mu$s time delays with inferred temperatures of 6800, 6100, and 5800 Kelvin, respectively.

the fits shown in Figure 1, the diatomic line strength method has the capability to calculate and fit highly resolved spectra which gives the method the ability to include many rotational lines. Taken in this context the line strength method for calculating diatomic spectra provides a viable option for quantifying diatomic spectraand should be viewed as useful for combustion studies which often employ laser-induced florescence as a diagnostic method with spectra that often have comb-like structures. In such spectra the highly resolved nature of a spectra calculated from the line strength is applicable [11]. This is found to be particularly useful in studies of combustion with high temperature flames [12].

## 4. Conclusions

In this work, we have inferred the temperature of laser-induced plasma following optical breakdown in laboratory air from NO emission spectra. The plasma temperature was inferred by fitting experimental to theoretically calculated spectra with the use of a Nelder-Mead algorithm. The theory spectra were calculated using the method of diatomic line strengths and the temperatures are found to be 6800, 6100, and 5800 Kelvin for 25, 50, and 75 $\mu$s time delays. In comparison to previous experiments in which NO spectra were fit using the NEQAIR program, the determined temperatures are found to closely agree for similar time delays. Given the ability for the diatomic line strength method to calculate highly resolved spectra, the ability to observe highly resolved spectra, and close agreement with other methods, the diatomic line strength method is a viable method to quantify diatomic, molecular spectra.

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