Time-resolved plasma spectroscopy of diatomic molecular cyanide

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Abstract. In this work, measurements of cyanide (CN) molecular spectra following laser-induced optical breakdown are communicated. The recorded time-resolved data are Abel inverted to determine the spatial distributions of the maximum CN signals and to evaluate molecular excitation temperatures. The experiments are conducted in a 1:1 CO₂:N₂ gas mixture contained in a cell kept at atmospheric pressure, and the micro-plasma is generated using 150 mJ, 6 ns Q-switched Nd:YAG laser radiation. The optical emissions from the micro-plasma are dispersed using a 0.64 m spectrometer and are recorded along the wavelength and slit dimensions using an intensified charge-coupled device.

1. Introduction

The cyanide (CN) molecule has been of interest in a variety of research areas [1, 2, 3] including spectroscopic characterization. Cyanides are connected to various living organisms, but they are highly toxic. There are several detection methods [4] yet molecular emission spectroscopy allows one to detect presence of CN in a minimally invasive manner [5, 6].

In this work, results from experiments using nanosecond LIBS are communicated that focus on molecular emission spectroscopy [7]. The interests include carbon cyanide (CN). The recombination radiation of CN occurs within the first 100 nanoseconds for laser-induced breakdown in 1:1 CO₂:N₂ gas mixtures when using nanosecond laser pulses to create the laser plasma. Aspects of the analysis including Abel inversions and computational modeling of the plasma are discussed together with how to obtain inferences of molecular excitation temperatures. For nominal 6 nanosecond laser pulses and for pulse-energies in the range of 100 to 800 mJ, expansion dynamics and turbulence due to shock phenomena are usually measured. Determination of spatial distributions serves the purpose of investigating the level of homogenous distributions. Local thermodynamic equilibrium is frequently supposed to be valid for diagnostics with atomic and molecular species emission spectroscopy.

2. Results and discussion

The experimental arrangement consists of a set of components typical for time-resolved, laser-induced optical emission spectroscopy [8, 9, 10], or nanosecond laser-induced breakdown spectroscopy (LIBS). The experimental series for the separate measurements of CN molecular distribution after optical breakdown includes evacuating the cell to a nominal mercury pump
vacuum of $10^{-4}$ Pa ($10^{-6}$ Torr) and then introducing the N$_2$:CO$_2$ mixture. Figure 1 illustrates the wavelength-calibrated, sensitivity-corrected and background-subtracted maps of captured time-resolved data following optical breakdown in the ultra-high pure N$_2$ and research grade CO$_2$. And the figure shows a single measured [9] and computed [10] spectrum at the center of the plasma. The fitted spectral resolution, $\Delta \lambda$, amounts to $\Delta \lambda = 0.44$ nm.

**Figure 1.** Time delay 950 ns; (a) pseudo-colored contour map, and (b) measured and fitted spectrum at a slit height of 7 mm, inferred temperature: $T = 9.04$ kK.

Signatures of the 0-0, 1-1, 2-2, 3-3, 4-4 band heads begin to emanate for time delays of the order of 100 ns from optical breakdown. Moreover, the plasma typically propagates towards the top or laser side. The recorded data indicate a ~ 0.8 mm upward CN-signal propagation in the 370 to 393.5 nm spectral, ~ 7 mm object window during the first 5 microseconds, from a delay of 200 ns to 5200 ns.

The detector pixels are binned in 4 tracks along the slit direction, resulting in obtaining 256 spectra for each time delay. The average of accumulated data from 100 consecutive optical breakdown events is recorded for 21 different time delays using a gate width of 125 ns. In Figure 1, the vertical axis indicates the slit-height. With 1:2 imaging, and a pixel resolution of 13.6 µm, the clearly discernable plasma size in the cell amounts to ~ 3 mm. The figure shows that the CN band heads of the $\Delta v = 0$ sequence are well-developed, and it also shows an atomic line near 386.2 nm that likely is the carbon CI 193.09-nm atomic line recorded in second order. The electron density, $n_e$, can be determined from the Stark full-width at half-maximum, $\Delta \lambda_{\text{Stark}}$, or from the Stark shift, $\delta \lambda_{\text{Stark}}$, of the carbon line [11],

$$\Delta \lambda_{\text{Stark}} = 2w \, n_e \left[10^{17} \, \text{cm}^{-3}\right], \quad \text{or} \quad \delta \lambda_{\text{Stark}} = d \, n_e \left[10^{17} \, \text{cm}^{-3}\right], \quad (1)$$

where the width parameter, $w$, and shift parameter, $d$, amount to $w = 0.00291$ nm and $d = 0.00294$ nm [11], respectively, at an electron temperature of 40 kK. At 200 ns time delay, the full width of $\sim 0.4 \pm 0.1$ nm in 2nd order reveals an electron density of $\sim 34 \times 10^{17}$ cm$^{-3}$. The shift of $0.2 \pm 0.05$ nm in 2nd order yields a consistent result for the electron density. The accuracy of the Stark width parameter is listed at 30% [12].

Figure 2 displays measured and fitted spectra at the center versus the top of the spectra at 2200 − ns time delay. The plasma shows a spatial temperature variation with the center being at 8.42 kK, while the temperature at the top is hotter at 9.03 kK. The higher temperature near the edge versus the center indicates higher electron density. Additionally, the presence of the CI 193.09-nm atomic line recorded in second order as displayed in Figs. 1(b) and 2(b) indicates an electron density that is larger near the edges than at the center of the plasma.
Figure 2. Time delay 2200 ns; (a) center, $T = 8.42$ kK, and (b) top, $T = 9.03$ kK.

Near the edges of the expanding plasma, the CN signals are lower than near the center. Computations of equilibrium CN distributions versus temperature [9] indicate about a factor of 3 smaller CN mass fractions at 9 kK than at 8 kK. Moreover, application of Abel inverse integral transforms [9] reveal slightly lower CN temperature in the plasma center for time delays of the order of 1000 ns. Near the plasma edges at the top and the bottom (see Fig. 1(a)), the signals of the likely atomic carbon line are spectrally wider, show larger shifts, and are stronger than the CN 0-0 band head.

3. Conclusions

Measured CN recombination spectra following laser-induced optical breakdown show spatial temperature variations. Noteworthy is the early occurrence of CN for time delays less than 1 µs. The likely presence of the CI 193.09-nm atomic line in second order suggests higher electron density near the edges of the plasma. Stark widths and shifts can be used to determine the electron density, but higher spectral resolutions of the order of 0.02 nm would be desirable for determination of accurate values for electron density from the carbon line. Time-resolved CN recombination spectra at better than 0.1 nm spectral resolution would also result in improved assessment of the molecular excitation temperature distribution.

References

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