Analysis of Atomic and Molecular Superposition Spectra Following Laser-Induced Optical Breakdown

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ABSTRACT: The methods of laser induced breakdown spectroscopy offer a quick and reliable procedure for atomic and molecular identification. Micro-plasma parameters such as temperature and electron density can be inferred from emission spectra that occur subsequent to laser-induced optical breakdown. Molecular recombination and/or excitation of selected molecules can lead to simultaneous occurrence of atomic and molecular species. In order to advance the superposition spectroscopy technology, it is desirable to have available accurate theoretical atomic line profiles and molecular spectra. This study investigates Balmer Series atomic hydrogen spectra showing presence of C_2 molecular Swan bands, and it also investigates application of AlO diatomic emission spectroscopy in combustion plume studies. The AlO emissions are superposed to blackbody radiation from the flame.

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1. INTRODUCTION

We collect radiation intensity versus wavelengths following Laser Induced Optical Breakdown (LIOB) to infer both temperature and electron density [1-3], and accurately interpret broad hydrogen Balmer series emission spectra [4]. Further, Diatomic Quantum Theory allows us to precisely create synthetic spectra for various molecules following LIOB [5-8]. By employing both theoretical spectra predictions and analysis of experiments, it becomes possible to identify specific diatomic spectra superposed with atomic emissions and to determine micro-plasma parameters. We also examine flame emission spectra [9].

LIOB in gases, early in the plasma decay, can be diagnosed using the Stark broadening of hydrogen lines. We previously reported measurements [2] and detailed studies [3,5] of the use of atomic lines for characterization of micro-plasma. The typical electron density amounted up to 10^{19} cm^{-3} and excitation temperatures up to 10^5 K, or approximately 10 eV. Presence of carbon in the plasma, however, induces formation of C_2 molecules, and recombination radiation can be recorded superposed to the atomic emission lines. This can be seen, for example, when generating a laser spark in expanding methane [2]. The molecular signatures of C_2 Swan molecular emissions become clearly discernable at time delays of 2 µs. In this work, we apply fitting of the C_2 Swan molecular emission spectra [7]. We reported electron excitation temperature of typically 10,000 K [3], while the analysis discussed here reveals inferred molecular temperatures of typically 5,000 K. The molecular recombination spectra are recorded simultaneously and overlap the atomic emissions of the H-beta and H-gamma lines of the hydrogen Balmer Series.

In the analysis of superposition spectra, we further report our initial investigation of AlO flame emission spectra [9] that show a smooth background due to Blackbody Radiation. The initial analysis applies an at most quadratic fit of the background with subsequent fitting of the molecular emission. This approach is similar to the analysis of the molecular C_2 spectra: We model the wings of the H-beta and H-gamma lines by an at most quadratic fit.

Clearly, it will be desirable in future studies to use full atomic lines for the hydrogen emissions in the case of the modeling of C_2, and to use blackbody spectra for the modeling of AlO. However, in this work we present our results of using at most quadratic background models. This allows us to estimate molecular excitation temperatures from the recorded emission spectra, with a reasonable accuracy and precision. Modeling of spectra that are a superposition of a variety of species can in principle be accomplished, but it usually involves use of several parameters for individual species. For laser-induced optical breakdown in air, such multi-species superposition spectra have been modeled previously [10]. In our studies we find that accurate line-strength files [6,7] are preferred over use of molecular emission spectra computed using molecular constants [11]. Subtle spectroscopic details and results from comparisons (not reported here) of synthetic and measured emission spectra persuade us to better use our accurate line-strength files.

2. MODELING OF SPECTRA

Boltzmann plot techniques for atomic[3] and/or molecular transitions along with computations of diatomic molecular species allows us to infer temperature [6-8]. The spontaneous intensity radiated by excited molecules from upper level to lower level is given by the following equation

$$I_{ul} = \frac{16\pi^3 N_0}{3\varepsilon_0 c^3 Q} v_{ul}^4 S_{ul} e^{-E_u/k_B T} . \tag{1}$$

Here, Q indicates the partition function or state sum, S_{ul} is the line strength, E_u the upper level energy. N_0 is the population density of molecules, v_{ul} the transition frequency, k_B the Boltzmann constant, and T is the temperature.

Diatomic line strengths can be calculated by following several steps [12].

(a) Determine the number and numerical values of parameters for the upper and lower levels and then use these parameters to predict the positions of all spectral lines in the band system. One may compute vastly more line positions than there are actual spectral lines. Selection rules are then implemented to ensure that each line position represents an actual spectral line.

(b) For these spectral lines the Hönl-London factors are then calculated.

(c) Then the potential energy curves are calculated utilizing the rotational constants and vibrational term values for the upper and lower electronic states using the values obtained during step (a) along with the Rydberg-Klein-Rees (RKR) algorithm.

(d) These potential energy curves are used to numerically solve the one-dimensional Schrödinger equation for each vibrational level of the upper and lower electronic states to find the vibrational eigen-functions. The Franck-Condon factors and r-centroids are then computed.

(e) Finally, using a Taylor's expansion of the electronic transition moment, the Franck-Condon factors, r-centroids, Hönl-London factors, and electronic transition moment are combined to form the diatomic line strength.

The practical modeling of the molecular spectra of individual diatomic molecules includes use of non-linear fitting of measured spectra with synthetic spectra [6-8]. Here, we summarize the typical approach. Figure 1 illustrates the graphical user interface (GUI) for modeling of select transitions of specific diatomic molecules. The primary input, of course, includes the line-strength file, the measured spectra, specification of the background, and specification of spectroscopic parameters to be held constant or to be varied.

3. EXPERIMENTAL DETAILS

The hydrogen time-resolved measurements of LIOB comprised typical experimental arrangements for laser-induced breakdown spectroscopy (LIBS): nominal nanosecond Q-switched laser (8-ns, 75-mJ per pulse infrared 1064-nm radiation from a model Continuum YG680-10 Nd:YAG laser), spectrometer (1/2 m model 500 SpectraPro Acton
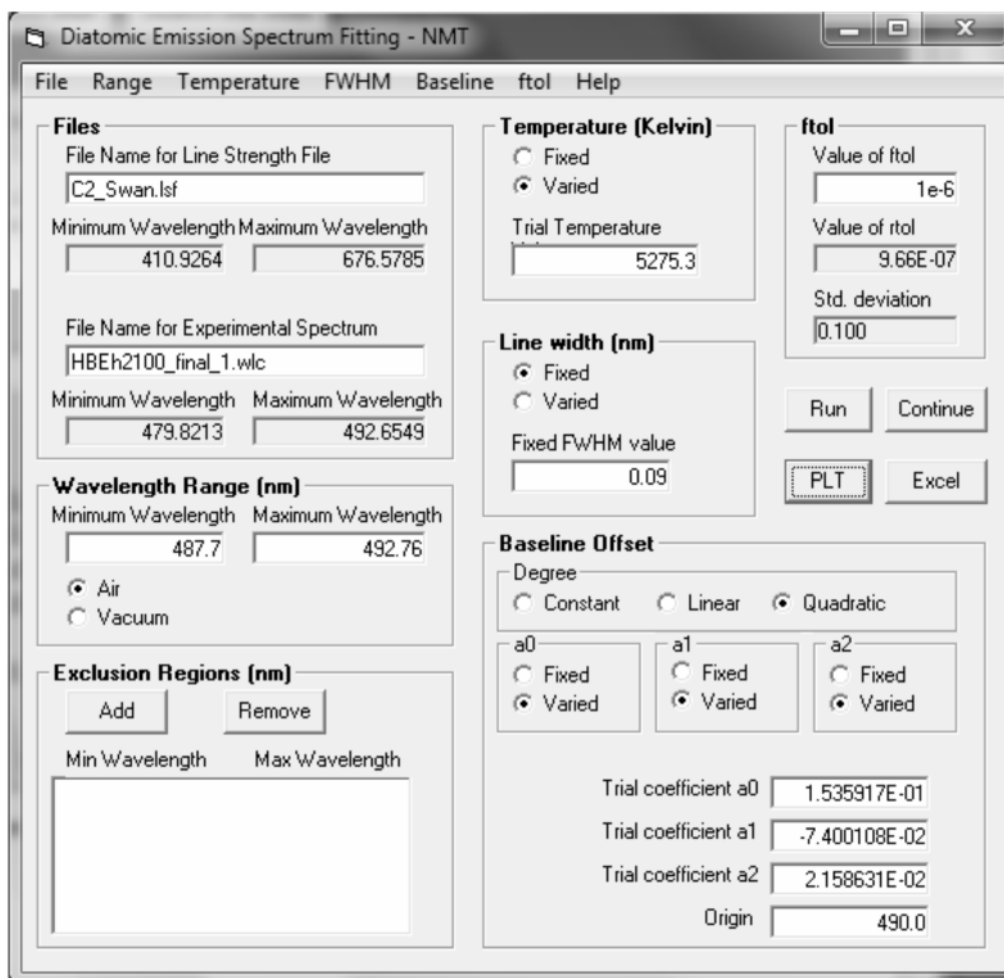
Figure 1: Graphical User Interface for the Nelder-Mead Temperature (NMT) program to fit diatomic emission spectra. The specific fixed parameter includes the instrumental full-width at half maximum (FWHM) of 0.9 nm for here fitting of a H-beta line profile at a delay of 2.1 μs (see Fig. 2). The inferred temperature of the C$_2$ Swan emissions amounts to 5,275 Kelvin

Research Corporation) and intensified linear diode array (model 1460 Princeton Applied Research detector/controller optical multichannel analyzer). Averaged over 100 individual LIOB events, the captured time-resolved data was detector-noise/background corrected and wavelength and detector sensitivity calibrated. The AlO flame emission spectra were recorded continuously for various positions along a large flame pool [9]. The AlO data was also wavelength and detector sensitivity calibrated.

Measurements of individual profiles of the Balmer series lines H-alpha, H-beta, and H-gamma, allow us to, in principle, infer electron excitation temperature. However, the inferred temperature will show reasonable error bars due to the broadened atomic emissions. Presence of the molecular emissions will add to the "background" for the hydrogen Balmer series diagnostic. Conversely, here we treat the H-beta and H-gamma lines as background in our analysis of molecular excitations. The blackbody radiation due to the emissions from a flame is modeled similarly.

Using the area of the incomplete H-beta and H-gamma lines and the area of the H-alpha line in constructing Boltzmann plots, the previously reported, inferred T$_e$ are in the 10,000 K (time delay 2.1 μs) to 20,000K (time delay of 0.4 μs) range [3]. For both gas pressures of 2.7×10^5 Pa and 6.5×10^5 Pa, almost identical results are found for T$_e$. The molecular excitation of the C$_2$ Swan band indicates temperatures of typically 5,000K (time delay 2.0 and 2.1 μs). Results of the flame temperature measured with a two-color pyrometer agree with the inferred temperature from spectroscopic analysis of AlO in the range of 2,700K to 3,000K [9].

4. RESULTS

In this section we present our first results from the fitting of C_2 Swan band emissions superposed to the H-beta and H-gamma atomic profiles. Figure 2 shows measured and fitted H-beta profiles for a time delay of 2.1 µs from laser-induced optical breakdown (LIOB). And Fig. 2 also shows the fitted C_2 Swan emission in the wings of the H-beta line. The experimental profile has been recorded in an expanding methane flow at pressure 6.5×10^5 Pa and at a time delay 2.1 µs. For comparison, the experimental profile at a pressure of 2.7×10^5 Pa was previously fitted, see Ref. [3]. The H-beta computation model was used from Ref. [15], for a center wavelength of 486.284 nm. Asymmetric H-beta profiles [16] were measured [2] earlier in the plasma decay up to time delays of 1.0 µs and for an electron density of typically 1.0×10^{17} cm^{-3}. The electron density for a time delay of 2.1 µs amounted to $N_e = 0.585 \times 10^{17}$ cm^{-3}, and the full-width-at-half maximum (FWHM) was 3.104 nm, with a center dip of 23.4%. The corresponding results for the high-pressure data are similar; here, we focus on analysis of the C_2 contribution. The inferred molecular excitation temperature amounts to 5,897 K.
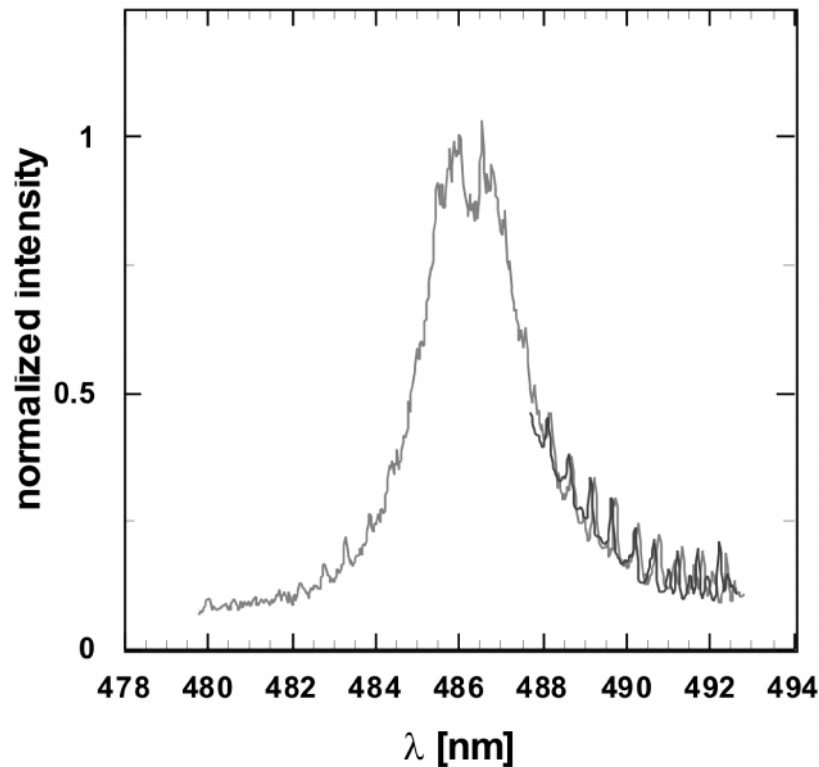

Figure 2: Measured H-beta and C_2 Swan Band fitted molecular emission. The fitted molecular emission shows a temperature of 0.59×10^4 K, while the electron excitation temperature amounts to 1.0×10^4 K

Figure 3 shows the results for C_2 fitting superposed to the H-gamma atomic line. The experimental flow conditions and time delay are identical to the ones for the recording of the H-beta emissions. The fitted temperature amounts to 4,846 K. The temperature difference of C_2 measured along with H-beta and along with H-gamma amounts to approximately 1,000 K. In the analysis of other H-beta and H-gamma profiles we find temperatures in the range of 4,000 to 6,000 K. In comparison the electron excitation temperature amounts to 10,000K, see Ref. [3], with an error in the order of 1,000 K to 2,000 K due to broad, incomplete line profiles of the hydrogen Balmer series used for the atomic Boltzmann plot. Consequently, the electron excitation and molecular excitation temperatures differ by about a factor of two.

Following measurements of AlO flame emissions [9] the analysis of the molecular spectra was accomplished similar to the approach used in the C_2 Swan band analysis: The blackbody radiation background was modeled with at most a quadratic background variation, see Fig. 1 that illustrated the layout of the fitting approach. Figure 4 shows the results.
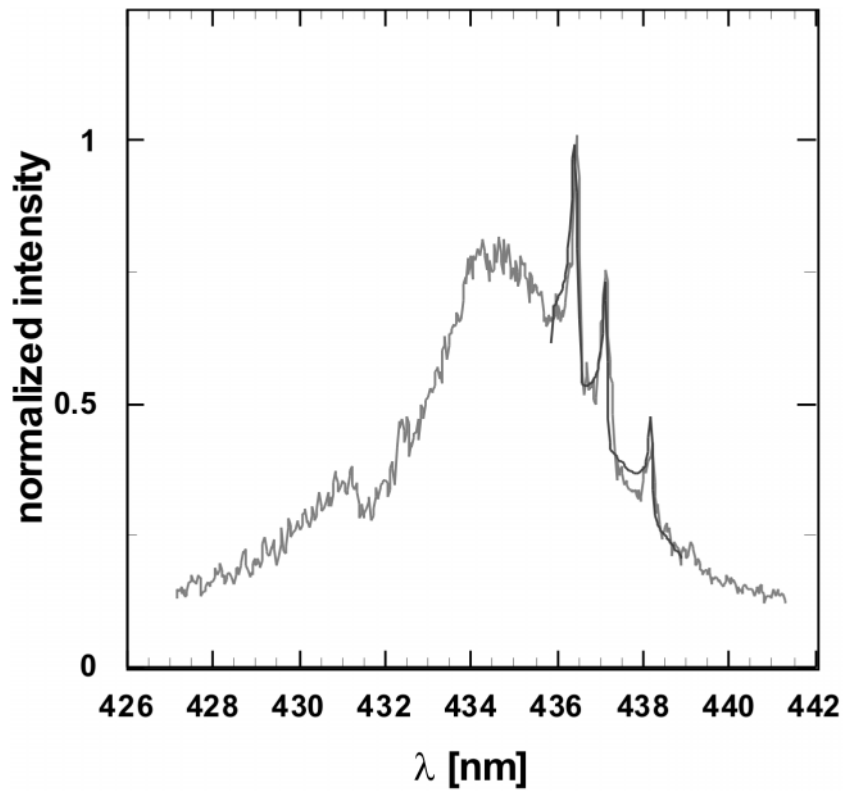
Figure 3: Measured H-gamma and C_2 Swan Band fitted molecular emission. The fitted molecular emission shows a temperature of 0.48×10^4 K, while the electron excitation temperature amounts to $1.0 \ 10^4$ K
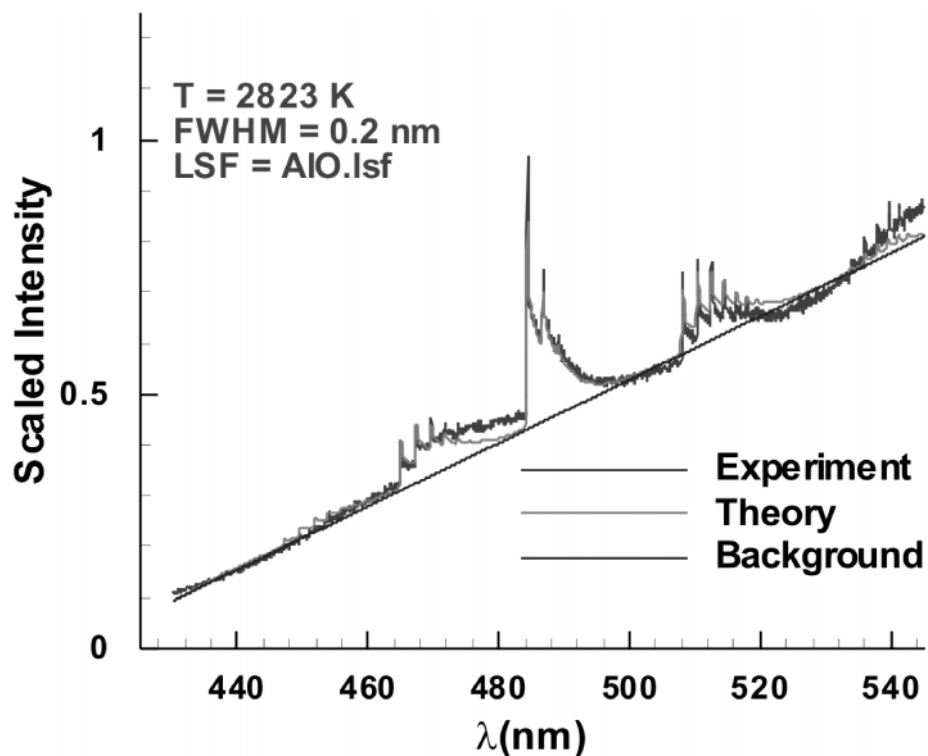

Figure 4: Measured and fitted molecular flame emission of aluminium monoxide. The fitted molecular emission shows a temperature of 2,823 K. The indicated background resembles blackbody radiation

The temperature results of the type illustrated in Fig. 4 are consistent with two-color pyrometer measurements [9]. Here, the background has been fitted using a linear approximation for the blackbody emissions for the region of interest. Multiple fitting of the blackbody radiation and of the AlO emission will be of interest in future studies.

5. CONCLUSIONS

We continue to model the C_2 Swan emissions superposed to the H-gamma and H-beta Stark broadened atomic lines. Ideally, complete profiles for the hydrogen Balmer series lines H-beta and H-gamma should be used for accurate fitting of the C_2 Swan spectra. Noteworthy is the temperature obtained from molecular recombination spectra in the 4,000 K to 6,000 K range for time delays of typically 2 μs following laser-induced optical breakdown in methane. For the AlO fitting, background modeling should include a blackbody radiation option. However, the molecular flame spectra recorded in the specific task carried out by Fire and Aerosol Sciences at Sandia National Laboratory, allowed us to map temperature of combusting aluminum as a function of height along a propellant plume. The continuing development of synthetic spectra for various atomic and molecular species promises to further the already expansive applications of superposition spectra and spectral identification as a diagnostic tool.

In our analysis we prefer the use of line strength files for accuracy of the fitting. Our interest includes diatomic molecular spectroscopy signatures from AlO, C_2, CH, CN, CrF, N_2^+ 1st Neg, N_2 1st Pos, N_2 2d Pos, NH, NO, OH, TiO, to name a few. Line-strength files for example for C_2, see Refs. [7] and [13], and AlO, see Refs. [6] and [8] show usually sufficient accuracy to address superposition spectra. Alternate approaches include use of a program package SPECAIR [11]. This program is designed for modeling the absolute intensity spectral radiation emitted by gases and plasmas of various compositions. It includes radiating species C, C_2, CN, CO, N, N_2, N_2^+, NH, NO, O, O_2, OH. The so-called NEQAIR program allows us to include select line-strength files as documented for example for AlO in Refs. [8,9] and OH in Ref. [10]. The program SPECAIR however allows one to evaluate spectra for different translational, electronic, vibrational and rotational temperatures individually. The code utilizes Boltzmann distribution factors at the electronic, vibrational, and rotational temperature to determine the population of the internal energy levels. It also allows one to evaluate effects of absorption by room air between the emitting gas or plasma and the detector. Important absorbing species in room temperature air at normal temperature and pressure are H_2O and CO_2 in the infrared and O_2 (O_2 Schuman-Runge continuum below 185 nm).

In the analysis of molecular superposition spectra, atomic hydrogen emissions are usually not included. Significant past experimental and theory work is noted on hydrogen, see for example Refs. [1-3], and future ongoing work on plasmas that contain hydrogen, see for example Ref. [14]. The analytical work on diatomic molecular spectroscopy, see for example Refs. [5,6], will be the basis of future analysis of molecular spectra that contain hydrogen Balmer series signatures. Equally, the modeling of flame emission spectra will continue to use the accurate line strength files for AlO to determine temperature from both molecular spectra and the underlying blackbody radiation.

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