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Article

Analysis of Laser Plasma Carbon Swan Emission Spectra

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Abstract: This article presents analysis of carbon Swan, C_2 , laser-plasma emission records using line strength data, C_2 -Swan-Isf, and the ExoMol astrophysical database. Line-strength data fitting of 0.25-nanometer spectral resolution ExoMol-computed spectra for a 6,000-Kelvin temperature C_2 Swan system, $d^3\Pi_g \rightarrow a^3\Pi_u$, $\Delta v = 0, \pm 1$, reveals a temperature of 5,640 Kelvin. The six per cent lower temperature is associated primarily with the accuracy of the transition wavelengths in the ExoMol vs. C_2 -Swan-Isf data. The analysis of experiment data examines spectra that are recorded following laser-induced optical breakdown in carbon monoxide. The laser plasma data are recorded with 0.35-nm spectral resolution. The temperature inferences are elaborated when using non-linear fitting with both databases. The results show temperatures in excess of 6,000 Kelvin for the $\Delta v = -1$ sequence, and for a time delay of 30 μs from laser plasma initiation. The accuracy of the C_2 Swan bands line strength data is of the order of 1 picometer. These line strength data are also utilized for analysis of laser-induced fluorescence experiments that employ a spectral resolution of 5.5 picometer, and a temperature of 2,716 Kelvin is inferred. Accurate C_2 databases show many applications in laboratory diagnosis and interpretation of astrophysical plasma records.

Keywords: diatomic molecules; carbon Swan bands; laser-plasma; data analysis; laser induced breakdown spectroscopy; combustion; time-resolved spectroscopy; spectra fitting program; astrophysics

1. Introduction

Signatures of the diatomic carbon molecule, C_2 , [1–3] occur in plasma-emission following the generation of laser-induced optical breakdown of carbon-containing materials, liquids, gases, including carbon monoxide gas [4]. Notable is of course, occurrence of C_2 Swan bands in combustion of hydrocarbons, emissions from white dwarf stars, e.g., Procyon B [5,6], to name two specific examples. Usually, accurate diatomic line strengths data are preferred in the analysis [7–9] of recorded data. However, recent interest in exo-planet spectroscopy motivates determination of new molecular databases, viz. the ExoMol [10] database. The ExoMol database lists various C_2 isotopologues, however this work focuses on $^{12}C_2$. The molecular transition of interest is the C_2 $d^3\Pi_g \rightarrow a^3\Pi_u$, $\Delta v = 0, \pm 1$ Swan band system [11].

Spectroscopy [11–17] of laser-plasma reveals clean C_2 Swan bands for of several dozens of microseconds from the initial laser plasma generation using pulse widths of a few nanoseconds. For diatomic carbon spectroscopy, one can utilize the ExoMol or other databases in conjunction with the PGOPHER program [18,19] for diatomic molecular spectroscopy. The ExoMol $^{12}C_2$ data files for the states and the transitions are converted in this work to line strength files for the purpose of comparison with previously communicated and extensively tested C_2 [7–9] line-strength data that are conveniently accessed with MATLAB [20] scripts.

2. Experiment and Analysis Overview

The laser plasma experiment for recording of C_2 Swan bands comprises a standard laser-induced breakdown spectroscopy arrangement [4]. A Continuum YG680S-10 Nd:YAG device is operated at the fundamental IR wavelength of 1064 nm, 7.5 ns pulse width, 300 mJ energy per pulse, and a

rate of 10 Hz. The laser beam is focused into a cell containing 99.97% purity carbon monoxide with at most 0.02% nitrogen gas impurity, at 22.4 kPa (3.25 psi) above atmospheric pressure. An optical multichannel analyzer manages electric gates and recordings of an intensified, 1024-pixels linear diode array mounted at the exit plane of a MonoSpec 27 Thermo Jarrel-Ash 0.275 monochromator. A 1800 grooves/mm holographic grating has a reciprocal linear dispersion of 2 nm/mm. Wavelength and sensitivity calibrations utilize standard light pen-ray and tungsten light sources, respectively. Typically, averages over 200 individual laser-plasma events are accumulated with a gate width of 1 μ s. The $\Delta v = -1$ sequence of the C_2 Swan system discussed in this work is recorded at a gate delay of 30 μ s. Over and above the 1- μ s average, the data represent a line-of-sight average of the expanding plasma.

The analysis of the diatomic molecular spectra utilizes line strength data, the Boltzmann equilibrium spectral program (BESP) and the Nelder-Mead downhill simplex, non-linear fitting algorithm [21] in conjunction with the Nelder-Mead temperature (NMT) program for computation and fitting of theory and experiment spectra. The molecular C_2 Swan line strengths “ C_2 -Swan-lsf” [8] are established using the Wigner-Witmer diatomic eigenfunctions [22,23] and standard molecular spectroscopy methods [7]. In turn, the ExoMol states and transition files for C_2 [24,25] are utilized for the generation of line strength data that can be used with BESP and NMT. The ExoMol data show Einstein A-coefficients that are converted to line strengths [26–29].

The C_2 -Swan-lsf and ExoMol databases show vacuum wave numbers. In both BESP and NMT programs, air wavelengths are computed by including refractive index of air variations with wave number [30]. Details are elaborated in Refs. [8,26] including preference of considering Gaussian-profiles. Extensions to combined Lorentzian and Gaussian profiles, or Voigt profiles, can be implemented using standard spectroscopy approaches [31].

3. Results

This section focuses on the diatomic molecular $C_2 d^3\Pi_g \rightarrow a^3\Pi_u, \Delta v = 0, \pm 1$ sequences and progressions. First, recorded spectra of the $\Delta v = -1$ sequence [4] are re-evaluated by fitting a linear, spectroscopically broad background in addition to minimizing the difference of theory and experiment spectra for the C_2 -Swan-lsf data. Second, fitting of the recorded data is accomplished with ExoMol data that are transformed from Einstein A-coefficients to line strengths. Third, ExoMol C_2 data in the range of 440–590 nm are computed and then analyzed with C_2 -Swan-lsf line strengths. And finally, comparisons are included of laser induced fluorescence (LIF) data and C_2 -Swan-lsf computed spectra in order to exhibit the accuracy of that theory data set. For these comparisons, a separate LIF-program (not communicated here) is utilized as for LIF the wave numbers for the lower states of the transitions are needed [7].

3.1. Analysis of $\Delta v = -1$ Swan Spectra with NMT Program and C_2 -Swan-lsf Line Strengths

A previous analysis of the $\Delta v = -1$ sequence [4] shows a temperature of 6,745 K and for a spectral resolution of 0.35 nm (11.5 cm^{-1}) when assuming zero background contributions. Over and above clearly developed Swan spectra for a time delay of 30 μ s from laser-plasma initiation, there are background contributions from other radiating species. This background radiation is modeled to vary linearly with wavelength. The background contributions are computed simultaneously with fitting the spectra for temperature determination while keeping the same spectral resolution. The NMT script would allow one to also fit the spectral resolution in the fitting of theory with experiment data.

Figure 1 illustrates spectra determined from temperature fitting with constant Gaussian line-width, $\Delta\lambda$. The simulated spectrum utilizes the C_2 -Swan-lsf data in the experimental range 528 nm–565 nm. Analysis of the measured data leads to a C_2 excitation temperature of $T = 7,360\text{ K}$.

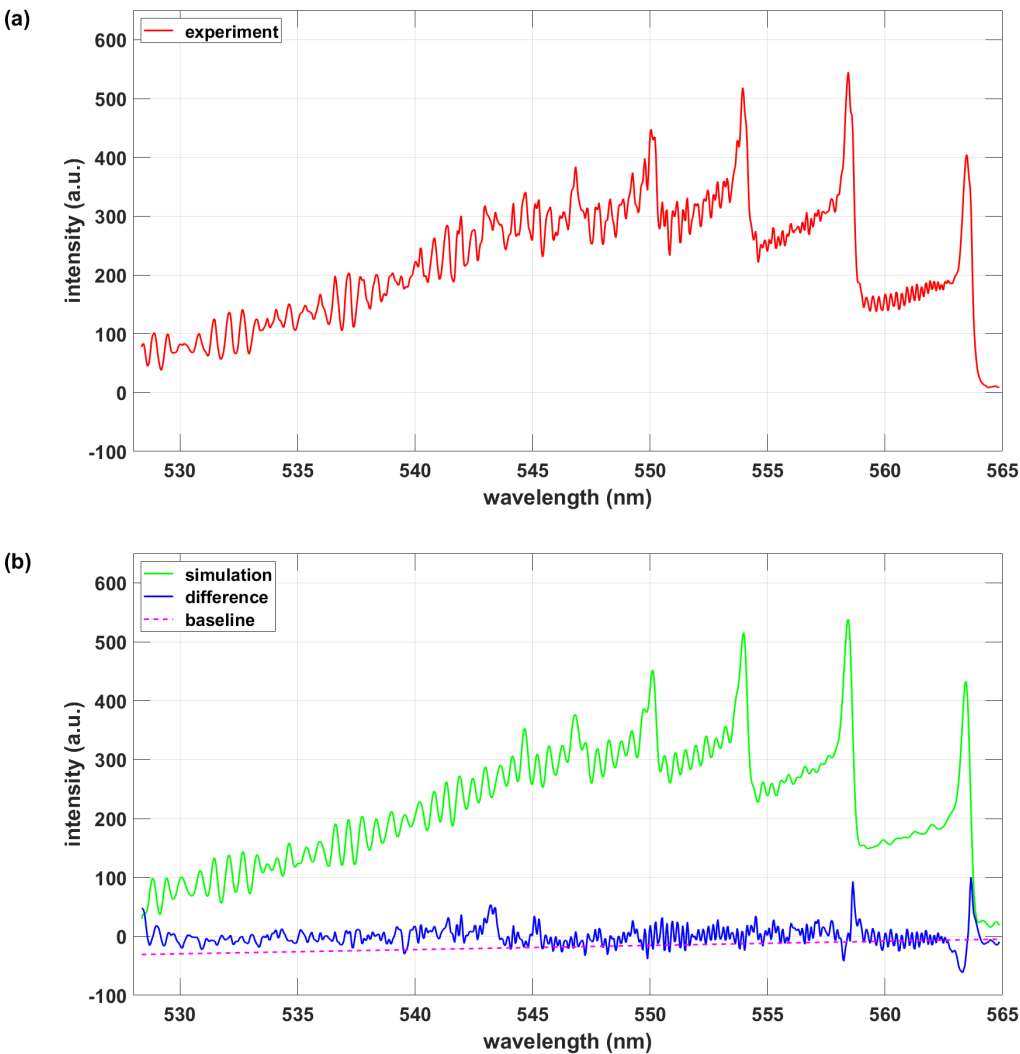


Figure 1. (a) Experiment. (b) NMT fitting with C₂-Swan-lsf data, T = 7,360 K, fixed $\Delta\lambda = 0.35$ nm.

3.2. Analysis of $\Delta v = -1$ Swan Spectra with NMT Program and ExoMol C₂ Line Strengths

For the analysis with ExoMol C₂ data, the states and transition files for C₂ [24,25] are collated in a table that is compatible with the NMT program, including conversion of Einstein A-coefficients to line strengths. Tables 1 and 2 reveal the number of lines that agree within specified wave number values and the number of transitions, respectively.

Table 1. Subset of the C₂ ExoMol data that agree within $\Delta\tilde{\nu}$ of 5,032 transitions in the C₂-Swan-lsf data in the range 528.36–564.85 nm (17,704–18,926 cm⁻¹).

Database	$\Delta\tilde{\nu} < 0.05\text{ cm}^{-1}$	$\Delta\tilde{\nu} < 0.2\text{ cm}^{-1}$	$\Delta\tilde{\nu} < 0.5\text{ cm}^{-1}$	$\Delta\tilde{\nu} < 2.0\text{ cm}^{-1}$	$\Delta\tilde{\nu} < 10.0\text{ cm}^{-1}$
ExoMol C ₂	1,147	2,215	2,980	4,073	4,789

Table 2. Number of transitions in the range 528.36–565.85 nm (17,704–18,926 cm⁻¹).

Database C ₂ Swan	528–565 nm	528–565 nm $A_{\text{coeff}} > 10^3\text{ s}^{-1}$
ExoMol C ₂	283,005	37,696
C ₂ -Swan-lsf	5,032	5,032

Figure 2 illustrates spectra determined from temperature and linear background fitting with constant Gaussian line-width, $\Delta\lambda$. The results indicate a temperature of $T = 5,740$ K that is 1,890 K lower than that obtained with C_2 -Svan-lsf fitting, see Figure 1. The temperature discrepancy is attributed to the spectroscopically different line positions.

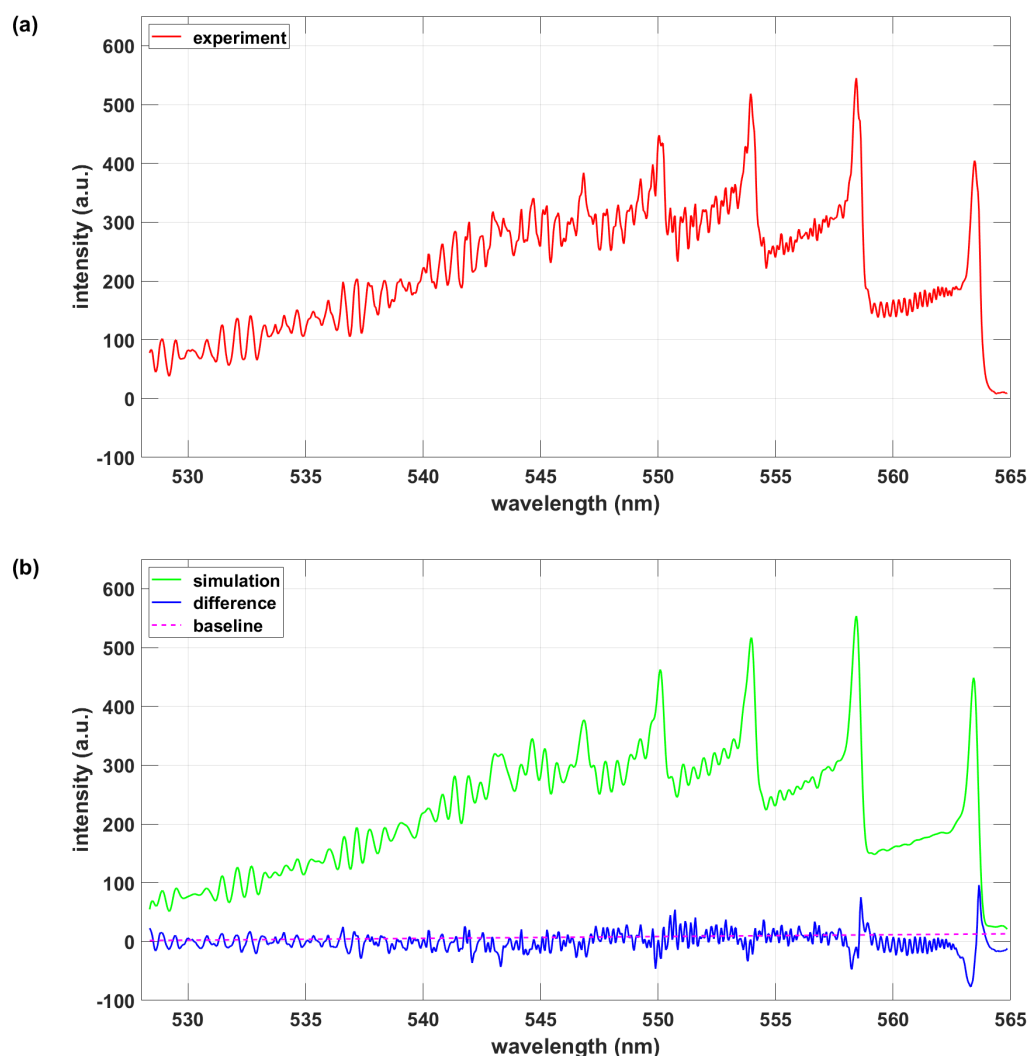


Figure 2. (a) Experiment. (b) NMT fitting with ExoMol C_2 data, $T = 5,740$ K, fixed $\Delta\lambda = 0.35$ nm.

The ExoMol C_2 data appear to successfully model in part the apparent differences near 543 nm in Figure 1 that suggest presence of so-called 6-7 high pressure band of C_2 , a known intensity anomaly in the C_2 Swan system. However, subtle differences occur for the 2-3, 3-4, 4-5 bands near 554 nm, 550 nm, 547 nm, respectively. The 0-1 and 0-2 bands near 564 nm and 558 nm, respectively, reveal similar differences between experiment and theory spectra.

3.3. Swan Spectra $\Delta v = 0, \pm 1$: ExoMol C_2 and C_2 -Svan-lsf Data Comparisons

The number of transitions in the range of 440–590 amount to well over one million for the ExoMol C_2 data base, or of the order of 100 times more transitions than those in the C_2 -Svan line strength data. Table 3 illustrates the comparisons, and it also indicates that for Einstein A-coefficients larger than 10^3 s^{-1} there are of the order of 10 times more lines that are included in the ExoMol C_2 database than that for C_2 -Svan data.

Table 3. Number of transitions in the ranges 440–540 nm (16,950–22,725 cm⁻¹).

Database	Swan	440–590 nm	440–590 nm $A_{\text{coeff}} > 10^3 \text{s}^{-1}$
ExoMol C ₂		1,251,235	169,566
C ₂ -Swan		17,689	17,689

Table 4 displays agreements of lines within the indicated wave number range for otherwise the same identification for upper and lower levels of the transitions. Of the 169,566 ExoMol C₂ transitions, 16,988 or about ten per cent are within ten wave numbers of those listed in the 17,689 C₂-Swan data. However, only 3,123 of 169,566 transitions, or about 2%, are in agreement within the accuracy of 0.05 cm⁻¹.

Table 4. Subset of the C₂ ExoMol data that agree within $\Delta\tilde{\nu}$ of 17,689 transitions in the C₂-Swan-lsf data in the range 440–590 nm (16,950–22,725 cm⁻¹).

Database	$\Delta\tilde{\nu} < 0.05 \text{ cm}^{-1}$	$\Delta\tilde{\nu} < 0.2 \text{ cm}^{-1}$	$\Delta\tilde{\nu} < 0.5 \text{ cm}^{-1}$	$\Delta\tilde{\nu} < 2.0 \text{ cm}^{-1}$	$\Delta\tilde{\nu} < 10.0 \text{ cm}^{-1}$
ExoMol C ₂	3,123	6,901	9,617	14,094	16,998

Figure 3 illustrates ExoMol C₂ computed, or numerical experiment data, in the wavelength range 440–590 nm that are fitted using the NMT script and C₂-Swan-lsf data. The differences in temperature of 360 K can be associated with primarily the wave numbers that are listed in the ExoMol C₂ database. There may also be differences in the Frank-Condon factors and r-centroids, but this is not further evaluated in this work. Figure 3b exhibits obvious differences near the heads of the various Swan bands.

3.4. Laser-induced fluorescence and C₂-Swan Line Strengths

The C₂ line strength database has been extensively tested [9] including in the analysis of laser-plasma emission spectra. The use of accurate line strengths extends to analysis of LIF data [32] of the $\Delta v = 0$ sequence, and comparisons with Doppler-limited dye laser excitation spectra of the $\Delta v = +1$ C₂ Swan band [32,33]. Figure 4 displays recorded and fitted LIF spectra of C₂ in the range of 507.723–516.696 nm. Analysis and fitting of laser induced fluorescence data requires knowledge of lower state wave numbers, and consequently a different script (not communicated here) as discussed in Ref. [7]. The laser step size in the experiment amounted to 0.002 cm⁻¹ (0.05 picometer), and the full-width-half-maximum of the fitted spectrum amounts to 0.22 cm⁻¹ (5.5 picometer) or about four times larger than the typical resolution of the C₂-Swan-lsf data.

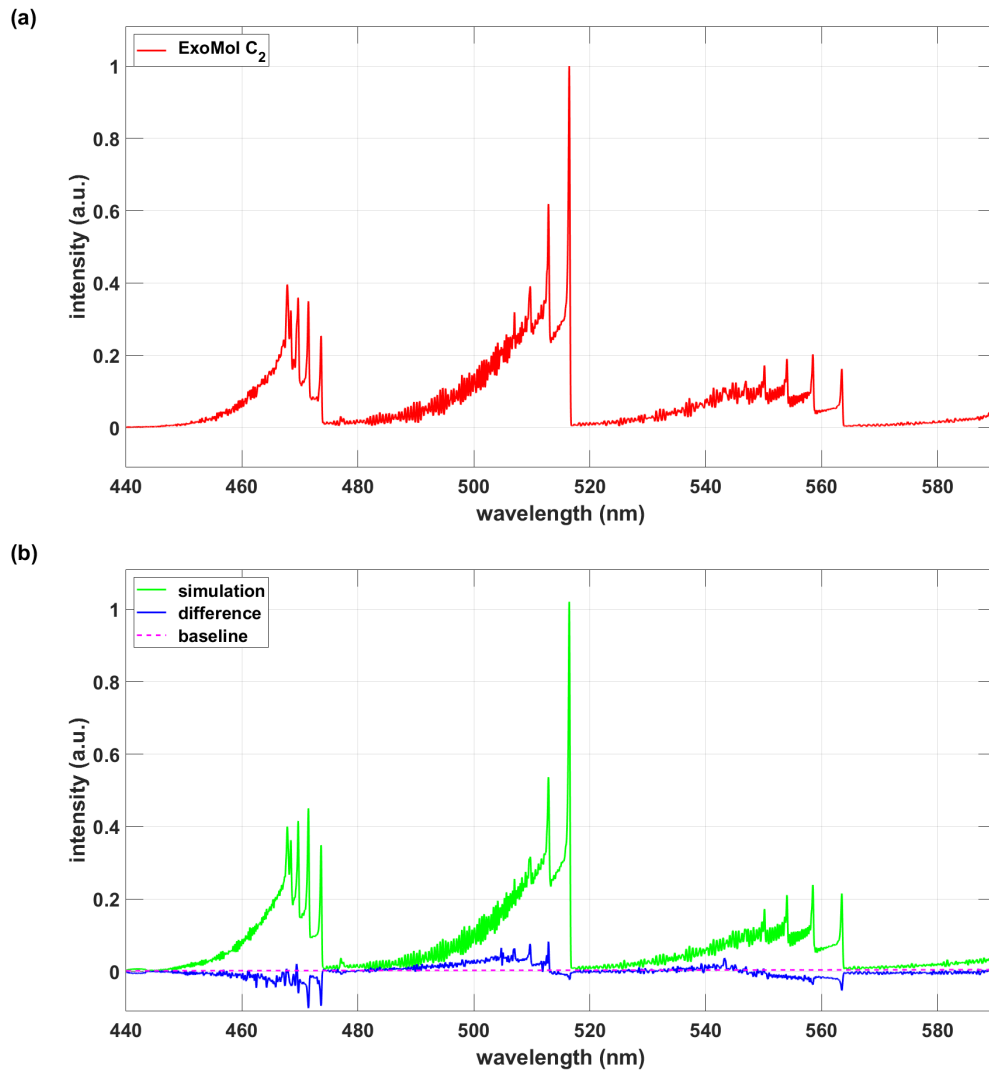


Figure 3. (a) Numerical experiment data, $T = 6,000$ K, $\Delta\lambda = 0.25$ nm. (b) NMT fitting with C_2 -Swan-lsf data, inferred temperature from fixed line-width fitting: $T = 5,640$ K.

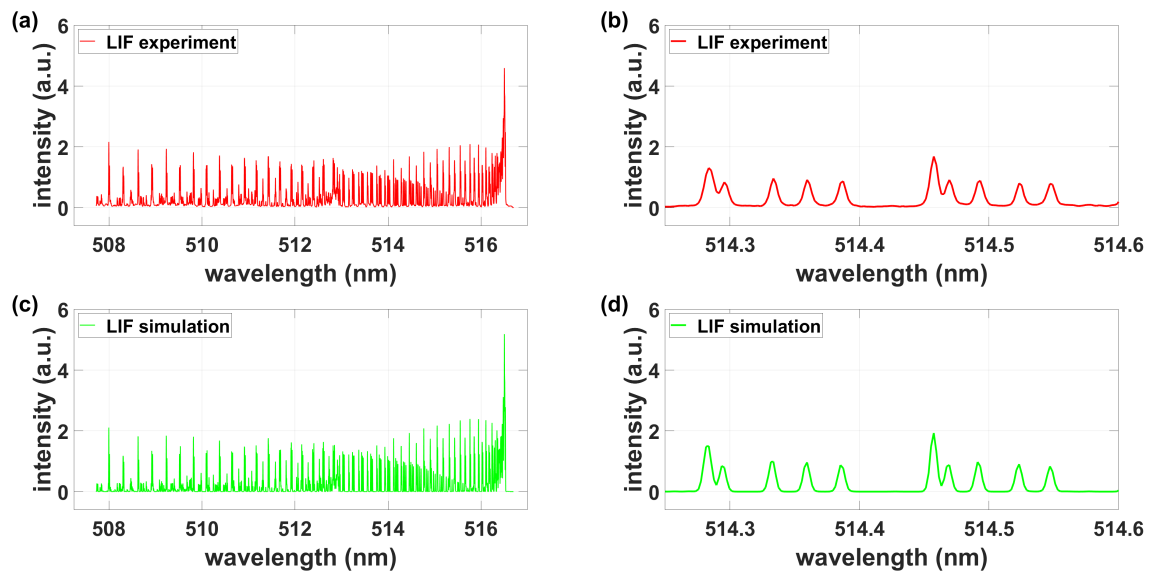


Figure 4. (a) Laser-induced fluorescence data, $T = 2,716$ K, laser step size: 0.00005 nm. (b) Expanded experiment data region. (c) Fitted data, $T = 2,716$ K, $\Delta\lambda = 0.0055$ nm. (d) Expanded fitted data region.

Table 5. Number of transitions in the range 507.723–516.696 nm (19,354–19,696 cm⁻¹).

Database Swan	507.723–516.696 nm	507.723–516.696 nm A _{coeff} > 10 ³ s ⁻¹
ExoMol C ₂	77,832	8,708
C ₂ -Swan	1,535	1,535

Table 6. Subset of the C₂ ExoMol data that agree within Δν̃ of 1,535 transitions in the C₂-Swan-lsf data in the range 507.723–516.696 nm (19,354–19,696 cm⁻¹) .

Database	Δν̃ < 0.05 cm ⁻¹	Δν̃ < 0.2 cm ⁻¹	Δν̃ < 0.5 cm ⁻¹
ExoMol C ₂	651	1,194	1,337

4. Discussion

The agreement of the ExoMol C₂ and C₂-Swan-lsf databases line position is marginal when using accuracies of the order of 0.05 cm⁻¹, or of the order of 1 picometer. For spectral resolutions of 10 cm⁻¹, or about 0.25 nm, and for the Δv = 0 ± 1 sequences and progressions, about 6% lower temperature is inferred when fitting 6,000 K, Exomol C₂ theory data with C₂-Swan-lsf data. Consequently, use of the C₂-Swan-lsf database is recommended. For measurements with spectral resolutions of 11.5 cm⁻¹, or an average resolution of 0.35 nm, significant differences occur as well, namely, a 25% lower temperature would be predicted when using the Exomol C₂ database. The C₂-Swan-lsf line strength table is generated by fitting high resolution Fourier-transform data rather than computation from first principles.

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