



Computation of diatomic molecular spectra for selected transitions of aluminum monoxide, cyanide, diatomic carbon, and titanium monoxide



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ABSTRACT

Laser ablation studies with laser-induced breakdown spectroscopy (LIBS) typically emphasize atomic species yet fingerprints from molecular species can occur subsequently or concurrently. In this work, selected molecular transitions of aluminum monoxide (AlO), diatomic carbon (C₂), cyanide (CN), and titanium monoxide (TiO) are accurately computed. Line strength tables are used to describe the radiative transitions of diatomic molecules primarily in the visible, optical region. Details are elaborated of the computational procedure that allows one to utilize diatomic spectra as a predictive and as a diagnostic tool. In order to create a computed spectrum, the procedure requires information regarding the temperature of the diatomic transitions along with other input such as the spectral resolution. When combined with a fitting algorithm to optimize such parameters, this procedure is used to infer information from an experimentally obtained spectrum. Furthermore, the programs and data files are provided for LIBS investigations that also reveal AlO, C₂, CN, and TiO diatomic spectra.

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1. Introduction

The generation of micro-plasma with laser radiation and the application of laser-induced breakdown spectroscopy (LIBS) are major interests in applied physics [1,2]. LIBS emerged from optical emission spectroscopy (OES) and has gained considerable popularity in the analysis of laser-induced plasma. Yet spark-induced breakdown spectroscopy (SIBS) continues to be of interest [1], equally use of double beam LIBS and/or combinations of laser-induced and electrical discharge generated plasma. Atomic emission spectroscopy (AES) allows one to evaluate the composition of a sample by analyzing specific wavelength regions of the radiation emanated from a flame, plasma, arc or spark. Over and above the occurrence of atomic species in recorded optical breakdown spectra, molecular emission characteristics can occur simultaneously. The origin of such spectra can be due to recombination of atomic species but can be due to removal of molecules that are excited during the interaction with laser radiation. In many instances, when using 1 to 10 nanosecond laser pulses and time-resolved detection [2], strong background from free electron radiation is measured first, emergence of atomic spectra occurs next, and then signatures of molecular species can be detected. LIBS experiments

with short-pulsed laser radiation, on the order of several tens of femto-seconds, can however immediately reveal molecular spectra that are especially of interest in combustion diagnostics [3]. Recent work in connection with laser ablation molecular isotopic spectrometry (LAMIS) [4] shows extensions of LIBS applications from exclusively elemental atomic spectra analysis to include molecular spectra as diagnostic tools. Laser ablation experiments with carbon-containing samples, such as coal [5,6], graphene [7], organic materials [8], or soil [9–11], can also reveal diatomic carbon Swan bands [12]. The determination of temperature is frequently of primary concern for description of the plasma and/or chemical state. Laser ablation and/or combustion of aluminum together with occurrence of aluminum monoxide [13,14], titanium laser ablation and occurrence of titanium monoxide [15], and/or laser-induced breakdown spectroscopy of carbon containing samples in air typically lead to cyanide [16,17] and diatomic carbon spectra [18]. For these reasons, it is important to have an accurate method of computing molecular spectra. The presented work includes spectra of AlO, C₂, CN, and TiO. In part due to the extensively tested predictions by laser–plasma experiments, the tools for computation and analysis of spectra from these species and for selected transitions are presented here.

There are several programs and codes that allow one to predict molecular spectra by utilizing standard molecular constants. These programs include, to name a few, NEQAIR [19], SPECAIR [20], and

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LIFBASE [21]. The application of NEQAIR has been previously discussed [22], to allow one to predict and fit multi-species non-equilibrium air radiation measurements. Equally, the programs SPECAIR and LIFBASE focus on various aspects of computing molecular spectra. For analysis of superposition spectra of hydrogen Balmer series hydrogen-beta and hydrogen-gamma lines [23], our C_2 line strength data are preferred after the computed spectra were compared [23] with the ones obtained by use of SPECAIR. Our C_2 carbon Swan line strength data nicely agree with recently published work [24]. Predictions with the LIFBASE software, which includes provisions for CN, appear to be less useful for temperatures that are on the order of 6000 to 8000 K. In turn, the measured CN spectra are predicted well with our accurate line strength data [25,26] for the $^{12}C^{14}N$ diatomic molecule, yet other isotopologues $^{13}C^{14}N$ and $^{12}C^{15}N$ are of interest in LIBS [27] and also in astrophysics [28]. It is important to precisely predict wavelength positions and rotational Hönl–London factors, together with accurate electronic transition moments that include so-called r-centroids. In our work, we find that the modeling of atomic and molecular superposition spectra, encountered for example in LIBS studies of expanding methane, strongly relies on availability of a reliable molecular data base. In molecular emission spectroscopy the determination of rotational temperature, T_r , is of interest to possibly infer gas temperature due to rapid equilibration of rotational distributions, and independently, the vibrational temperature, T_v . It is not unusual that molecular OES shows by a factor of 10 differences in rotational and vibrational temperatures [29]. Yet in LIBS applications using 1 to 10 ns pulsed laser radiation, one frequently finds equal temperatures, T , or $T = T_r = T_v$, in the analysis of line-of-sight recorded spectra. It is noteworthy that the presented line strength data and associated programs to accomplish prediction of molecular spectra are also applicable to laser-induced fluorescence work and/or can be extended to the study of spectra from different isotope compositions such as for instance $^{12}C_2$, $^{12}C^{13}C$, or $^{13}C_2$ diatomic carbon spectra.

2. Computation of spectra

Molecular spectra are computed from line strength tables that are established for diatomic molecules, particularly for selected electronic transitions that have been the focus of extensive study. The most accurate available experimental data for the line positions are employed to determine the number and numerical values of parameters for the upper and lower transition levels. These parameters allow one to predict the positions, ν_{ul} , of the spectral lines. The spectral lines are subsequently utilized to calculate the so-called Hönl–London [30] factors $S_{ul}(J', J)$. The product of the Hönl–London factor and of the electronic–vibrational transition moments, composed of Frank–Condon

Table 1

Glossary of variables. It is customary in spectroscopy to use cgs units.

Variable	Description	Units
$S_{ul}^{(report)}$	Line strength/ $(e_{esu}a_0)^2$	
S_{ul}	Line strength	stat 2 cm 2
A_{ul}	Transition probability	s $^{-1}$
N_u	Number of radiators	cm $^{-3}$
g_u	Excited state degeneracy	
Q	Partition function	
N_0	Number of molecules	cm $^{-3}$
I_{ul}	Radiated energy	erg s $^{-1}$ cm $^{-3}$
$J_{ul}^{(meas)}$	Measured intensity	Counts
C_0	Calibration constant	Counts/(erg s $^{-1}$ cm $^{-3}$)
ν_{ul}	Transition frequency	s $^{-1}$
$\tilde{\nu}_{ul}$	Transition wavenumber, $\tilde{\nu}_{ul} = \nu_{ul}/c$	cm $^{-1}$
$\tilde{\nu}$	Wavenumber	cm $^{-1}$
$\delta\tilde{\nu}$	Wavenumber resolution	cm $^{-1}$
F_u, F_l	Term values	cm $^{-1}$
λ_{ul}	Transition wavelength	nm
λ	Wavelength	nm
$\delta\lambda$	Spectral resolution, $\delta\lambda = \lambda^2 \delta\tilde{\nu}$	nm
$\Delta\lambda$	Wavelength bin width	nm
c	Speed of light	cm s $^{-1}$
h	Planck constant	erg s
k_B	Boltzmann constant	erg K $^{-1}$
T	Temperature	K
G_λ	Line shape function	
σ	Gaussian standard deviation	nm

factors and electronic transition moments that contain r-centroids, is called the diatomic line strength. Non-vanishing Hönl–London factors serve as an indication of allowed molecular transitions. The calculation of diatomic line strengths is accomplished by utilizing a complete set of basis functions, i.e., Hund's case *a* basis, and it involves the steps:

1. Evaluate accurate line positions;
2. Determine the Hönl–London factors;
3. Compute the Frank–Condon factors with the vibrational eigenfunctions determined for the potential functions;
4. Expand the electronic transition moments using r-centroids;
5. Finally, form the product of Hönl–London, Frank–Condon, and of electronic transition moment factors.

In practice, accurate line positions are found by determining molecular parameters from high-resolution, measured spectra. This is accomplished by starting with trial values for each of the molecular parameters, diagonalizing upper and lower Hamiltonian matrices, evaluating the Hönl–London factors (here, for 1-photon transitions), and then iteratively finding improved molecular parameters to match

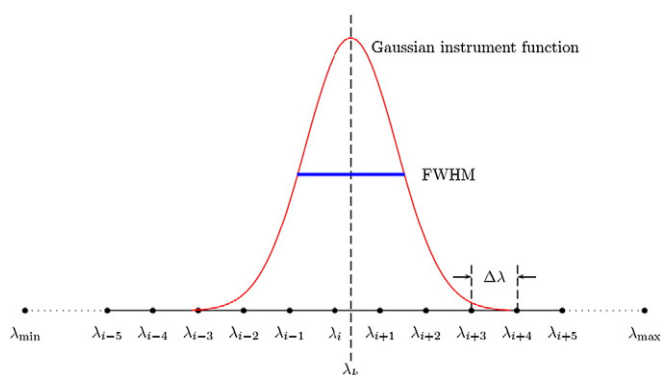


Fig. 1. Contributions of each spectral line to various wavelength bins.

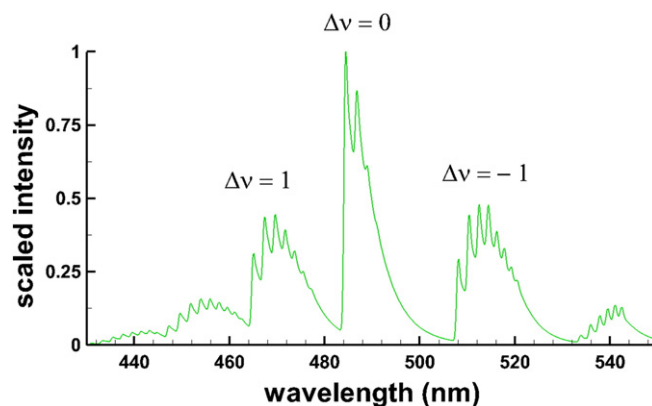


Fig. 2. AIO $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ band spectrum, $T = 4000$ K, spectral resolution $\delta\lambda = 0.8$ nm [37].

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