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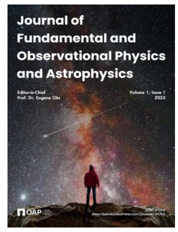

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Personal Retrospective on the Laser-Induced Breakdown Spectroscopy (LIBS)

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Abstract The interests in laser-induced breakdown spectroscopy, LIBS, comprise the spatio-temporal formation and evolution of the optical breakdown kernel, the fluid dynamic expansion, and of course experiments' diagnoses of measured atomic and molecular species signatures. Moreover, fundamental research aspects include line-shape analysis and the computation and prediction of atomic and molecular spectra.

Keywords laser induced breakdown spectroscopy, atomic and molecular spectroscopy; analytical chemistry; astrophysics

1. Introduction

The topics, laser plasma and laser-induced breakdown spectroscopy and atomic-molecular- optical physics, are contents of a volley of selected books [1–13]. The physics activities and works by the author CGP lead to the inclusion in the most recent August 2024 Stanford University career list of World's Top 2% Scientists [14].

This communication summarizes research on the subject of laser-induced transient micro- plasma diagnoses and selected publications during the years 2018 to 2025. Time-resolved spectroscopy elucidates plasma dynamics and species distributions that are generally of value in analytical chemistry. Aspects of electron density, atomic and molecular distributions are contents of the summarized work. Applications extend from analyses of laboratory to stellar plasma. Of particular interest is the spectroscopy of the hydrogen Balmer series and several diatomic molecules. In most of the publications, nominal nanosecond radiation from table-top laser devices is employed for generation of the micro-plasma, and spatio-temporal experimental methods capture phenomena that occur at well-above hypersonic, supersonic, and subsonic plasma and gas expansion speeds.

2. Research Focus

The research focus is on recent 2018 to 2025 investigations [15–17] that were primarily conducted [18] at the Center for

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Laser Applications at The University of Tennessee Space Institute. However, a few selected publications with international collaborators are also included. The author, Dr. Christian G Parigger, has been engaged in laser plasma research at The University of Tennessee from 1987 to 2023, and subsequently, at CGP Consulting, LLC, from 2023 to 2025 [17]. Recent publications in Multidisciplinary Digital Publishing Institute (MDPI) journals Atoms, Molecules, Foundations and Symmetry encompass various research aspects. During the 2018-2023 period of time, twenty-one MDPI articles referenced in this summary reflect scientific open-access peer-reviewed engagements. Various conference contributions including in the Journal of Physics: Conference Series further portray recent re- search associated with the biannual and well-established International Conferences on Spectral Line Shapes (ICSLS). The transition from previous archived journals such as Applied Optics, Optics Letters, Spectrochimica Acta Part A and/or Part B and Journal of Quantitative Spectroscopy and Radiative Transfer to peer reviewed open access journals is in accord with world-wide transition to open-access viz. access-for-everyone. In addition, the moderated Cornell University https://arxiv.org and MDPI https://www.preprints.org preprint servers convey aspects of research as well. And, of course, the Auburn University electronic International Review of Atomic and Molecular Physics (IRAMP) journal https://www.auburn.edu/cosam/departments/phyiscs/iramp/index.htm communicates peer reviewed research activities.

3. Research Summary Works

Three fundamental works in 2020 and 2024 comprise a book chapter [15] on molecular laser-induced breakdown spectroscopy and e-books on Diatomic Spectroscopy [16, 17]. The former communicates molecular spectroscopy and applications to plasma-, combustion-, astro-physics- analyses. Primary interests include plasma in gases; however, the book chapter [15] includes laser ablation, including co-authors' work on laser-ablation molecular isotopic spectrometry (LAMIS). Diatomic molecules include cyanide (CN), aluminum monoxide (AlO), titanium monoxide (TiO), Swan bands of C2, and the hydroxyl radical (OH). Aspects of spherical aberrations from focusing with a single lens are elaborated, and Abel inversion techniques are discussed for determination of spatial molecular distribution. The latter derives diatomic spectroscopy transition strengths [16] employing the Wigner- Witmer diatomic eigenfunction. The diatomic line strength is composed of electronic-, vibrational-, and rotational- transition terms including Franck-Condon, H¨onl-London and r-centroid factors. The second edition of the e-book on Diatomic Spectroscopy [17], published in 2024, shows ten additional chapters, one on fundamentals and nine on applications. Appendices communicate programs for computation of molecular spectra and for Abel in- version. Comparisons are included of predictions of molecular spectra when including other databases. In addition, the second edition discusses the connections of shadow graphs and of measured emission spectra.

4. Laser-Plasma Spatio-Temporal Expansion

The generation of an optical spark requires sufficient peak irradiance usually achieved with pulsed, coherent radiation with appropriate optical focusing [19–21]. Expansion dynamics at hypersonic, supersonic, and subsonic are usually measured by taking shadow graphs and spatio-temporal spectroscopy [19–27]. At or near optical breakdown threshold in gases, single or multiple optical breakdown beads are measured due to spherical aberration of a single focusing lens. Subsequently, absorption of the remaining pulse causes expansion that appears initially similar to opening an umbrella. However, for typically one to ten microsecond after the optical pulse, the shadow graphs appear almost spherically symmetric. For time delays of the order of one to several hundred microsecond, the breakdown kernel evolves towards the laser device, or the tip of the mentioned umbrella snaps towards its handle, and vortices appear in the shadow graphs.

5. Atomic and Molecular Spectroscopy

Hydrogen and selected diatomic emission spectroscopy include analysis of laboratory and stellar astrophysical plasma, e.g., from white dwarfs [28–33]. These works include self- absorption assessments. Fundamental aspects of diatomic molecular spectroscopy [34] lead to consistent data analyses without invoking the concept of reversed angular momentum - programs Nelder-Mead temperature (NMT) and Boltzmann Equilibrium Spectra Program (BESP) are freely available [35] as clear-text scripts with data files. Plasma diagnosis is elaborated with selected diatomic molecules including comparisons of the published data base with other readily available data bases for OH, CN, C2, AlO [35–41]. In addition, the collaboration with University of Prayagraj (formerly Allahabad), India, on meteorite and gypsum laser-induced breakdown spectroscopy (LIBS) [42, 43] and on medical applications that include gallstone and pointed gourd leaves analyses [44, 45]. Collaborations with The University of Cairo include research on plasma involving silver nano-particles [46–48]. Recent collaborations with the Chemical Research Center in Hungary focus on microwave plasma methylidyne (CH) cavity ring-down spectroscopy [49].

6. Discussion

Both atomic and molecular species can be readily discerned from comparisons of measured and computed atomic line shapes and molecular band appearances. Several of the investigations elucidate experimental spatially- and temporally-resolved LIBS records' analysis details. The molecular emission spectroscopy comparisons requires accurate data bases. The established and well-tested data bases for selected electronic, vibrational and rotational diatomic transitions and the associated analysis programs are now published for applications in LIBS research [35]. The 2018 to 2025 summary shows a research focus in molecular diagnosis with accurate line strengths and with other corresponding data bases [50, 51], including ExoMol [51]. Comparisons of diatomic spectra analysis for selected diatomic bands include carbon Swan and AlO molecules [52, 53].

Future activities in atomic and molecular LIBS certainly should focus on fundamental line shape research of atomic and molecular species. The contributions in the wings of atomic lines, viz. hydrogen, can increase the background in molecular spectra, viz. superposed hydrogen and carbon Swan spectra, and consequently, can lead to systematic errors in the inference of molecular emission temperature. Spectral broadening of individual transitions can affect the analysis of observed spectra., viz. Voigt line shapes for individual lines in a molecular band. Of interest are as well detailed high resolving power spectra of isotopologues for the purpose of predicting accurate molecular spectra of diatomic species, e.g., see chapter seven on Molecular LIBS of the recent book by Singh and Thakur [13]. Generally speaking, LIBS relies on line-of-sight gathering of plasma spectra; however, for spherical and prolate spheroid symmetries, spatially recorded data can be Abel inverted for the extraction of spatial species temperature distributions. Future experimental laboratory arrangement may include significant asymmetric plasma kernels requiring a few simultaneous stereographic measurements for Radon inversion of recorded data. The inversion of the integrated line-of-sight data would yield atomic and molecular data that would correspond to a narrower range of temperature for otherwise optically thin plasma. Consequently, the comparisons of computed and measured spectra within a narrow temperature range will provide fundamental insight in the accuracy of the employed data bases. Applications of LIBS in combustion, environmental, and planetary and space exploration, will benefit from using laboratory, well-tested data bases.

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