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Diagnostics and simulations of molecular formation in laser-induced plasmas

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Abstract

The formation of diatomic molecules or radicals in the cooling phase of laser-induced plasmas is mainly determined by thermodynamic parameters as the local plasma temperature, pressure and particle density. Better understanding of the molecular formation can be used for deeper material analysis and research. We adapted the well-established method reactive force field (ReaxFF) to simulate the formation of molecular bonds in time-resolved LIBS experiments.

Instead of standard quantum mechanical or continuous simulation methods, ReaxFF uses a hybrid form based on the calculation of the bond order. The main advantage is the short computational time of molecular bonds compared to standard approaches. This allows the simulation of molecular formation at fixed temperatures in thermodynamic equilibria as well as temperature ramp simulations to get temperature dependent molecular concentration profiles. Molecular simulations enable the explanation of observed molecular band emission in LIBS experiments, the investigation of molecular interferences with other elements in the sample, and the signal optimization of molecular LIBS experiments. Furthermore, we show that the presented method can be used for a rough molecular temperature estimation of the plasma.

As an application, we simulated the temperature behavior of the formation of calcium oxide (CaO) and compared the results to the law of mass action. Calcium and oxygen are the main constituents in cement, whose analysis is of high economic importance as it is part of concrete infrastructure buildings. LIBS measurements of CaO at different gate delays reveal the dynamic behavior of atomic and molecular emission. Furthermore, multivariate methods can be used for a cement separation on the basis of the molecular emission of CaO at 600.4 nm.

Keywords
Molecular LIBS; Molecular dynamic simulation; ReaxFF

1. Introduction

Temporal resolved observation of native and recombining molecules by laser-induced breakdown spectroscopy (LIBS) enabled a great advantage for the analysis of elements with weak atomic emission [1,2]. In combination with other elements contained in the sample and the surrounding atmosphere diatomic molecules and molecular radicals can be formed during the plasma cooling phase and emit characteristic molecular bands.

Investigation of the formation process of molecules inside the cooling plasma can lead to a proper understanding of the molecular emission and allows an advanced material analysis. This process is mainly determined by thermodynamic parameters as the plasma temperature, ambient pressure and particle density. Many theoretical [3-5] and experimental [6-12] studies on the role of chemical reactions of e.g. CN or AlO reactions in laser induced plasmas have been presented. Various simulation methods and approaches, specified pressure dependencies and cooling rates have been reported. In order to receive an additional insight into dynamical behavior on atomistic scales, we have performed molecular dynamic simulations at fixed temperature equilibria as well as temperature ramp simulations to reveal temperature dependent molecular concentration profiles of CaO. These profiles help to explain the observed molecular band emission, to investigate molecular interferences and interactions with other elements in the sample, and to determine the parameters of LIBS experiments in order to obtain high molecular formation rates. Furthermore, we show that the presented method can be used for a temperature estimation in the plasma cooling phase.

Instead of standard quantum mechanical approaches [13] like ab-initio or density functional theory and continuous methods [5], we use the well-established method reactive force field (ReaxFF), originally presented by Adri van Duin [14]. ReaxFF is a bond-order based hybrid tool for exploring, developing and optimizing material properties [15]. Primary targets of our simulations are confirming the reliability of the temporal-resolved LIBS measurements and identifying possible limitations caused by critical element concentrations, which cannot be easily revealed by the spectroscopic measurements themselves. The simulations aim on a better understanding of molecular dynamic processes and on deriving