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Kinetic modeling study of the laser-induced plasma plume of cyclotrimethylenetrinitramine (RDX) ☆

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Abstract

A kinetic model of a laser-induced breakdown spectroscopy (LIBS) plume of cyclotrimethylenetrinitramine (RDX) was developed for the analysis of processes responsible for the LIBS signature of explosives. Air and argon were considered as buffer gases. The model includes a set of processes involving ion chemistry, as well as excitation, ionization, and other processes affecting neutral and ion species. Modeling results show that the overall reaction process can be considered a two-stage process. The first stage corresponds to a fast approach to a quasi-stationary state, while the second stage corresponds to the change of quasi-stationary species concentrations due to the change in temperature. As a result of the two-stage process, the initial mechanism of explosive decomposition is not important in determining its signature in the LIBS measurement time window (1–30 μs). The main processes responsible for generation of excited states for the LIBS emission are electron-excitation impact processes. A mechanism for the appearance of a double peak of the C_2 species concentration in the RDX plasma plume was suggested. Double-peak behavior of the C_2 species was previously experimentally observed during laser ablation of graphite.
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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an emerging diagnostic method for many applications. A LIBS operates with a high power laser pulse focused on small spot of a sample material. The interaction of the pulsed laser beam with a sample material produces high-temperature ionized plasma containing electronically excited elements which radiate the characteristic emission lines of corresponding elements. It is important to note that the laser energy release time occurs in the femtosecond–nanosecond temporal range. However a plasma kernel with high temperature exists for 10–100 μs, as a result of chemical reactions and recombination processes, releasing energy on the microsecond time scale and sustaining the plasma.

The direct detection of energetic materials and explosives in real time is an important practical problem [1–3]. The LIBS technique is mainly considered to be a method of analytical element analysis. However, the LIBS technique allows one to identify certain chemical compounds with chemometric analysis. Results of recent LIBS studies of energetic materials demonstrate that the simultaneous registration O, N, H and C_2 signals [1–3] and analysis of the ratios of peak intensities allows one to make definite conclusions on the presence of energetic material.

The aim of the present work was to develop a kinetic model of the LIBS plume of RDX for the analysis of processes responsible for the RDX LIBS signature. RDX (1,3,5-trinitrohexahydro-s-triazine) is an explosive nitroamine widely used in military and

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industrial applications. It is considered one of the most powerful military explosives. The developed model includes processes of formation and quenching of excited H, N and O atoms, and a submodel for formation of the C_2 molecule. The observation of LIBS C_2 signals was used to discriminate organic samples from inorganic targets during detection of energetic materials [2]. Together with peak ratios, the data on C_2 emission was used for the detection of a number of explosive materials. In future studies, we plan to reduce suitably the developed model for detailed CFD modeling studies of RDX LIBS plume. The results of the present kinetic modeling suggest that the assembled model can be used for understanding the reaction behavior in the LIBS plume of other C/H/N/O-containing explosive materials.

2. Kinetic model

As the first step in the analysis of processes responsible for the emission lines in the plasma plume of explosives, a kinetic model of RDX reaction behavior in the LIBS plume was developed. Air and argon were considered as buffer gases. Earlier we developed a kinetic model of lead reactions in air and argon [4,5] to describe the chemical reactions and collisional processes that occur within the high-temperature mixture in the LIBS plume. These processes were included as a part of the current model. The model includes a set of processes involving ion chemistry, as well as excitation, ionization, and other processes affecting neutral and ion species.

The kinetic model of RDX reactions in the plume includes the following main reaction subsets: RDX decomposition reactions, high-temperature air and argon plasma reactions of neutral species, reactions of ionization and reactions of charged species (e−, H^+, O^+, O_2^+, N^+, NO^+, N_2^+, H_2^+, OH^+, H_2O^+, O_2^-, O^-, C^+, CO^+, CO_2^+, CH_3^+, CH_4^+, CH^+, CH_2^+, $C_2H_3^+$, $C_2H_2^+$, N_4^+, $N_2O_2^+$, N_3O^+, N_2O^+, N_3^+, NO_2^+, NO_3^+, NO^-, N_2O^-, NO_2^-, NO_3^-), reactions generating the electronically excited atoms N, O, and H and their reactions in the plasma plume. Table 1 contains the electronic states of atomic N, O, and H included in the model. For example, the following excited states of the oxygen atom were included in the kinetic model: ground state $O(^3P)$, two metastable states $O(^1D)$ and $O(^1S)$ and excited states 3s ^5S, 3s ^3S, 3p ^5P, and 3p ^3P, which participate in the 777 nm and 844 nm O atom transitions.

Table 1
States of atomic nitrogen, hydrogen and oxygen included in the kinetic model

Atom	Level	Energy, cm^{-1}	Emission line, nm
N	$2p^3\ ^4S^0$	0	(L)520,347,120,113.4
N*2	$2p^3\ ^2D^0$	19,226	(U)520,(L)149
N*3	$2p^3\ ^2P^0$	28,839	(U)347,(L)175
N*4	$2p^23s\ ^4P$	83,337	(U)120,(L)(870),(821),747,742
N*5	$2p^23s\ ^2P$	86,192	(U)149,175,(L)135,947,(940),742.861
N*6	$2s^22p^4\ ^4P$	88,134	(U)113
N*7	$2p^23p\ ^2S^0$	93,582	(L) 947,939,(857–866)
N*8	$2p^23p\ ^4D^0$	94,839	(U)(868–874)
N*9	$2p^23p\ ^4P^0$	95,511	(U)821
N*10	$2p^23p\ ^4S^0$	96,752	(U)745,947
N*11	$2p^23p\ ^2D^0$	96,834	(U)740.9,939.5
N*12	$2p^23p\ ^2P^0$	97,793	(U)861
O	$2p^4\ ^3P$	0	
O*2	$2p^4\ ^1D$	15,865	
O*3	$2p^4\ ^1S$	33,795	
O*4	$3s\ ^5S^0$	73,769	(L)777
O*5	$3s\ ^3S^0$	76,794	(L)844
O*6	$3p\ ^5P$	86,626	(U)777
O*7	$3p\ ^3P$	88,642	(U)844
O*8	$4s\ ^5S^0$	95,498	
H	*n=1*	0	(L)102.5, 121.6
H*2	*n=2*	82,259	(L)656,(U)102.5
H*3	*n=3*	97,492	(U)121.6, 656

Table 2
Kinetic models of RDX decomposition used in this work

Kinetic model	Model details
Gas-phase decomposition model	Model of initial RDX decomposition of Chakraborthy et al. [8]
Initial gas composition on the surface from RDX decomposition and detailed gas-phase model of this work	Decomposition products at the surface, experimental data of Fetherolf and Litzinger [11]
Two overall subsurface reactions and gas-phase mechanism of this work	Subsurface decomposition model from [12]
Overall reaction of decomposition and detailed mechanism of this work	Overall decomposition reaction from [10]

Thus the model includes the following reaction subsets:

1. Initial decomposition reactions of RDX (or explosive products at the surface of target material)
2. High-temperature reactions of products of explosive decomposition in the buffer gas under the LIBS conditions (buffer gas: Ar or air).
3. Reactions of excited states species responsible for the LIBS signature, including the generation and quenching of excited states (O, H, N) and the subset of reactions of excited species with the decomposition products of RDX and with buffer gas species.

The kinetic model was assembled from several sources. Main sources of data are identified below. When absent, kinetic data were estimated based on analogy or with the use of empirical rules. The kinetic model contains overall 137 species, with 577 reactions. To describe RDX decomposition, several mechanisms were used [6–10] (Table 2). A plasma kinetic model for the H/N/O/Ar system was taken from our previous work [4,5]. Plasma chemistry reactions related to the C/H/O/N system came from several sources [13–15]. Reactions involving the C_2 species were added on the basis of the results of Kruse and Ross [16,17]. Kinetic data for electronically excited O, H and N atoms (electron-impact excitation cross sections, radiative quenching rates, etc) were taken from [18−21]. Table 3 contains the block of reactions describing the kinetics of C_2 formation and consumption, and a block of ion reactions involving carbon-containing species. The kinetic submodel describing the formation and decay of electronically excited H, N and O atoms will be presented in a separate publication. Note that the kinetic model doesn't currently include excited C atom states. The excited states of carbon atom will be considered in a future work.

Of course, at these high temperatures, a large number of rate constant values was obtained by extrapolation from rate