

LASER-SUPPORTED IGNITION, COMBUSTION AND GASIFICATION OF AP-BASED PROPELLANTS

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ABSTRACT

The paper is devoted to the study on the molecular level the chemistry of ignition and combustion of the composite AP-based propellants under laser support, including determination of the products of reactions in the gas and in the condensed phases of propellant and their concentrations as a function of time. The method of the investigation of ignition chemistry of solid propellants has been developed. The molecular beam mass-spectrometry (MBMS) was used for the identification of the products evolving directly from the condensed phase of the propellant during the ignition and following further combustion as function of time of laser acting. The initial distance between the orifice of the probe and the surface of propellant was equal to 2 or 0.1 mm. Earlier the MBMS method was successfully used for investigation of the chemical structure of the flame of solid propellants based on AP, HMX, RDX and other ingredients. The method of microthermocouples was used for the measurements of the temperature of the gas near the surface of the propellant. The composite pseudopropellants AP/HTPB and AP/PMMA were chosen as an object of the research. The ignition of the solid propellant and its transition to the combustion under CO₂ - laser radiation was investigated at 0.1 MPa of argon. The key species of solid propellant gasification during its ignition and combustion were determined. Besides, the dependencies of mass peak intensities of gasification products on time during and after propellant ignition were determined. The data on propellant gasification during the ignition with simultaneous measurement of temperature of gas phase near the burning surface were obtained in some experiments. Obtained data will be useful for the modeling of ignition process and its transition to the combustion on the molecular level. Described experimental technique can be used for ignition chemistry study of other energetic materials (EM).

Key Word: ignition, combustion, laser, composite propellant, AP, HTPB

NOMENCLATURE

Pa	= pressure in Pascal
wt	= weight
s	= second
m/e	= ratio mass ion to him charge
L	= distance from the burning surface
mm	= millimeter
P	= pressure
W	= watt
cm	= centimeter
°C	= degree Celsius
³⁵ Cl, ³⁷ Cl	= isotopes of the chlorine atom
μm	= micron
ar.un.	= arbitrary unit
kg	= kilogram
t	= time
ntp	= normal temperature and pressure
T	= temperature

INTRODUCTION

Ignition of solid propellants involves a number of physiochemical processes and has been subject of many investigations. Many theoretical models have been developed to study the ignition of solid propellants and explosives. They can be divided into three groups: solid phase, heterogeneous, and gas-phase reaction models. Laser irradiation is widely used for study of ignition and combustion of solid propellants and explosives¹⁻⁴. The recent paper¹ is devoted to a comprehensive analysis of laser-induced ignition of RDX monopropellant. The paper¹ attempts to establish a general framework for study of the key physiochemical processes involved in the laser-induced ignition and combustion of RDX monopropellant. Detailed chemical kinetics and transport phenomena in the gas-phase region, as well as thermal decomposition reactions have been included in model. Generally, the main experimentally measured characteristics of laser-induced ignition are ignition delay and surface temperature of solid propellant as a function of heat flow. However, there are no experimental data except paper^{5,6} on the gasification products and species concentrations near the propellant surface as a function of time. But they are necessary for understanding of the mechanism of solid propellant ignition and its transition to the combustion on a molecular level and for development of the comprehensive ignition and combustion models. Earlier for study of flame structure at self-sustained⁷⁻¹⁴ and laser supported^{5,6,15} combustion of solid propellants the molecular beam mass spectrometry (MBMS)⁷⁻¹¹ and microprobe technique^{5,6,9,12-15} were successfully applied. The objective of present work is to extend method (MBMS) for study of the laser-induced ignition of solid propellants and its transition into the combustion.

EXPERIMENTAL

The investigation of laser-induced ignition of solid rocket propellants was conducted using molecular beam mass spectrometry (MBMS), microthermocouple techniques and video recording. The scheme of set-up is presented in Fig. 1. Earlier this set-up was successfully used for study of flame structure of solid propellants^{7,8,10,11} and their thermal decomposition at high heating rates⁸. The ignition of solid propellant is a fast process. The characteristic time of ignition can vary from 0.01 to several seconds. In this work the ignition of ammonium perchlorate NH₄ClO₄ (AP)-based not cured solid propellants was studied., Hydroxyl-terminated

polybutadiene HO-[-C₄H₆-]_n-OH (HTPB) and polymethylmethacrylate [-CH₂C(CH₃)(CO₂CH₃)-]_n (PMMA) were used as a fuel. In previous our experiments rich and stoichiometric compositions of HTPB/AP propellants were used for flame structure study using microprobe technique¹²⁻¹⁴. For these experiments the propellants with minimal amount of fuel (3.5 wt% HTPB and 4.5 wt% PMMA) were chosen. They provide self-sustained steady-state combustion at pressure of 0.1 MPa and initial temperature of 20°C. AP/HTPB propellant mixtures were prepared by mixing of ~ 2 g of AP powder (with particle size of ~ 20-30 μm) with HTPB in short glass vessel during 5 minutes and then - in jasper mortar during 20 minutes. Specific density of propellant strands was 1.52 g/cm³. Side surface of propellant strand was covered by solution of linoleum. AP was mixed with PMMA (particle size of PMMA was ~ 3-7 μm) in jasper mortar during 20 minutes. Propellant strands were produced by pressing of propellant mixture. Specific density of these strands was 1.83 g/cm³. For measurement of the burning rate at self-sustained combustion of these propellants they were placed in pyrex glass tube with diameter of 4 mm and wall thickness of 0.9 mm. The burning rate at *ntp* was

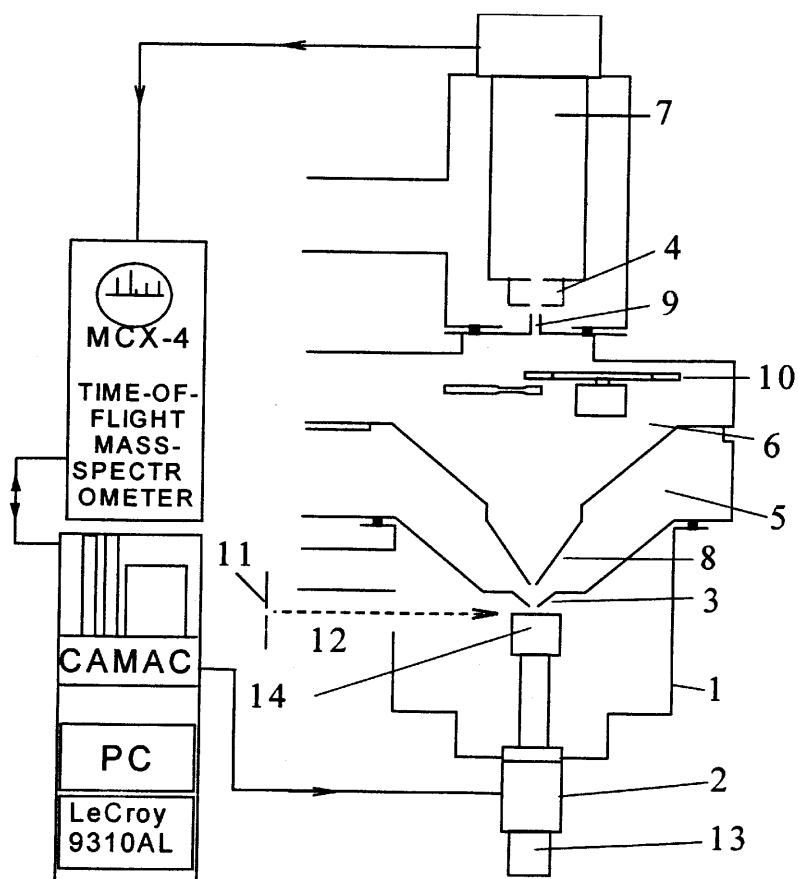


Figure 1. Molecular beam mass spectrometric set-up for study the laser-induced ignition and combustion of solid propellant: 1) combustion chamber; 2) scanning system; 3) heated quartz probe; 4) ion source; 5) skimmer chamber; 6) collimator chamber, 7) drift tube, 8) skimmer 9) collimator; 10) slotted disk; 11) chopper; 12) laser beam; 13) stepper motor; 14) propellant strand.

equal to 0.58 mm/s for HTPB based propellant and 0.38 mm/s for that based on PMMA. The gasification products from the strand surface were sampled continuously using heated probe with diameter of sampling orifice of 0.04 mm. Diameter of the tip of the probe was equal to 3 mm. Internal opening angle of the probe was equal to 50°. Heater for the probe was produced from nichrome wire with diameter of 0.2 mm. Time of heating-up of the probe to temperature of 500° C was ~ 30 s. Temperature of surface of the face plane of the probe was controlled in preliminary experiments using 20 μm Pt/PtRh thermocouple. Contact between the junction of thermocouple and the face plane of the probe was maintained by a spring. The maximal frequency of measurement of peak intensities of gaseous products was 25 Hz. The data acquisition system on

the basis of apparatus CAMAC was used in this investigation. It allows to measure intensities of 10 selected mass peaks in mass spectrum as a function of time. The whole mass-spectrum of ignition products over the range from $m/e = 30$ to $m/e = 91$ was measured using digital memory oscilloscope LeCroy 9310AL. Application of molecular beam mass spectrometry on the basis of time-of-flight mass spectrometer (MSCh-4) provides correct sampling of species evolved from surface of the propellant strand and fast method of their detecting during the laser-induced ignition.

The strands were ignited using CO₂-laser (APOLLO LASER, Model 500) with power of 12 W. The laser alignment provided the hit of laser beam on the burning surface at angle of $\sim 60^\circ$ or $\sim 78^\circ$ to the surface normal. The region under the probe near the sampling orifice with area of diameter ~ 3 mm was irradiated. Heat flux on a propellant surface was equal to 36 or 12 W/cm² taking into account an angle of inclination of beam to a propellant surface. The place of a hit of a laser beam was controlled before every experiment. The ignition was monitored using video camera Panasonic-M3000. One of two variants of scheme of experiment is shown in Fig. 2. A filament heater was located at the external side of the tip of the probe. It provides the warming-up of the tip of the probe to the temperature close to that of the propellant burning surface. It was necessary to prevent clogging of the sampling orifice by the products of AP sublimation, that formed during laser heating of the strand surface. During the warming-up of the probe, the minimal distance between tip of the probe and the strand surface was equal to ~ 2 mm.

The temperature of the tip of the probe during the experiment was $\sim 500^\circ\text{C}$.

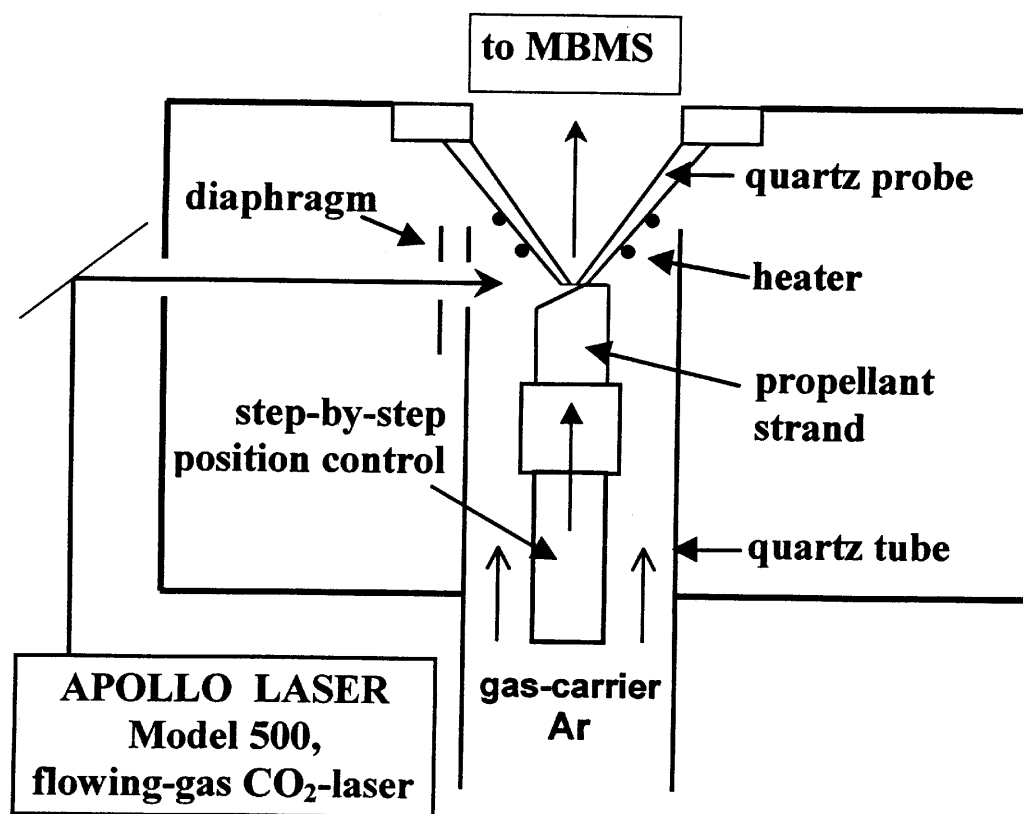


Figure 2. Part of experimental set-up for study laser-induced ignition and combustion of solid propellant.

Temperature of the burning surface of propellants investigated is close to 500°C . Therefore the probe was heated to the temperature $\sim 500^\circ\text{C}$ in order to minimize thermal influence of the probe on propellant surface and on gasification products before inflammation. During the expansion of sampled gas in the probe, fast freezing of reactions occurs. Besides, skimmer cuts out central part of gas jet formed by the probe, which is free from possible catalytic reactions on the walls of the probe. Truncated cylindrical strands of special form with height of 4-5 mm and diameter of 5 mm were prepared and used. Side surface of the strands was not coated. The part of the strand top was truncated at angle of 30° or 12° to the ground surface as it is shown in Fig. 2. The strand was placed on the holder of the rod of step-by-step motor of the scanning mechanism in a

flow tube with diameter of 16.5 mm. The spring was located between the holder and the rod to prevent possible destruction of the probe. The flow of argon in a tube was $41 \text{ cm}^3/\text{s}$ (*ntp*). The velocity of argon along the strand side surface was equal to $\sim 20 \text{ cm/s}$. After warming-up of the probe the strand was rapidly ($t \sim 1.0 \text{ s}$) moved to the probe and automatically stopped at the distance of 0.1-0.3 mm from the tip of the probe. Then shutter of laser beam was opened and surface of the strand began to be heated up under the laser irradiation. The mass-peak intensities of products of ignition sampled by the probe were measured as function of time. After ignition the burning surface of strand moved from the probe with the burning rate. Then after short time (1-2 s) the strand was moved to the probe with velocity exceeding the burning rate of the propellant on $\sim 1 \text{ mm/s}$ until burning surface contacted with the probe. This allowed to investigate the propellant flame structure (the profiles of mass peak intensities of species in flame zone). In some experiments the temperature of gasification products evolving from the surface was measured using ribbon Pt-Pt(10%Rh) thermocouple of 6 micron thickness simultaneously with the measurement of profiles of mass peak intensities. The time response of thermocouple was 4 ms according to our estimations. The thermocouple was located at the distance of 0.25 mm from the strand surface. In this case the strand was placed at the distance of 2 mm from the cold probe, and laser beam fell to the strand surface at angle of 60° to the strand surface normal. Heat flux on propellant surface was equal to 36 W/cm^2 .

RESULTS AND DISCUSSION

Fig. 3 represents time dependencies of temperature of gas near the propellant surface and peak intensities of mass with $m/e = 36$ and $m/e = 32$ during the laser-induced ignition and combustion. In this case the strand surface was located at the distance of 2 mm from the tip of the probe and the thermocouple – near the propellant surface. Fig. 3 shows that the time of propellant ignition (the time from beginning of the heating to abrupt growth of the temperature) is about $\sim 1.5 \text{ s}$. There are two regions on the temperature curve attributed to the propellant ignition: 1) growth of the temperature near the surface from 20°C to $\sim 400^\circ\text{C}$ for about 1.5 s; 2) increase of the rate of temperature growth from $\sim 400^\circ\text{C}$ to $\sim 1500^\circ\text{C}$ for about 0.1 s. In these experiments measurement of intensity of only selected mass peaks was conducted

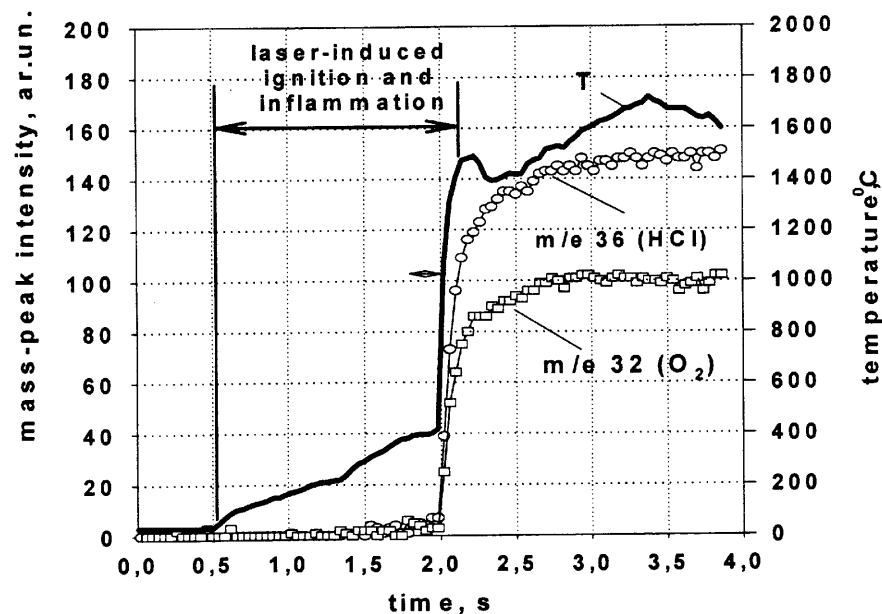


Figure 3. Time dependence of temperature near the propellant surface and mass peak intensities at distance of 2 mm from the propellant surface during laser-induced ignition and combustion of AP/HTPB (96.5/3.5) propellant at 0.1 MPa.

Time dependence of temperature, measured by thermocouple in the zone 1, characterizes growth of propellant surface temperature during its heating by laser irradiation because the junction of thermocouple was located near the propellant surface. An inflammation (zone 2) occurs at the certain critical value of surface temperature. In zone 2 an abrupt increase of intensities of mass peaks with $m/e=36$ (HCl) and $m/e=32$ (O_2) is observed. Intensities of these peaks are proportional to concentrations of HCl and O_2 –

products of gasification and final combustion products. Due to this we also can not distinguish in Fig.3 HCl and O₂, formed during the propellant gasification, from these products formed during the combustion of HClO₄ in flame of propellant. As the probe was not heated and was located at the distance more than width of the flame zone the key species of gasification of AP-based propellant HClO₄, and NH₃ was not detected in this experiment. Similar behavior of temperature and peak intensity of mass with m/e=36 and 32 was observed also for propellant with PMMA. The inflammation takes place as in the case of propellant with HTPB after 1.5 s at temperature of 400°C. Besides the growth of mass peak with m/e = 41 was observed before ignition. This mass peak is connected probably with ion CH₂=C-CH₃⁺. This ion is fragmentary one formed from molecular ion of methylmethacrylate (MMA). The latter is product of PMMA destruction. The abrupt decrease of this peak during the inflammation was observed.

The time dependence of mass peak intensities obtained by probe located near the propellant surface during

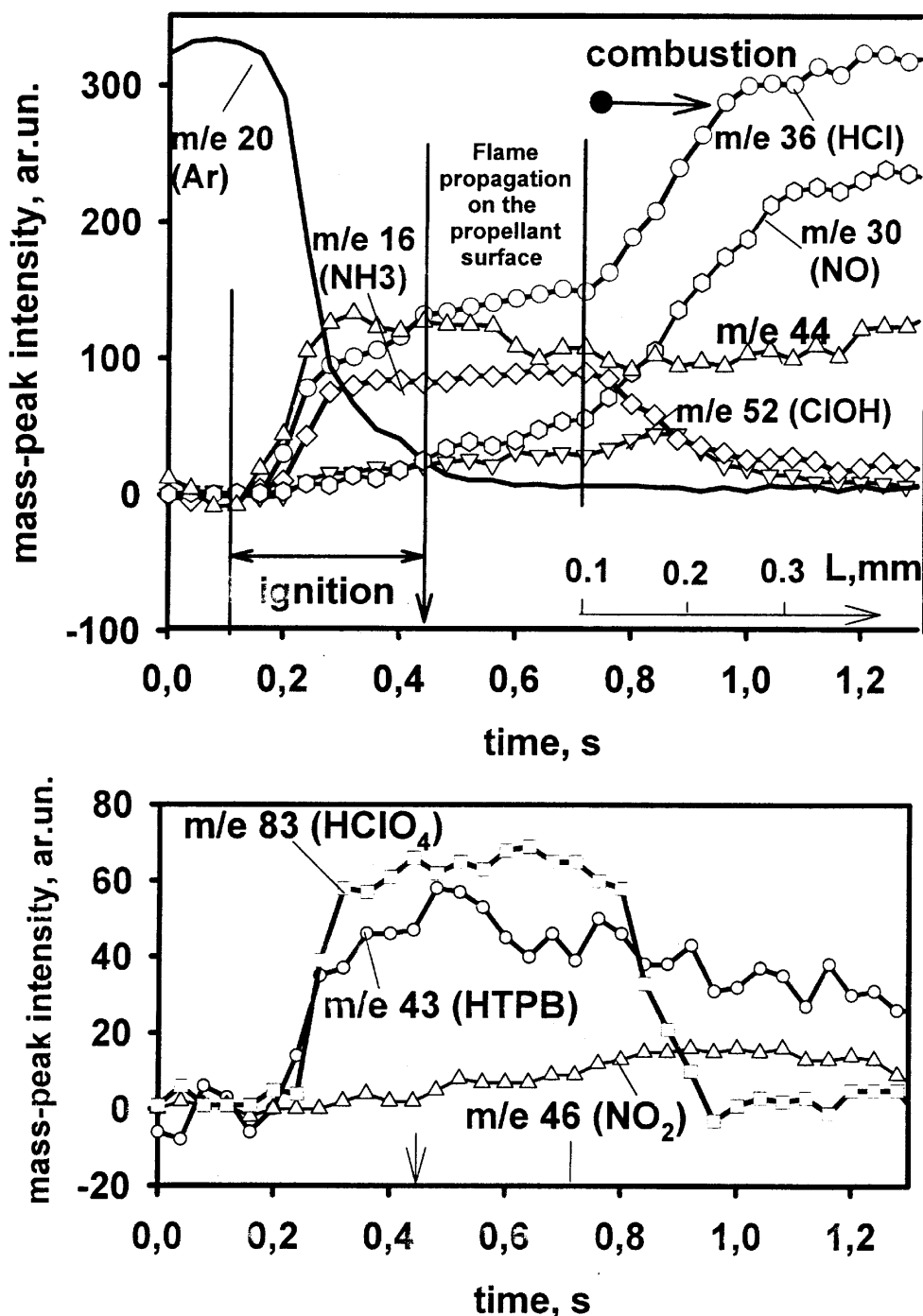


Figure 4. Time dependence of mass peak intensities obtained by probe located near the propellant surface during the laser-induced ignition and combustion of AP/HTPB (96.5/3.5) propellant at 0.1 MPa.

the laser-induced ignition and combustion of AP/HTPB (96.5/3.5) propellant at 0.1 MPa is shown in Fig. 4. Heat flux was equal to 12 W/cm². The distance between the tip of the probe and the strand surface was equal to 0.1 mm, and the temperature of the tip of the probe was 500°C. The mass peaks 83 (HClO₄), 46 (NO₂), 36 (HCl), 52 (ClOH), 16 (NH₃), 20 (Ar), 30 (NO, N₂O, NO₂), 44 (N₂O, CO₂), 43 -were detected. Mass peak 43 is connected probably with HTPB decomposition products. In other experiments mass peaks: 32(O₂), 67(ClO₂), 70(Cl₂) have been measured too. Above mass peaks except mass 43 were detected and identified earlier in flame zone of AP and AP/PMMA by MBMS¹⁰. Video recording showed that behavior of intensity of the peaks from 0,45 to 0,75 s corresponds to the flame propagation along the strand surface. Subsequent decrease of intensities of mass peaks 16, 52, 43, 83 relates to moving of burning surface of strand from the probe with rate equal to the burning rate of propellant. In this connection the spatial axis in Fig.4 was put to the place corresponding t=0.75 s. The beginning of gasification corresponds to the moment of opening of the laser beam shutter. Mass peaks 16 and 83 correspond to the products of AP sublimation NH₃ and HClO₄, while the mass peaks 44 (N₂O and CO₂) and 43 are connected with products of HTPB decomposition. Other peaks - 36 (HCl), 52 (ClOH), 46 (NO₂), 30 (NO, N₂O, NO₂) correspond to the products of AP decomposition in the condensed phase. Intensity of mass peak 30 (NO, N₂O, NO₂) is close to that of mass peak 36 (HCl) in combustion products. Ratio between these peaks well corresponds to the ratio between them in the flame of pure AP⁸. Intensities of mass peaks near the propellant surface at the moments of ignition and the combustion are presented in Table 1. It can be seen that ratios between intensities of mass peaks near the propellant surface at t=0.45 and 0.75 s, which are proportional to the ratios of concentrations of gasification products of propellant at ignition and combustion are close except for NO and NO₂. Their percentage at ignition is less than that at combustion.

Table 1.

Intensities of mass peaks near the surface of AP/HTPB propellant during its ignition and combustion.

Time t, s	Mass peaks (m/e)							
	83 (HClO ₄)	46 (NO ₂)	43 (HTPB)	52 (ClOH)	36 (HCl)	16 (NH ₃)	44 (N ₂ O, CO ₂)	30 (NO)
0.45 (Ignition)	64	3.5	52.5	23	131	82.5	126	29.5
0.75 (Combustion)	62.5	10.5	44.5	31.5	156	87.5	103	64

The overall mass-spectrum of products of laser-induced propellant ignition obtained using digital oscilloscope at a moment t=0.45 s over a mass range from 65 to 105 is shown in Table 2. This moment is shown by arrow on fig.4. Intensities of all peaks are normalized to intensity of mass peak 83.

Table 2.

Intensities of mass peaks near the surface of AP/HTPB propellant during its ignition over a mass range 65-105, obtained using digital oscilloscope LeCroy.

m/e	83	67	100	85	69	102	70	72	95	79
I, %	100	63	44	35	30	21	14	6	13	6

Mass peaks are following: 67 (³⁵ClO₂), 69 (³⁷ClO₂), 70 (³⁵Cl₂), 72 (³⁷Cl₂), 100 (H³⁵ClO₄), 102 (H³⁷ClO₄), 83 (³⁵ClO₃), 85 (³⁷ClO₃), and also 79, 95. The two latter peaks probably correspond to products of HTPB decomposition as they are not connected with products of AP decomposition. Earlier the mass range with these peaks was not investigated because of their low intensities. Our experiments on mass-spectrometric investigation of thermal decomposition of HTPB using method described in⁸ confirmed this assumption. We did not compare data obtained in this work for lean AP/HTPB propellant with data obtained earlier¹²⁻¹⁴, because they relate to stoichiometric and rich propellants.

CONCLUSIONS

Experimental method for investigation of ignition chemistry of EM using CO₂ laser and molecular beam mass spectrometric diagnostics in situ was developed.

It allowed to identify key species evolving from propellant at its ignition and to obtain intensities for main species (which are proportional to their concentrations) near the surface of composite solid propellant based on AP. The detection of significant amount of HClO₄ and NH₃ in products of laser-induced ignition of propellants is the first experimental confirmation of an important role of AP sublimation during the AP based propellant gasification before its inflammation. The ratios between intensities of mass peaks for key species near the propellant surface at ignition and combustion are close. Developed technique can be used for study of laser-supported ignition of other EM and for development and validation of ignition models based on detailed consideration of ignition at molecular level.

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DISCUSSION

Questions/Comments:

Reviewer No. 1

1. The *EXPERIMENTAL* section needs details about the method of preparation and structure of samples, the AP particles dimensions, the form which the binders are employed, methods of mixing and pressing, density of the charges, and so on.
2. Concerning the next section *RESULTS AND DISCUSSION*, a big quantity of oxygen is depicted in Figure 3 but no oxygen is reported in Figure 4. The contradiction between these findings is related in the text to different temperatures of the probe, but no explanation of this strong influence is offered. The product concentrations, as well as temperature, are related to the time axis; to understand the events in flame, the space coordinate should also be used. No chemistry is observed in the text. Comparison of the species presence and distribution with previously obtained steady state burning data is not implemented. The ignition time is not related to data of previous publications for different AP propellants.

Author's Reply:

1. Concerning the *EXPERIMENTAL* section:

AP/HTPB propellant mixtures were prepared by mixing of ~ 2 g of AP powder (with particle size of ~ 20-30 μm) with HTPB in short glass vessel during 5 minutes and then - in jasper mortar during 20 minutes. Specific density of propellant strands was 1.52 g/cm³. Side surface of propellant strand was covered by solution of linoleum. AP was mixed with PMMA (particle size of PMMA was ~ 3-7 μm) in jasper mortar during 20 minutes. Propellant strands were produced by pressing of propellant mixture. Specific density of these strands was 1.83 g/cm³. Heat flux on the propellant surface was 36 or 12 W/cm² taking into account the angle of inclination of the beam with respect to the propellant surface.

2. Concerning the *RESULTS AND DISCUSSION* section:

- We detected oxygen in products formed during ignition and combustion in the experiment, presented in Fig. 3. In the experiment presented in Fig.4, oxygen was not detected because of limited possibilities of measuring apparatus.
- A spatial axis has been added in Fig.4 using video recording. Since the beginning of burning surface regression is seen to correspond to 0.75 s, the spatial axis in Fig.4 begins at $t=0.75$ s.
- We agree that chemistry of ignition is not discussed in details. Combustion chemistry of AP and AP-based propellants were discussed earlier in our papers and confirmed in this paper. It is established that products of gasification of AP are the products of its dissociative sublimation, i.e. NH₃ and HClO₄. Reactions between them and binder gasification products are responsible for main processes in flame. In this paper, the key species of propellant gasification at ignition were identified and were shown to be the same as the key products of gasification in the combustion wave.
- Earlier in literature there were no data on flame structure of AP/HTPB propellant obtained using MBMS. There were data obtained for similar propellants using microprobe technique. Nevertheless our data are in satisfactory qualitative agreement with published data^{9,10,15} on flame structure for AP/HTPB, AP/PMMA and other AP-based propellants, including species detected in flame.
- We did not compare the ignition time of our investigation with previous publications because the experimental conditions and propellant compositions are different.

Questions/Comments:

Reviewer No. 3

1. The authors note that their samples were "unpolymerized," which I take to mean that they were not cured. If my interpretation of their statement is correct, they should address the possible effects of using uncured propellants on their results. Were any anomalous behaviors noticed during burning? Some past work with nitramines and uncured binders using laser heating led to anomalous burning rates due to the presence of voids in the samples.
2. The authors report quite different burning rates for AP/HTPB and AP/PMMA strands. It would be

interesting to include a short statement on the source of this difference, which was a bit surprising since the samples are largely AP. Was it simply due to the weight percent of binder or do chemical differences in HTPB and PMMA play a role?

- 3. The laser hits only a small area of the strand, $1.5 \times 3 \text{ mm}^2$. The authors refer to the use of their data for model development and validation, but the fact that they are only heating a small portion of the surface may make modeling of these experiments problematic.*
- 4. Heating of the tip of the probe to 500°C is required in these experiments to avoid clogging of the probe. However, use of such a high temperature raises concerns about possible reactions occurring inside the probe in the region of the probe tip. How have the authors convinced themselves that this is not a problem?*
- 5. On page 7 the authors note that many of their mass peaks "obviously correspond to products of HTPB decomposition." They make this statement without any justification or references. It would be useful for them to at least give a reference here so that interested readers could understand the source of the mass peaks to which they refer.*

Author's Reply:

- 1. Yes, the strands were not cured. However, we did not observe any anomalous behavior of propellant burning rate.*
- 2. Difference in burning rates for AP/HTPB and AP/PMMA strands is probably connected with difference in gasification mechanism of binder. For HTPB-based propellants heat release in the condensed phase is higher than for PMMA-based propellants, as PMMA decomposes with formation of MMA (volatile product), but HTPB partly decomposes with formation of nonvolatile or low volatile products, which react with AP in condensed phase.*
- 3. Laser beam passed through ellipsoidal orifice ($1.5 \times 3 \text{ mm}^2$), however on the strand surface there was spot with diameter of 3 mm because of incline surface of strand. Yes, we heated only small part of the strand surface, but the probe sampled products from significantly less surface (inside the irradiated surface). Besides burning rate of strand 3 mm in diameter is the same as for strand of 4 mm in diameter.*
- 4. Temperature of the burning surface for propellants investigated is close to 500°C . Therefore the probe was heated to the temperature $\sim 500^\circ\text{C}$ in order to minimize thermal influence of the probe on burning surface and on gasification products before inflammation. During the expansion of sampled gas in the probe, fast freezing of reactions occurs. Besides, skimmer cuts out central part of gas jet formed by the probe, which is free from possible catalytic reactions on the walls of the probe.*
- 5. The decomposition products of AP are very well known to authors, therefore all other peaks (for which these products are not responsible) were believed to relate to decomposition products of HTPB.*