XXXVI INTERNATIONAL CONFERENCE ON INTERACTION OF INTENSE ENERGY FLUXES WITH MATTER
MARCH 1-6, 2021, ELBRUS, KABARDINO-BALKARIA, RUSSIA

LABORATORY OF NONEQUILIBRIUM PROCESSES

INVESTIGATION OF PAHs FORMATION DURING SHOCK WAVE PYROLYSIS OF BENZENE AND DIMETHYL ETHER MIXTURES

A. Drakon, A. Eremin, M. Korshunova[@] and E. Mikheyeva
Joint Institute for High Temperatures RAS
[@] korshunova@labnp-jiht.ru

IIEFM 2021

Abstract

For the first time, the laser-induced fluorescence (LIF) was used to monitor polyaromatic hydrocarbons (PAHs) formed during the pyrolysis of hydrocarbons behind shock waves. The temperature dependencies and time evolution of the total spectral fluorescence signal from growing PAHs were obtained. To control the onset of the appereance of condenced phase, the laser light extinction of HeNe laser at 633 nm was registered. The optical density of investigated mixtures was measured. The mixtures of benzene and dimethyl ether (DME) were studied. It was shown that large PAHs consisting of four or more aromatic rings are the precursors for the appearance of condensed phase, and are probable nuclei of carbon nanoparticles. In a mixture of benzene with DME, more small aromatics consisting of one-two rings and fewer larger PAHs as compared to the pyrolysis of benzene in argon was detected. It was found that the DME presence significantly reduced the optical density of the mixture at 633 nm, which indicated a decrease in the soot yield. Kinetic modeling of PAHs and soot formation under experimental conditions was carried out. The influence of the DME presence on chemical reaction pathways PAHs formation is discussed.

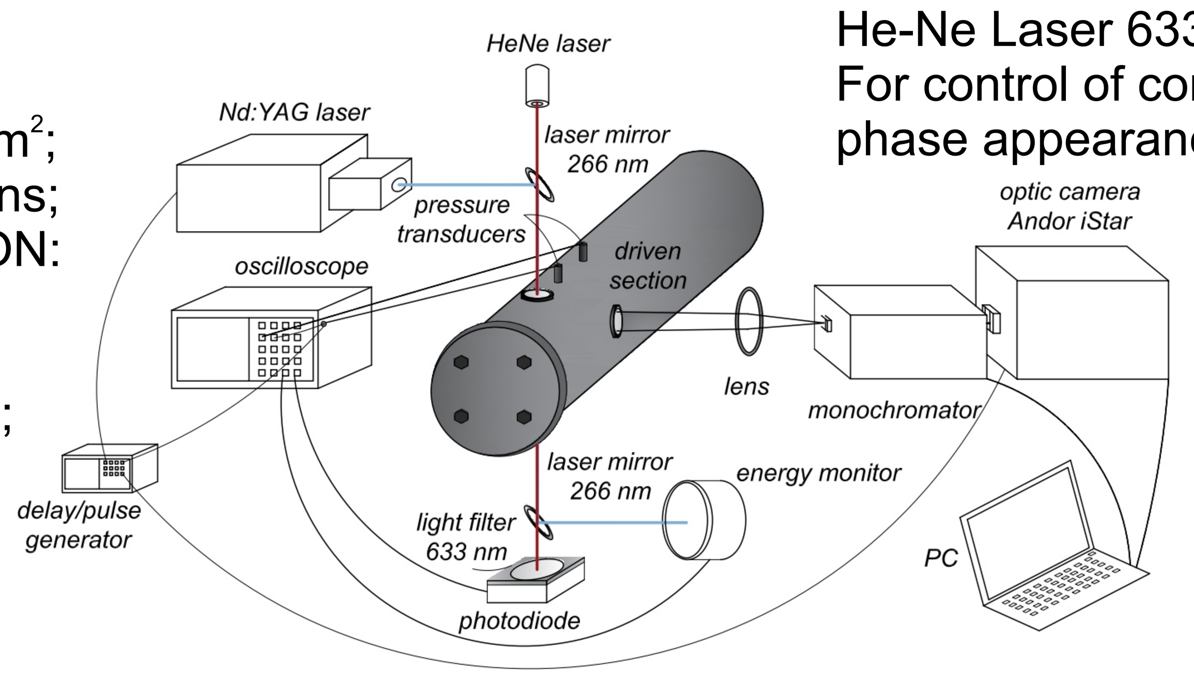
Motivation

PAHs are mainly formed from incomplete combustion processes and generally considered as precursors for soot particles [1, 2]. Precise measuring of PAHs formation and growth is significant for better understanding and developing of soot formation kinetics [3]. At the present time, great attention is paid to the study and development of new types of fuels. Biofuels are a promising trend in this field [4]. DME is a non-carcinogenic and non-toxic substance with a high calorific value, allowing it to be used as a fuel for diesel engines. The presence of oxygen in a compound improves the oxidation efficiency, which is expected to reduce soot emissions. Benzene is the simplest aromatic compound, the pyrolysis of which naturally produces PAHs efficiently. Therefore, the study of DME addition influence on the formation of PAHs during the pyrolysis of benzene seemed to be a highly relevant problem.

Experimental setup

Scheme of the shock tube with LIF and extinction techniques

LIF:
Pulse Nd:YAG laser
266 nm for exitation;
fluence of 25-35 mJ/cm^2;
duration of pulse - 12 ns;
Monochromator ACTON: 300 lines/mm;
ICCD camera iSTAR: explosure time 200 ns;
Calibrated by mercury lamp.

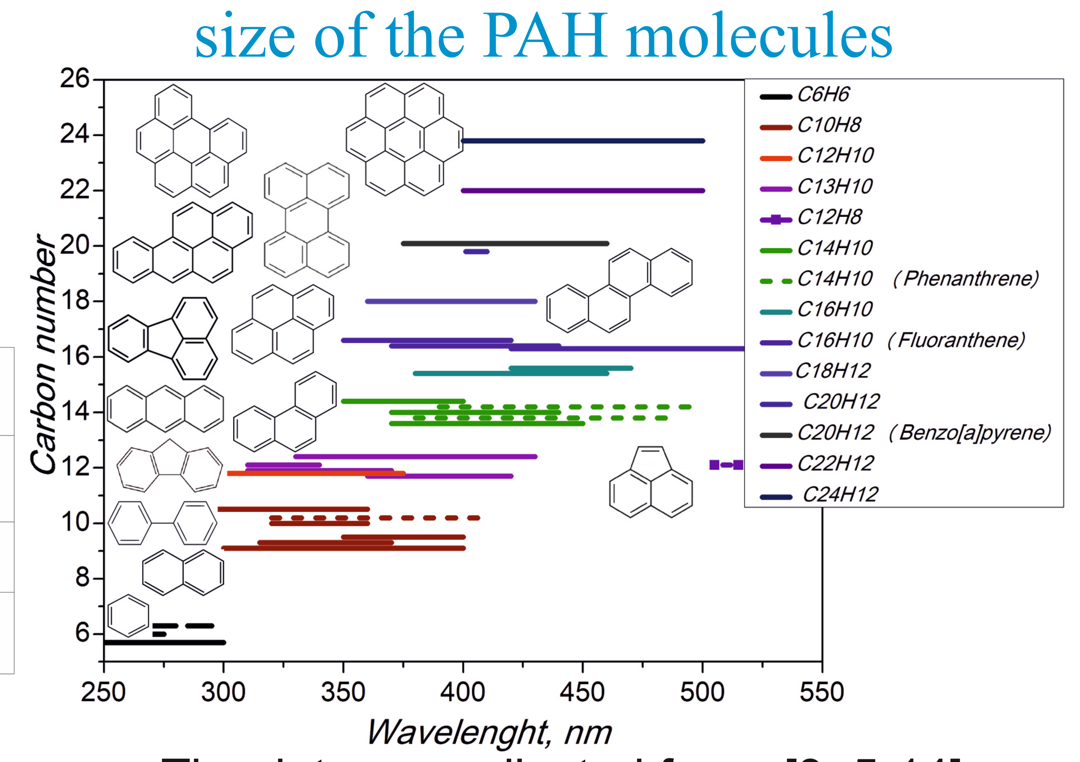


Extinction:
He-Ne Laser 633nm
For control of condensed phase appearance.

Experimental conditions:

Mixture composition	LIF measurements		Extinction measurements	
	Pressure range, P_5, bar	Temperature range, T_5, K	Pressure range, P_5, bar	Temperature range, T_5, K
1% C_6H_6 + 99% Ar	4.3-5.7	1330-1790	1.4-4.6	1643-2558
1% C_6H_6 + 5% DME + 94% Ar	3.6-4.6	1350-2000	2,7-3,3	2140-2425

LIF spectrum evolution with increasing size of the PAH molecules

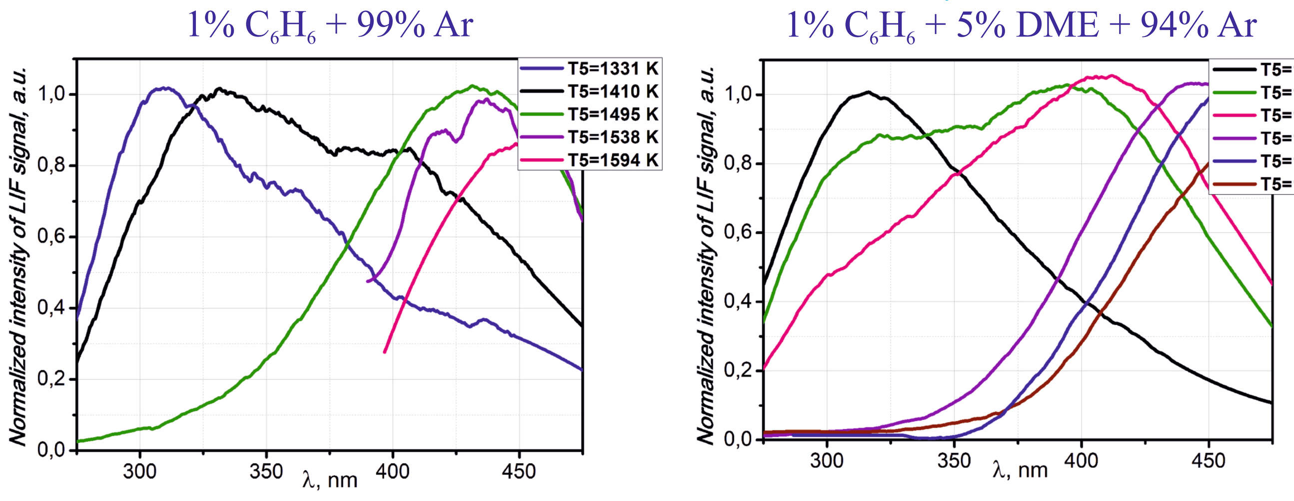


The data are collected from [3, 5-14].

Experimental results

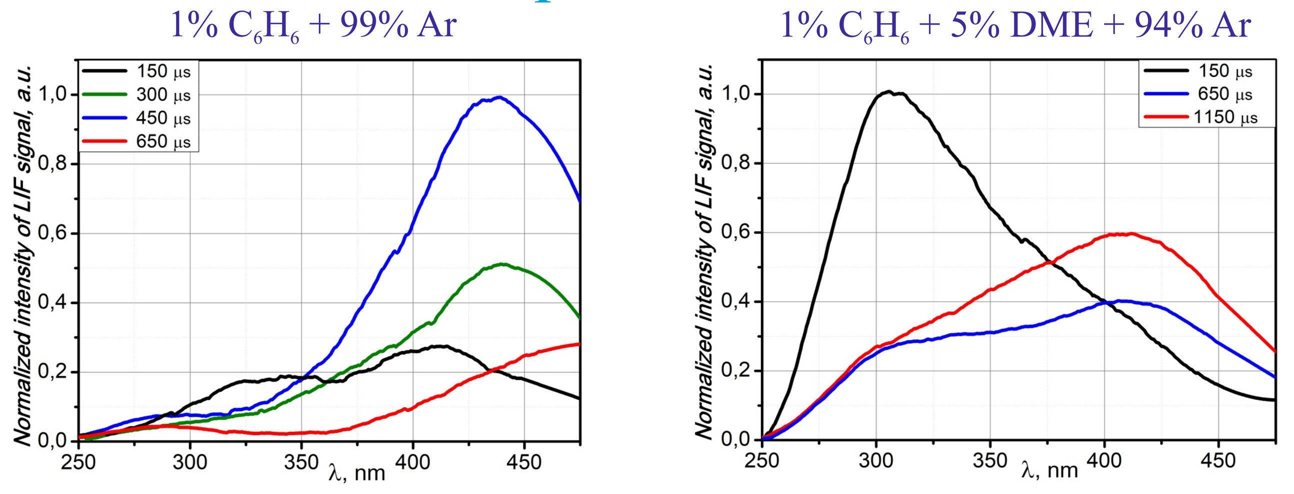
Temperature dependence of PAHs LIF spectrum at reaction time 1150 μs

1% C_6H_6 + 99% Ar | 1% C_6H_6 + 5% DME + 94% Ar

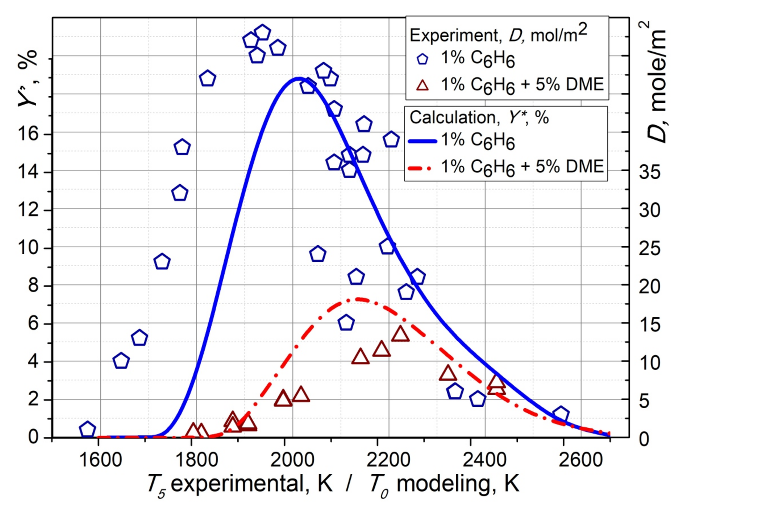


Time evolution of PAHs LIF spectrum at temperature 1650 K

1% C_6H_6 + 99% Ar | 1% C_6H_6 + 5% DME + 94% Ar



Optical density at 700 μs

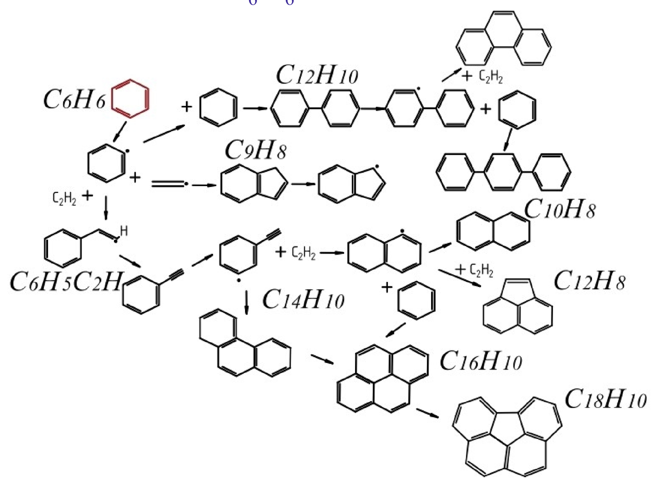


The DME presence leads to a shift in the LIF spectra of PAHs to shorter wavelengths compared to a mixture of benzene diluted in argon at the same initial temperature. The DME slows down the growth of large (consisting of 3-4 and more rings) PAHs. In a mixture of benzene with DME, more amount of small aromatics (consisting of 1-2 rings) PAHs were detected. Laser extinction measurements showed a significant decrease in optical density during benzene pyrolysis with the DME presence over the entire temperature range studied. Based on the obtained LIF spectra and exctinction measurements, it was concluded that the DME accelerates formation of the small aromatic compound and slows down the larger PAHs formation and soot particles.

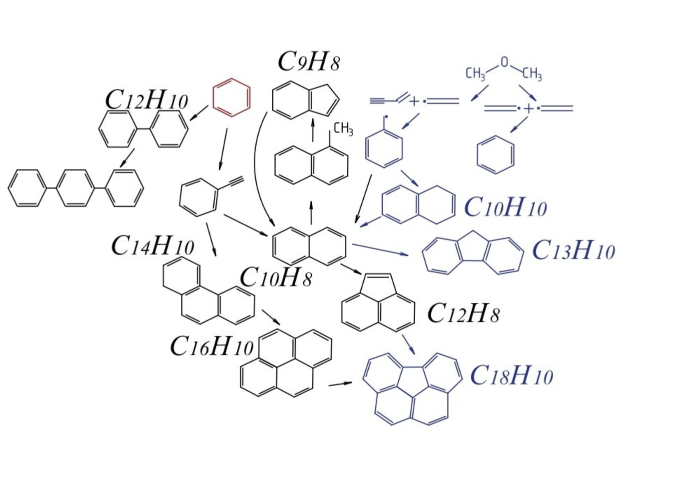
Kinetic modeling

Aromatic compound formation pathways at 1600-1800 K

1% C_6H_6 + 99% Ar



1% C_6H_6 + 5% DME + 94% Ar



The calculations were carried out using kinetics mechanisms [15, 16] in the 0-dimentional approximation under constant pressure conditions with OpenSmoke++ code [17].

Conclusions

LIF spectra were obtained for different temperatures (1300–2000 K) and reaction times of 150–1150 μs for diluted in argon benzene, DME and their mixture.

Large PAHs consisting of fore or more aromatic rings are the precursors for the appearance of condensed phase, and are probable nuclei of carbon nanoparticles.

DME additives increase the yield of "small" PAHs (1-2 rings) and slow down large PAHs and soot formation compared with benzene mixture.

Kinetic modeling has shown that DME presence leads to the formation of 5-membered aromatic ring (C_5H_5), $C_{10}H_{10}$, $C_{13}H_{10}$ as well as the emerging of alternative formationpathways for C_9H_8 and $C_{10}H_8$.

References

[1] K.Gleason et al. Combust. Flame V. 223, 2021.
[2] M. Frenklach et al. Symp. (Int.) Combust. 20 (1985).
[3] Y.Zhang et al. Appl. Phys. B. V. 125, 2019.
[4] H.K.S. Panahi et al. BRJ V. 23, 2019.
[5] F. Beretta et al. Combust. Flame V. 61, 1985.
[6] F. Ossler et al. Appl. Phys. B. V. 72, 2001.
[7] T. Aizawa et al. SAE Trans. V. 112, 2003.
[8] R. Sun et al. Opt. Lasers Eng. V. 48, 2010.
[9] K. Hayashida et al. Fuel V. 90, 2011.
[10] M. Orain et al. Appl. Phys. B. V. 102, 2011.
[11] S. Bejaoui et al. Combust. Flame V.161, 2014.
[12] B. Chen et al. Combust. Flame, V. 177, 2017.
[13] M. Taniguchi et al. Photochem. Photobiol. V. 94, 2018.
[14] Y. Zhang et al. Spectrochim. Acta, Part A V. 224, 2020.
[15] E. Ranzi et al. J. Chem. Kinet. V. 46, 2014.
[16] C. Saggese et. al. Combust. Flame V. 162, 2015.
[17] A. Cuoci et al. Comput. Phys. Commun. V. 192, 2015

RFBR RUSSIAN FOUNDATION FOR BASIC RESEARCH
The support from the Joint Project RFBR-DFG No. 20-58-12003