Experimental and kinetic modeling study of the positive ions in ethylene flames

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2022

Introduction

- Combustion hydrocarbons remains the main technology for generating energy in the foreseeable future. Problem: harmful emissions (PAHs, soot);
- Understanding the chemistry of ion conversion in flames is important for the development of new diagnostic methods (PAH detection).
- Electric field assisted combustion. Plasma-assisted combustion.

Introduction

Currently, detailed chemical-kinetic models for the combustion of hydrocarbons have been developed, taking into account the formation of charged species. Although, models are not perfect.
The main reactions embedded in the mechanism are the following:

Chemiionisation:

$CH+O \Leftrightarrow CHO^+ + e^-$

Formation H_3O^+ :

$CHO^+ + H_2O \Leftrightarrow H_3O^+ + CO$

Recombination:

$H_3O^+ + e^- \Leftrightarrow H + H + OH$

Proton transfer to neutral species :**$A+H_3O^+ \Leftrightarrow AH^+ + H_2O$**, For example, **$H_3OH+H_3O^+ \Leftrightarrow (CH_3OH)H^+ + H_2O$**, for flames with different ϕ the species (A) reacting with **H_3O^+** are slightly different.

$$\phi = \frac{F/O}{(F/O)_{st}}$$

- F – fuel flow
- O – oxygen flow
- St - stoichiometry

Introduction

Mechanisms involving ion chemistry

Team of authors	Year	Fuel	Number of compounds/reactions
T. Pedersen, Robert C. Brown (Combustion and Flame)	1993	Methane	36/86
J. Prager, U. Riedel, J. Warnatz (Proceedings of the Combustion Institute)	2007	Methane	38/208
J. Cancian , B.A.V. Bennett, M.B. Colket & M.D. Smooke (Combustion Theory and Modelling)	2012	Acetylene, Ethylen	136/1010
B. Chen et al. (Combustion and Flame)	2019	Methane	522/2801
Mechanism ICKC (Combustion and Flame)	2022	Methane	522/2831

Goal of the work

The aim of this work was to experimentally verify and improve the ion chemistry mechanism available in literature (ICKC mech.) for premixed ethylene/oxygen/argon flames.

Particular tasks

1)To measure the cationic structure of flames $C_2H_4/O_2/Ar$ in a wide range of equivalence ratio using MBMS.

2)To simulate the ion structure of the flames.

3) To further refine the model, if needed.

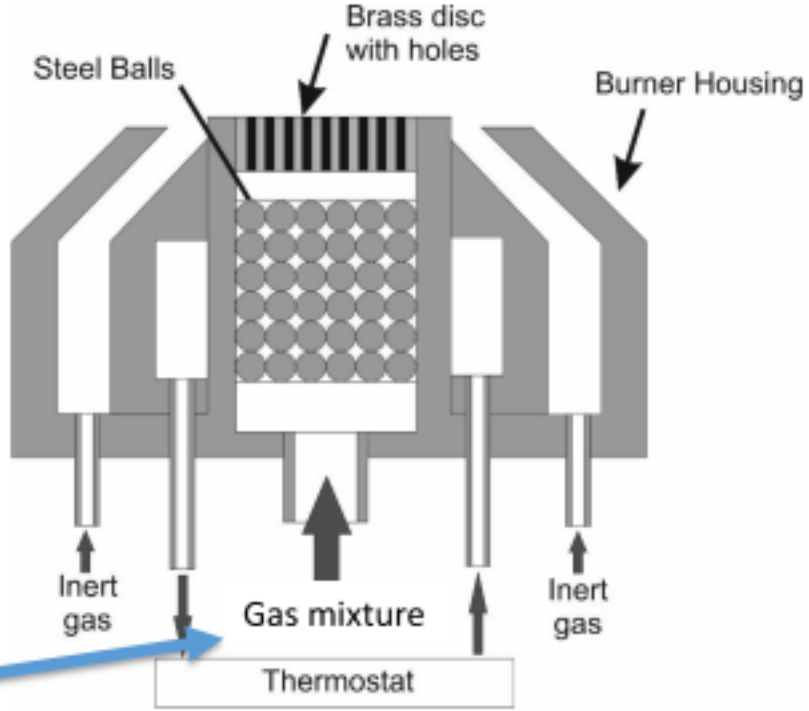
Experimental technique

Temperature at the burner surface:
T_0=95 ^{0}C

Pressure:
P=1 atm.

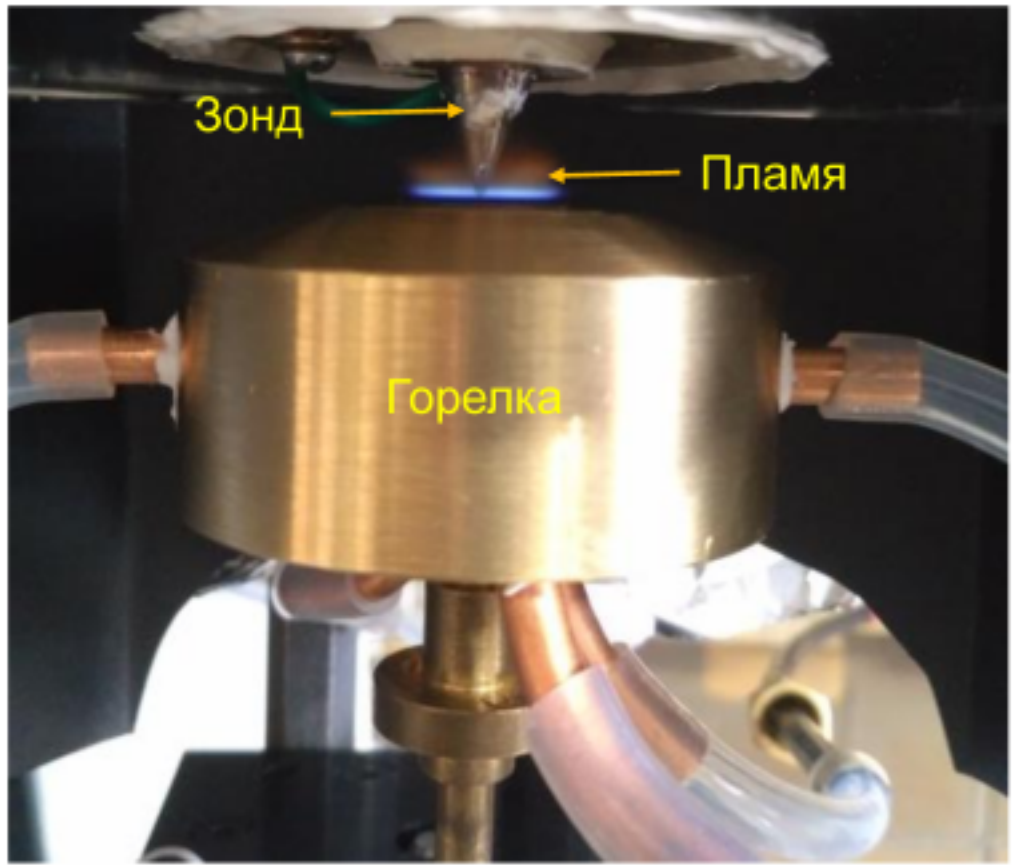
Total flow:
30 cm^3/c

Composition of fresh mixture



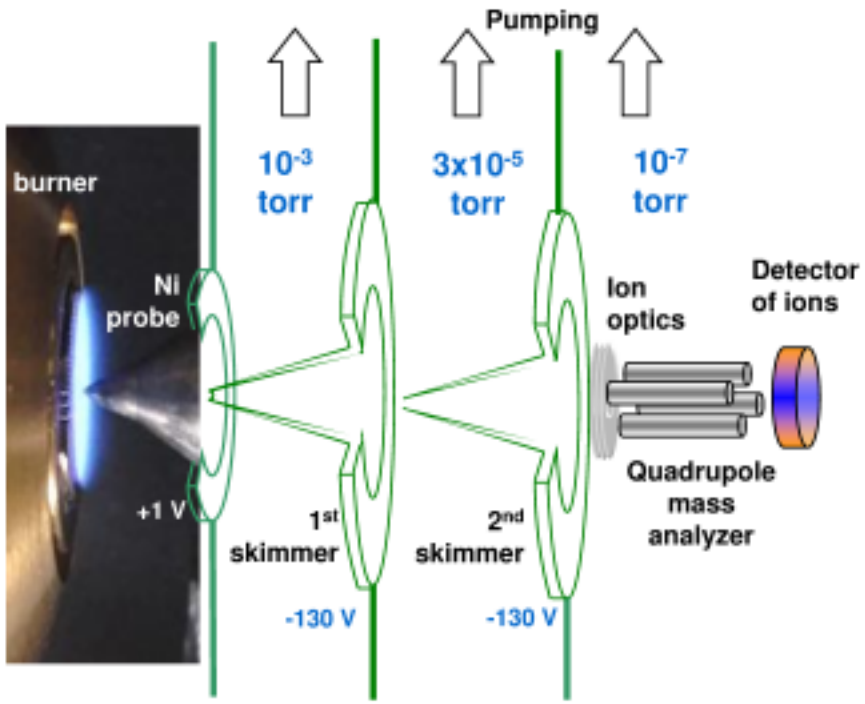
Flame №	Φ	Mole fraction		
		C_2H_4	O_2	Ar
1	0.4	0.035	0.265	0.7
2	0.7	0.056	0.243	0.7
3	1.0	0.075	0.225	0.7
4	1.25	0.088	0.212	0.7
5	1.5	0.1	0.2	0.7

Botha-Spalding Type Burner



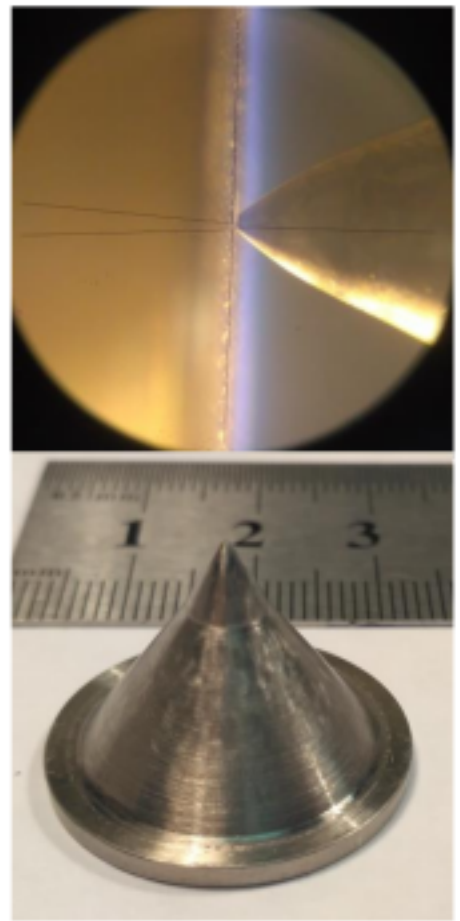
Experimental technique

MBMS setup (Hiden HPR60)

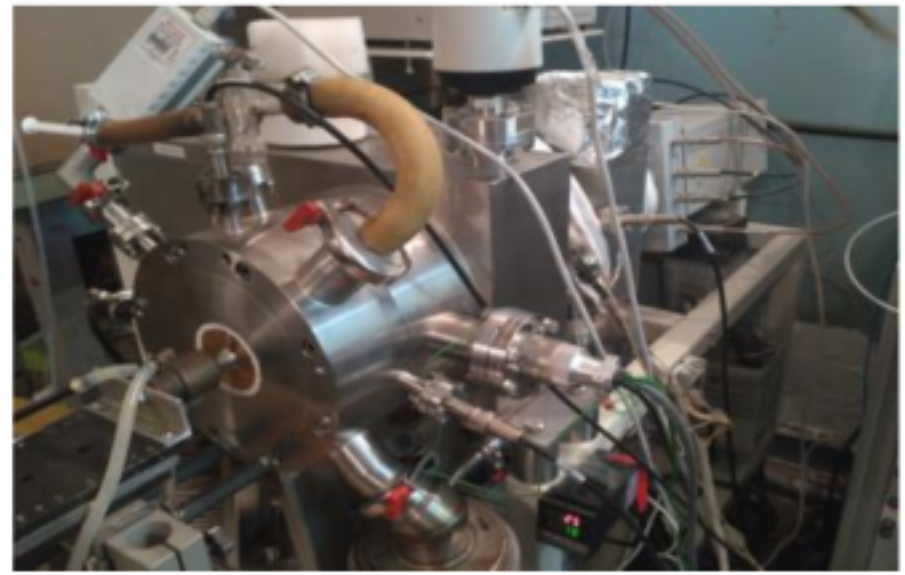


Schematics of the setup

Molecular beam mass spectrometric facility was used. The diameter of the probe orifice is 80 µm.



Ni sampling probe



General view of the setup

Modeling

- The simulation was performed using the Cantera (v.2.5.1)
- The kinetic mechanism includes:

  - The base mechanism for combustion of hydrocarbons (neutral species): AramcoMech 2.0 (493 species, 2716 reactions)

  +

  - Mechanism of reactions involving ions: Mechanism ICKC (31 species, 105 reactions)

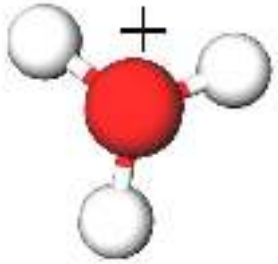
Mechanism ICKC [Combustion and Flame 241 (2022) 112106] is based on the mechanism of Chen et al. [Comb. Flame (2019)] (29 species, 85 reactions):

1) The thermochemical parameters of all cations are calculated by methods of quantum chemistry;

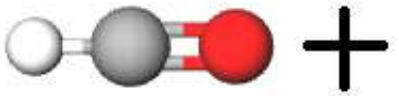
2) The reaction rate constants have been updated according to the astrochemical database UMIST Rate 12.

Results. Cations in ethylene flame

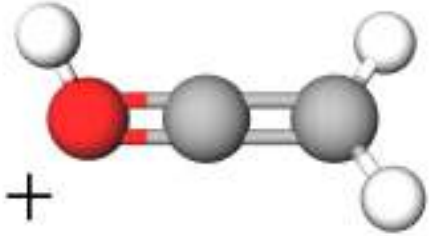
- H_3O^+: m/z = 19;



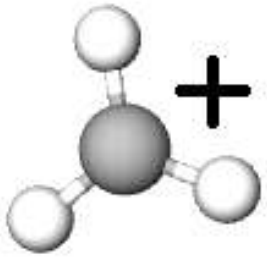
- HCO^+: m/z = 29;



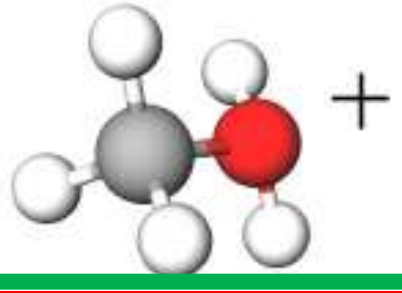
- $C_2H_3O^+$: m/z = 43;



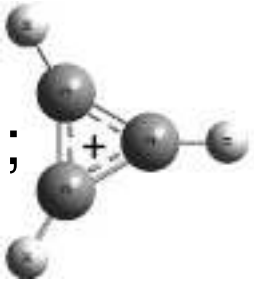
- CH_3^+: m/z = 15;

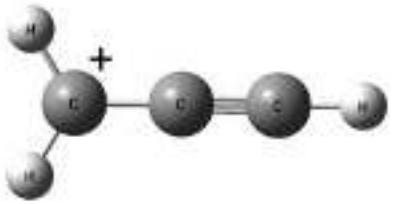


- CH_5O^+: m/z = 33;

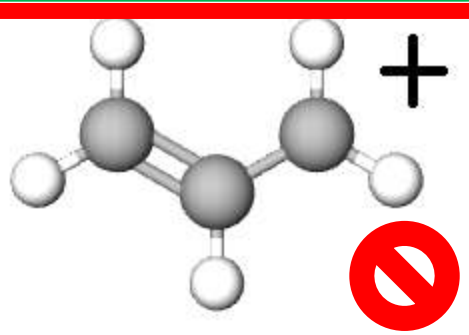


$C_3H_3^+$: m/z = 39;



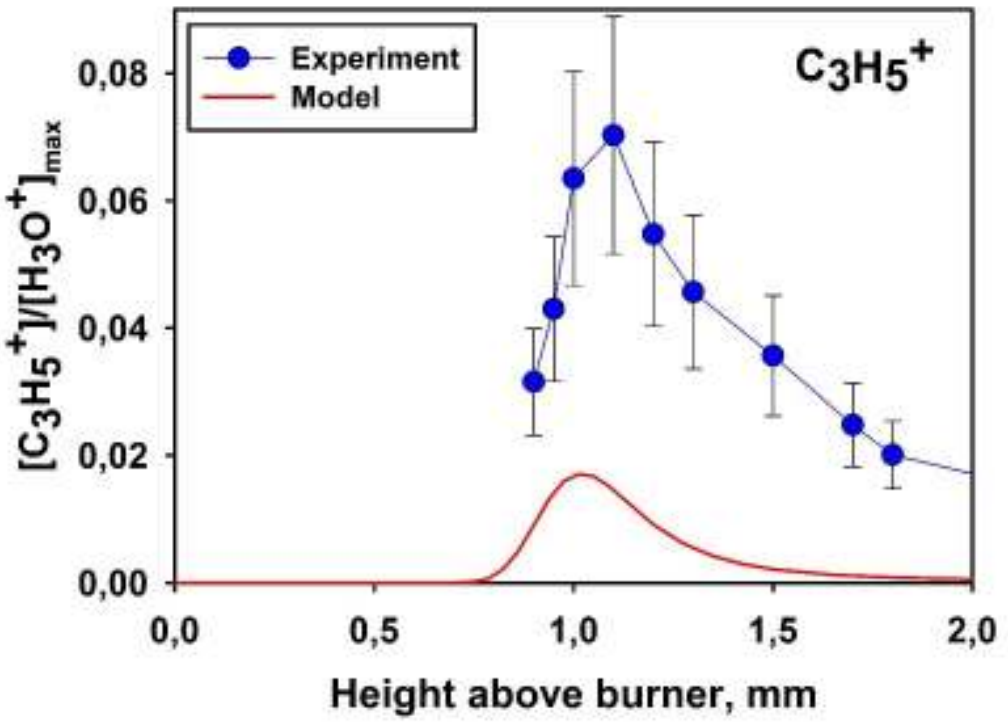


$C_3H_5^+$: m/z = 41.



Results. Cation $C_3H_5^+$

Rich ethylen flame



- Main cations: H_3O^+, $C_3H_3^+$, $C_2H_3O^+$, CH_5O^+, HCO^+, CH_3^+

$$kf = AT^B exp\left(-\frac{Ea}{RT}\right)$$

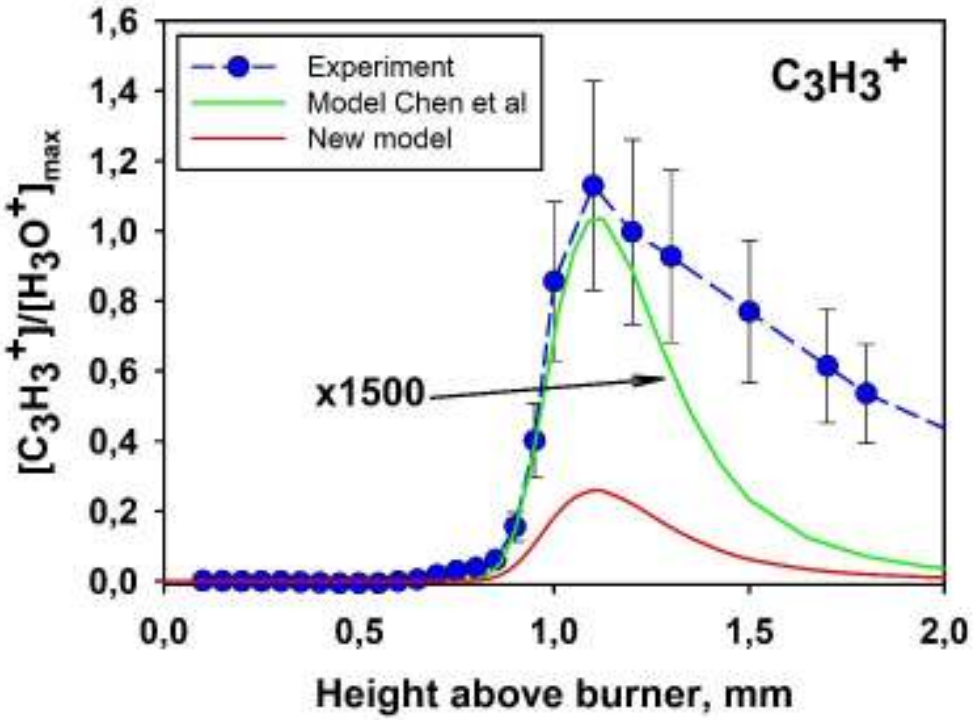
Reactions involving $C_3H_5^+$	A (cm3/s/mole)	B	Ea (kcal/mole)
$C_3H_5^+ + e^- <=> CH_3CCH + H$	$9.033*10^{16}$	-0.5	0
$C_3H_5^+ + e^- <=> C_3H_3 + H_2$	$9.033*10^{16}$	-0.5	0
$CH_3^+ + C_2H_4 <=> C_3H_5^+ + H_2$	$3.16*10^{14}$	0	0
$CH_3^+ + C_2H_6 <=> C_3H_5^+ + H_2 + H_2$	$8.45*10^{13}$	0	0
$H_3O^+ + CH_3CCH <=> C_3H_5^+ + H_2O$	$1.08*10^{15}$	0	0
$HCO^+ + CH_3CCH <=> C_3H_5^+ + CO$	$8.4*10^{14}$	0	0
$C_3H_3^+ + C_3H_6 <=> CH_3CCH + C_3H_5^+$	$6.02*10^{14}$	0	0
$C_2H_3O^+ + CH_3 <=> C_3H_5^+ OH$	$6.02*10^{14}$	0	0

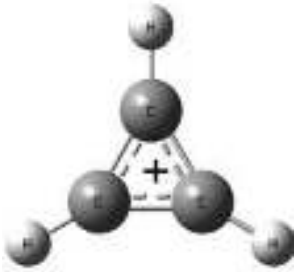
The thermochemical parameters $C_3H_5^+$

Enthalpy of formation at 298K (Kcal/mol)	Entropy at 298K (Kcal/(mol*k))
228,4	60,5

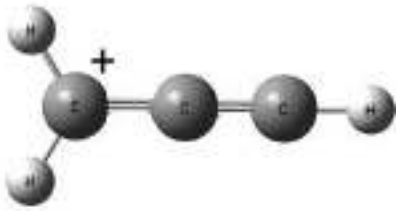
Results. Isomers $C_3H_3^+$

Rich ethylene flame





Cyclic



Linear

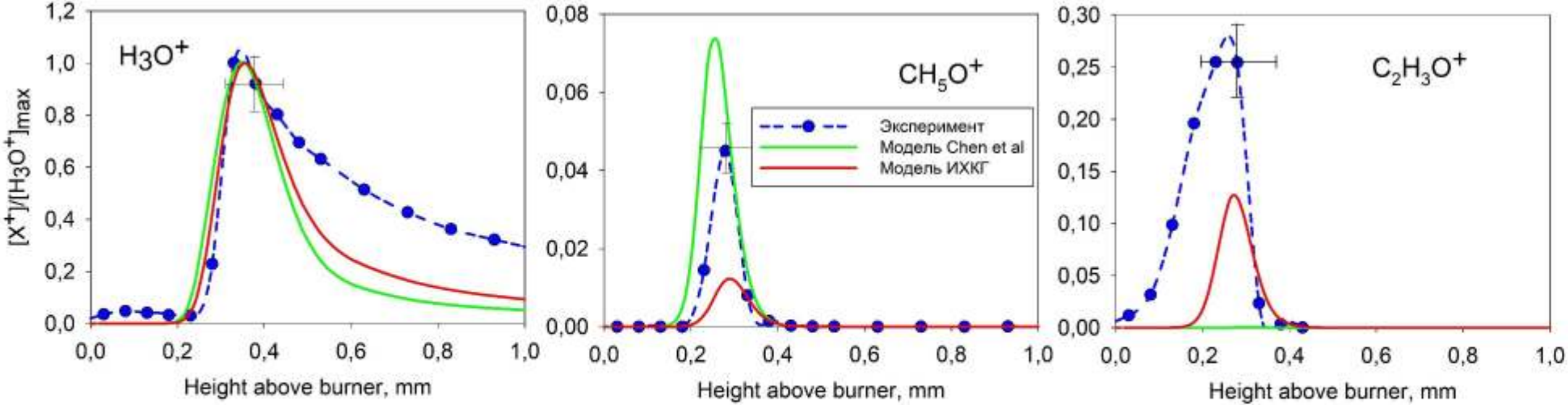
Previous model prediction is increased by 1500 times!

$CH_3^+ + C_2H_2 <=> CH_2CCH^+ + H_2$
$CH_3^+ + C_2H_4 <=> CH_2CCH^+ + H_2 + H_2$
$CH_3^+ + C_2H <=> CH_2CCH^+ + H$
$H_3O^+ + C_3H_2 <=> CH_2CCH^+ + H_2O$
$HCO^+ + C_3H_2 <=> CH_2CCH^+ + CO$
$CH_2CCH^+ + C_2H_2 <=> H_2C_3H^+ + C_2H_2$
$CH_2CCH^+ + E^- <=> C_2H_2 + CH$
$CH_2CCH^+ + E^- <=> C_3H_2 + H$
$CH_2CCH^+ + O <=> HCO+ + C_2H_2$
$CH_2CCH^+ + O^- <=> O + C_3H_3$
$CH_2CCH^+ + OH^- <=> OH + C_3H_3$
$CH_2CCH^+ + O_2^- <=> O_2 + C_3H_3$

Results. Main cations

Stoichiometric flame of ethylene, $\phi=1$

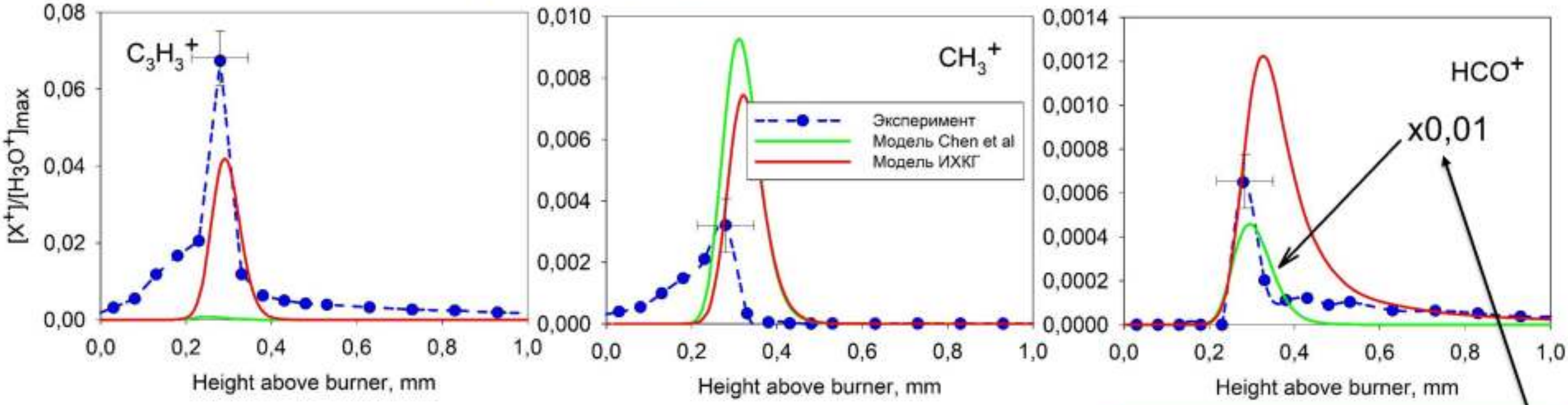
Relative molar fraction: $[X^+]/[H_3O^+]_{max}$.



Results. Main cations

Stoichiometric flame of ethylene, ϕ=1

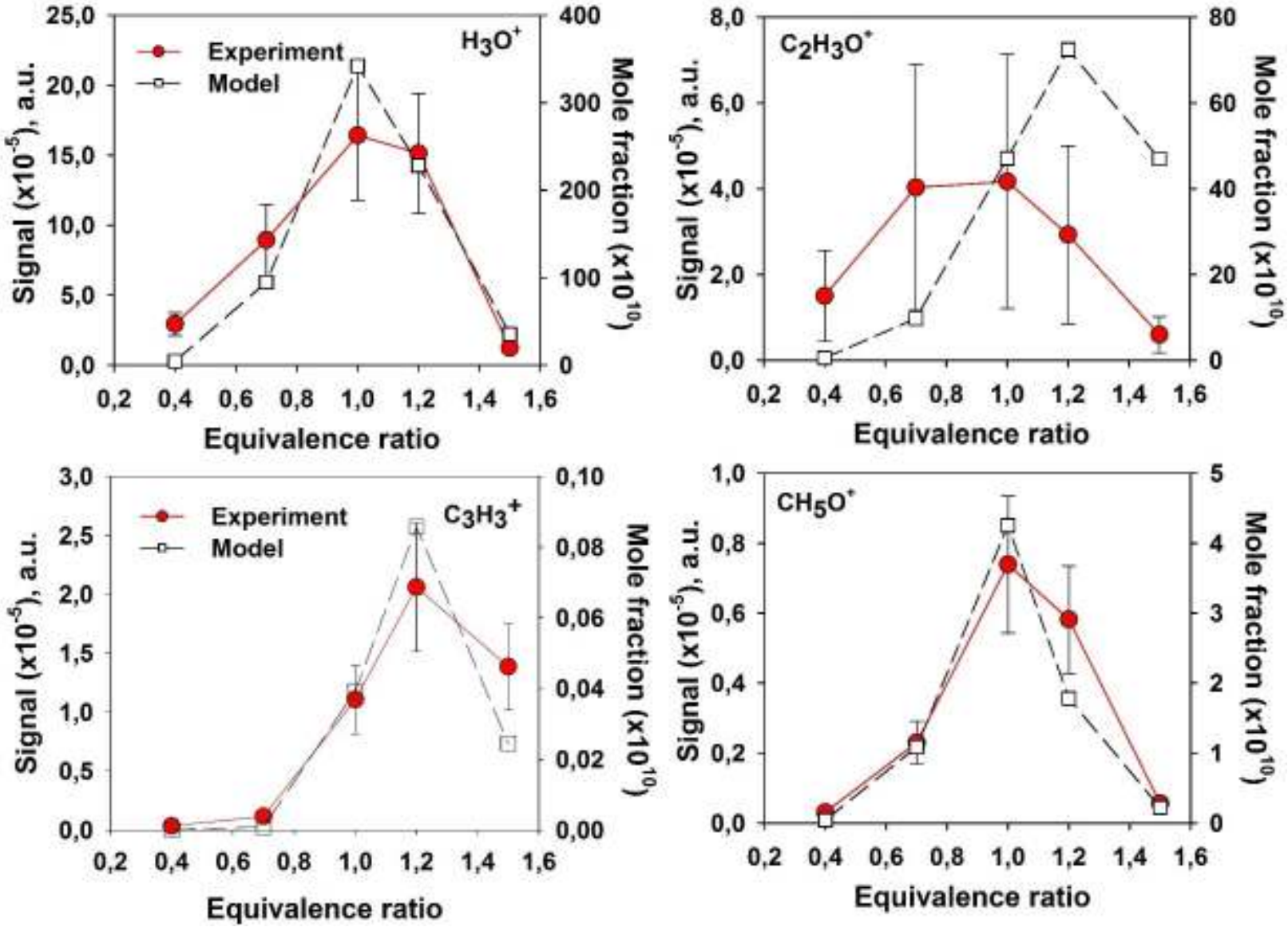
Relative molar fraction: $[X^+]/[H_3O^+]_{max}$.



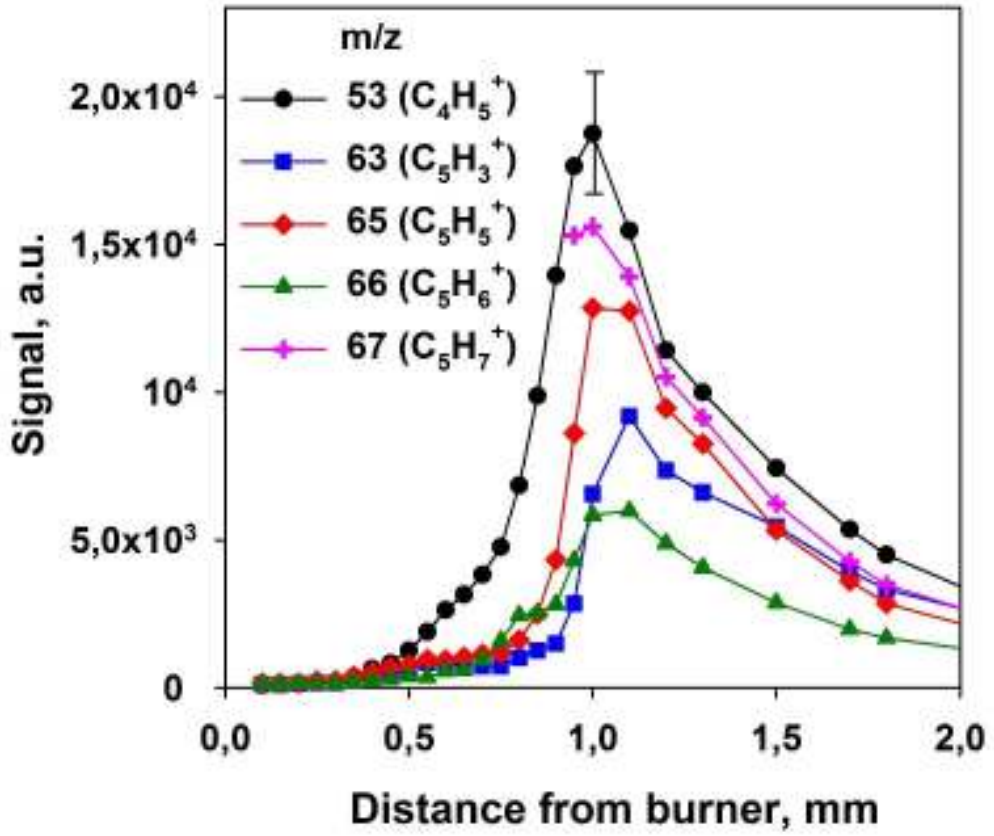
Updated model is much better in predicting $C_3H_3^+$!

Prediction of model of Chen et al. for HCO+ was decreased by 100 times.

Results. Maximum abundance of key cations



Results. Cations $C_4H_5^+$, $C_5H_3^+$, $C_5H_5^+$, $C_5H_6^+$, $C_5H_7^+$.



Possible reactions of formation:

$CH_3^+ + CH_2CCH \Leftrightarrow C_4H_5^+ + H$

$C_3H_3^+ + HC_4H \Leftrightarrow C_5H_3^+ + C_2H_2$

$HCO^+ + CH_3C_4H \Leftrightarrow C_5H_5^+ + CO$

$C_3H_3^+ + C_2H_4 \Leftrightarrow C_5H_6^+ + H$

$C_3H_5^+ + C_2H_4 \Leftrightarrow C_5H_7^+ + H_2$

- Main cations: H_3O^+, $C_3H_3^+$, $C_2H_3O^+$, CH_5O^+, HCO^+, CH_3^+

Conclusion

- Data on the cationic structure of ethylene/oxygen/argon flames (ϕ=0.4-1.5) were obtained experimentally and used to test the mechanism proposed earlier (ICKC) for reactions involving ions.

- The mechanism proposed earlier (ICKC) has been improved by adding reactions involving cation $C_3H_5^+$ (8 reactions), two isomeric forms of $C_3H_3^+$ (linear and cyclic) (12 reactions).

- The new experimental data and the modified mechanism will serve in the future for the development of an ion chemistry model for combustion of heavy hydrocarbons.

Thanks for your attention!

The work was supported by the RFBR under grant No 19-03-00589_a.