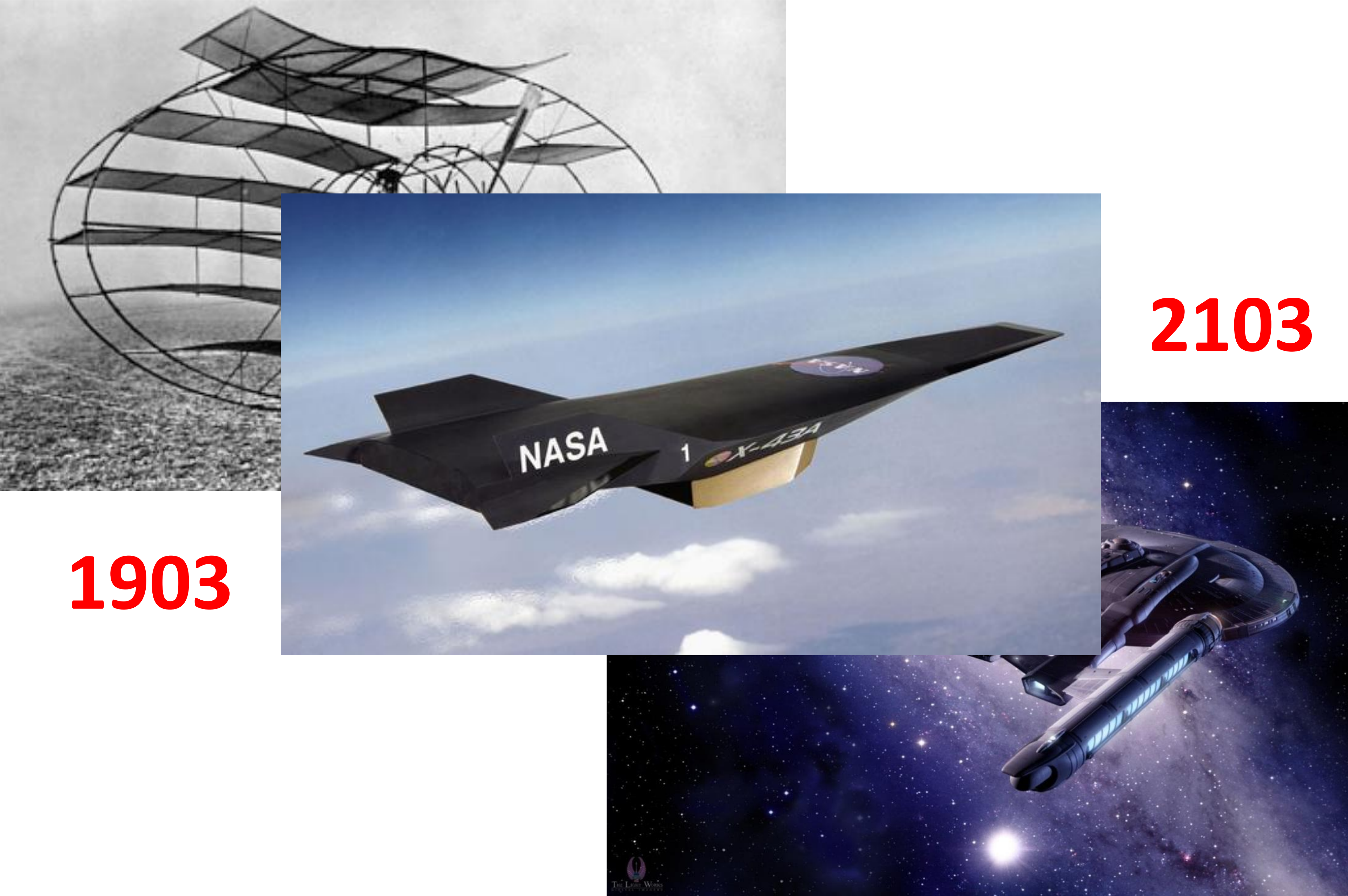
Effect of “Hot” Atoms on Active Species Production in High-Voltage Pulsed Discharges

Nikolay Aleksandrov, Alexander Ponomarev,
Andrey Starikovskiy

Oxygen Plasma Kinetics Workshop
Reykjavik 2016

Plasma Technologies for Aerospace



2103

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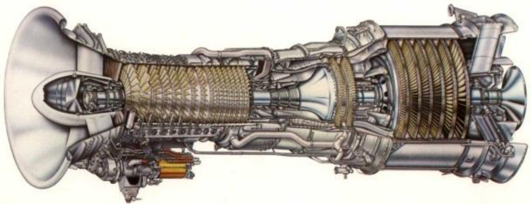
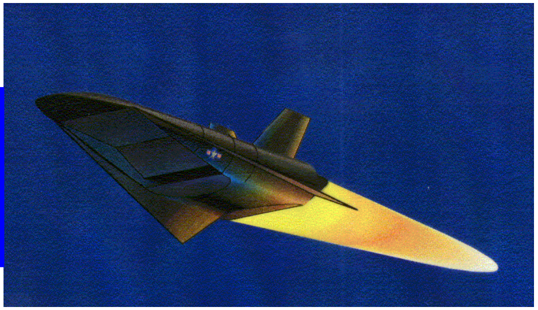
Nonequilibrium Plasma Aerodynamics

Dynamic
Flow Control

Hypersonic
Drag Reduction



Plasma
Assisted
Combustion



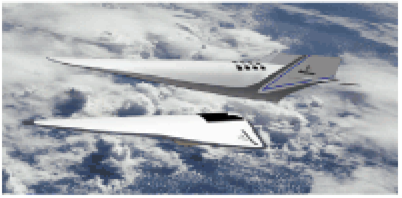
Internal
Aerodynamics

External
Aerodynamics

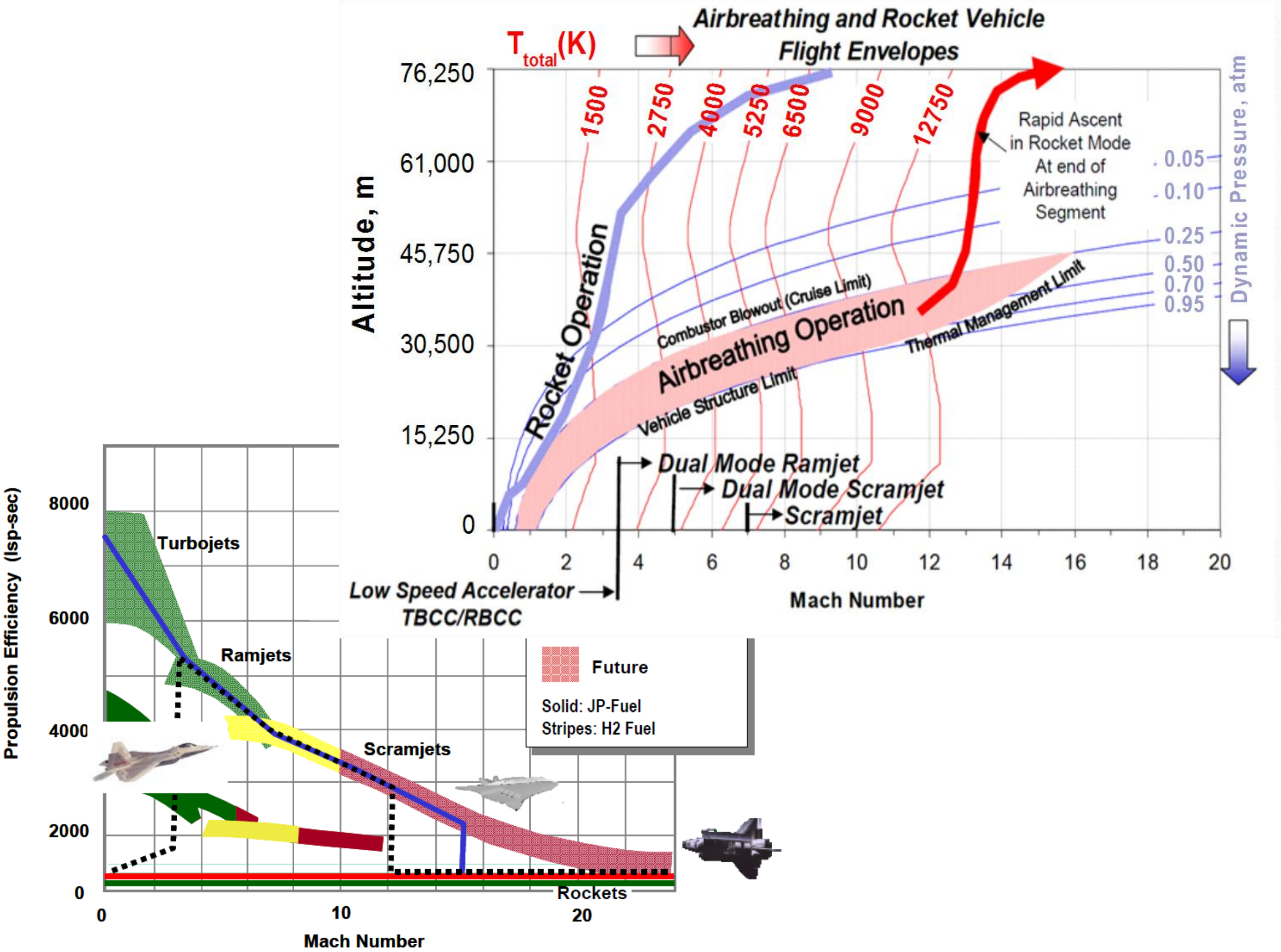
Propulsion Efficiency and Operating Regimes for Variety of Flight Systems

(a)

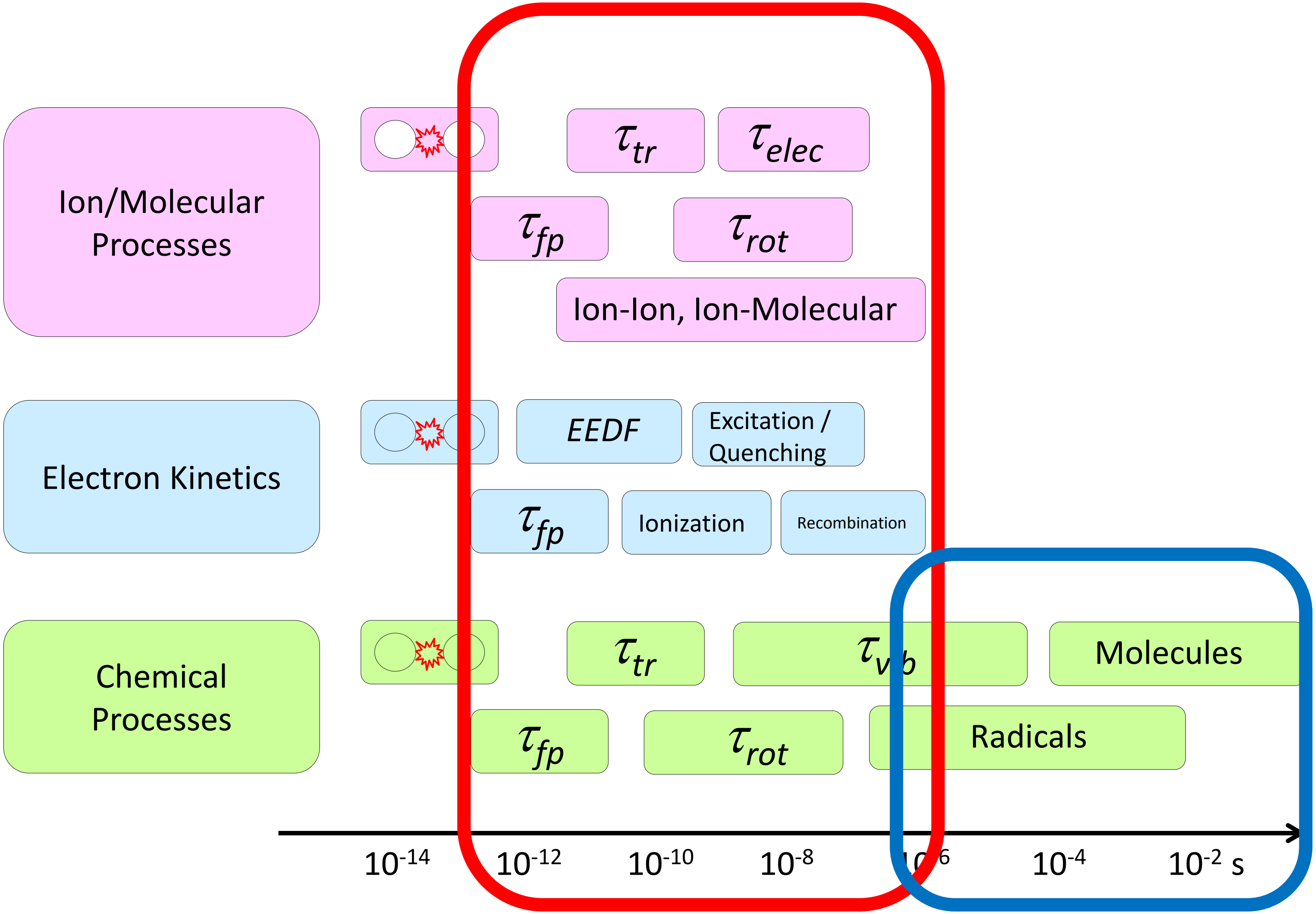
(b)



(c)



Short Time Scale Chemistry: Non-equilibrium Regimes



Ion/Molecular Processes

τ_{tr} τ_{elec}

τ_{fp} τ_{rot}

Ion-Ion, Ion-Molecular

Electron Kinetics

EEDF

Excitation / Quenching

τ_{fp}

Ionization

Recombination

Chemical Processes

τ_{tr} τ_{vib}

Molecules

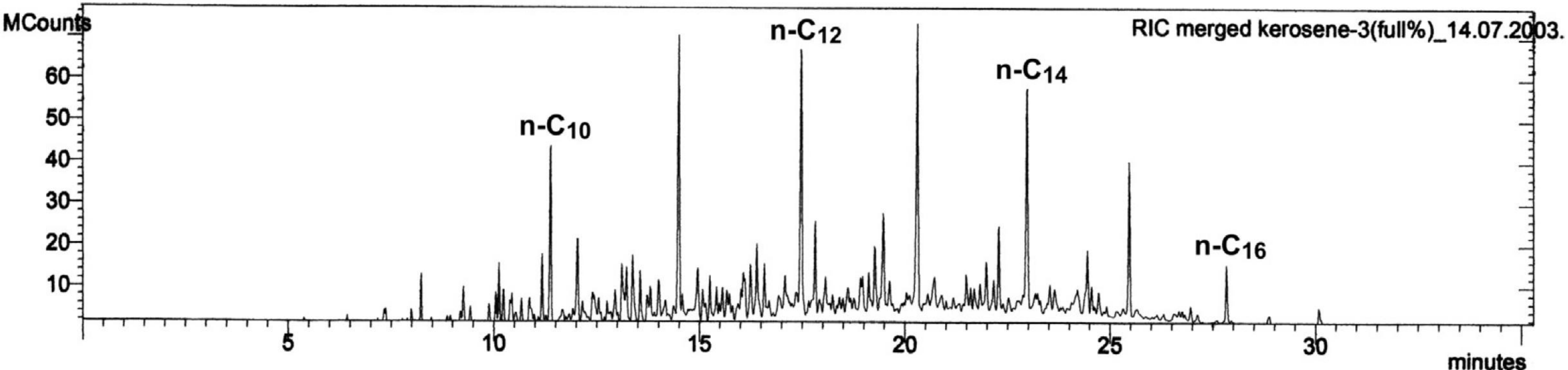
τ_{fp} τ_{rot}

Radicals

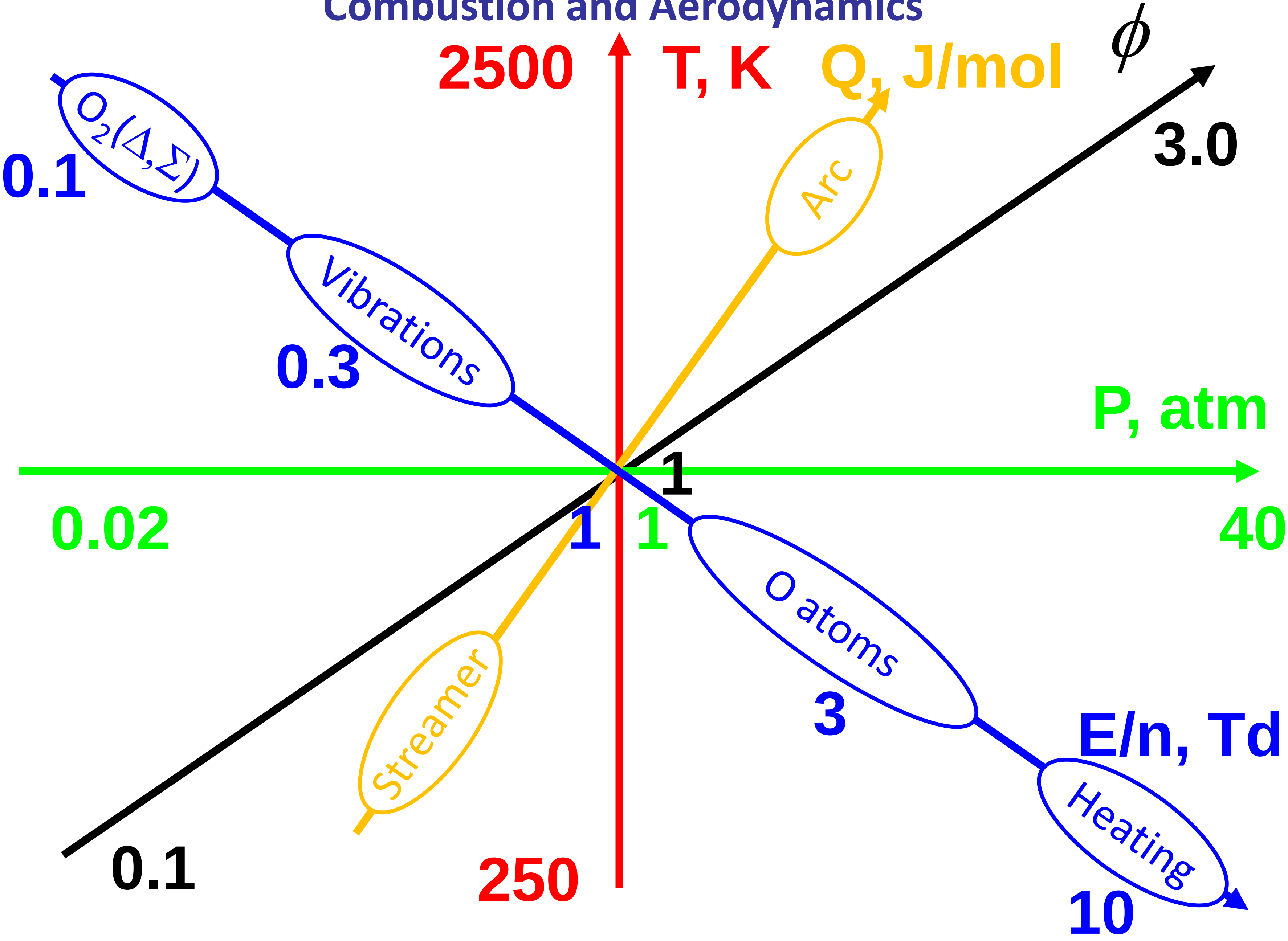
10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} s

Cross-sections Available

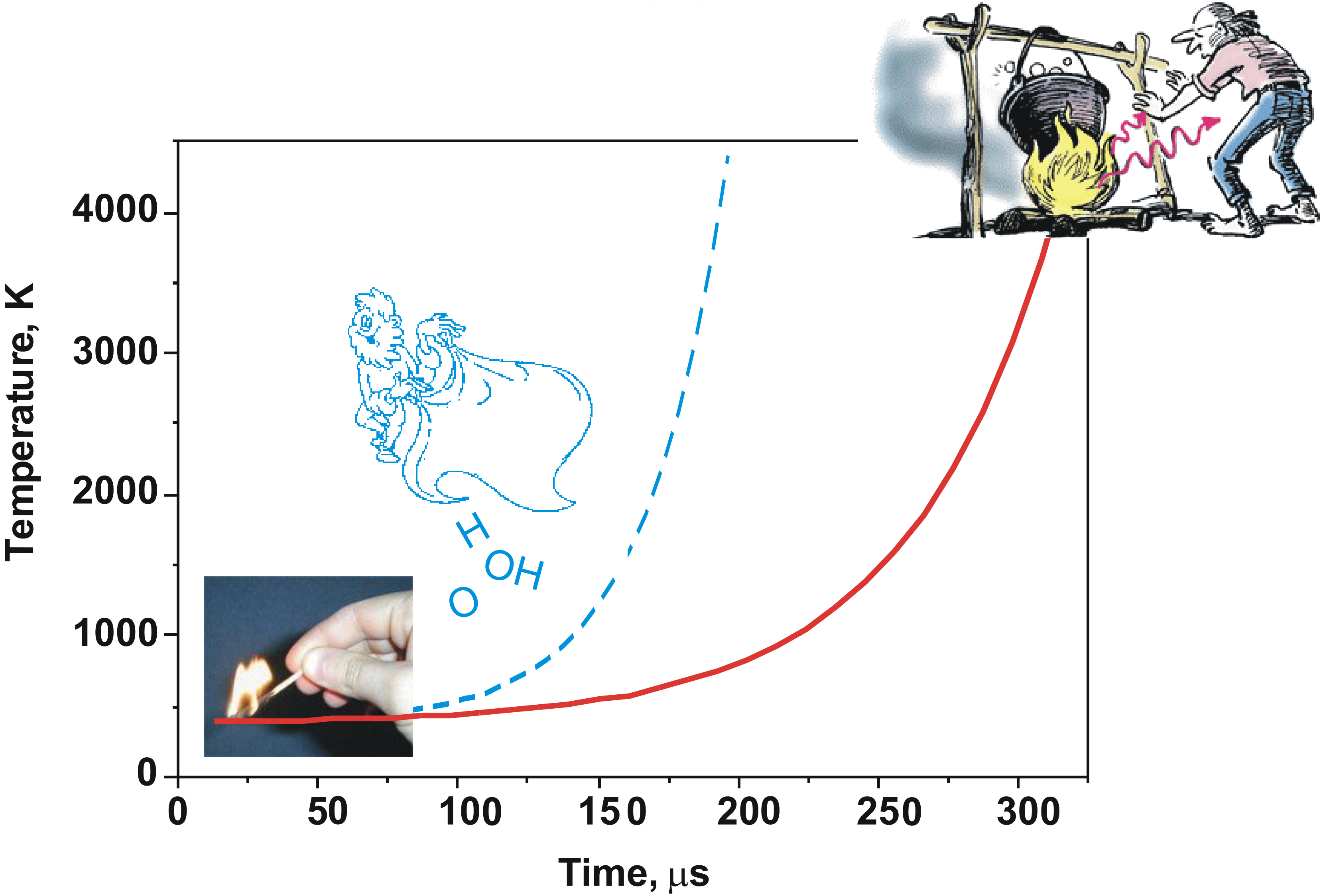
Atmospheric	Saturated	Unsaturated	Oxygenated	Isomers
N2	CH4	C2H2	CO	iso-butane
O2	C2H6	C2H4	CH3OH	iso-propane
CO2	C3H8	C3H6	C2H5OH	neo-pentane
H2O	C4H10		CH3OCH3 DME	
O3	C5H12			
Ar	H2			
N2O				



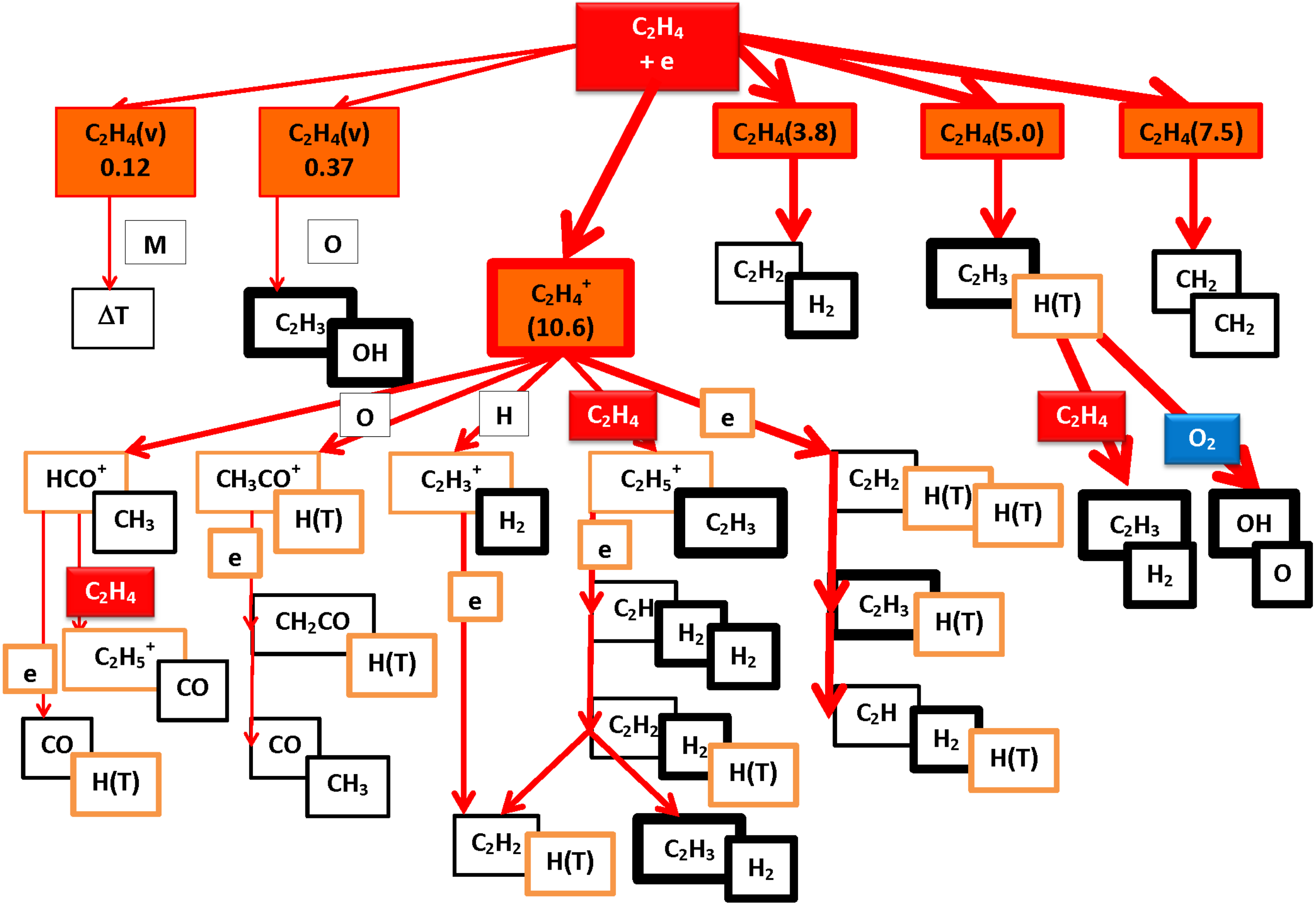
Nonequilibrium Plasma : New Dimensions in Combustion and Aerodynamics



Decreasing of Ignition Delay Time - 1994



PAC Pathways: C_2H_4-air



C_2H_4 + e

$C_2H_4(v)$ 0.12

M

ΔT

$C_2H_4(v)$ 0.37

O

C_2H_3

OH

$C_2H_4^+$ (10.6)

O

H

C_2H_4

e

HCO^+

CH_3

C_2H_4

e

$C_2H_5^+$

CO

CO

H(T)

CH_3CO^+

H(T)

e

CH_2CO

H(T)

CO

CH_3

$C_2H_3^+$

H_2

e

C_2H_2

H(T)

$C_2H_5^+$

C_2H_3

e

C_2H

H_2

H_2

C_2H_2

H_2

H(T)

C_2H_3

H_2

C_2H_2

H(T)

H(T)

C_2H_3

H(T)

C_2H

H_2

H(T)

$C_2H_4(3.8)$

C_2H_2

H_2

$C_2H_4(5.0)$

C_2H_3

H(T)

C_2H_4

O_2

C_2H_3

H_2

OH

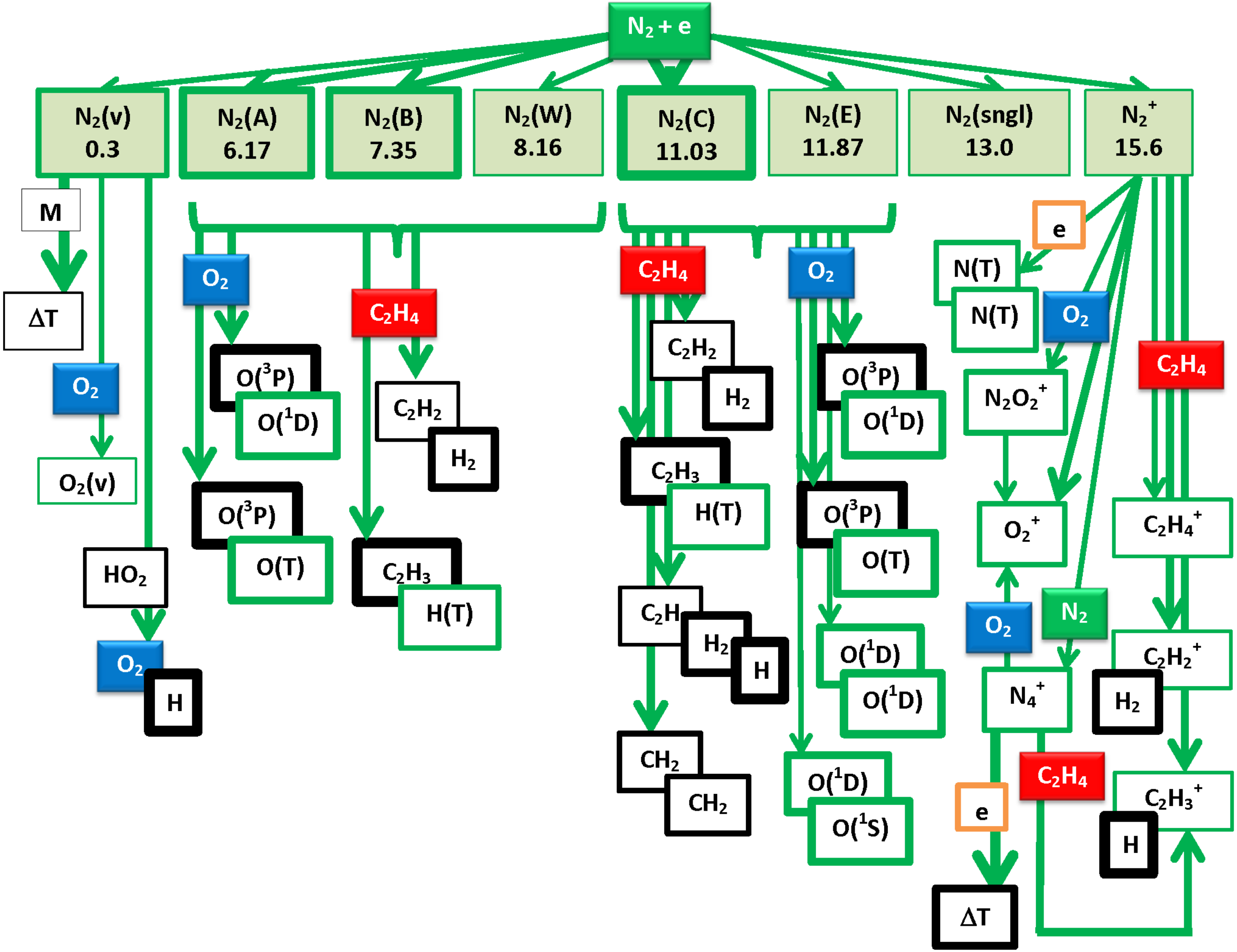
O

$C_2H_4(7.5)$

CH_2

CH_2

PAC Pathways: C_2H_4-air



$N_2 + e$

$N_2(v)$ 0.3

$N_2(A)$ 6.17

$N_2(B)$ 7.35

$N_2(W)$ 8.16

$N_2(C)$ 11.03

$N_2(E)$ 11.87

N_2(sngl) 13.0

N_2^+ 15.6

M

ΔT

O_2

$O_2(v)$

HO_2

O_2

H

O_2

$O(^3P)$

$O(^1D)$

$O(^3P)$

$O(T)$

C_2H_4

C_2H_2

H_2

C_2H_3

$H(T)$

C_2H_4

C_2H_2

H_2

C_2H_3

$H(T)$

C_2H

H_2

H

CH_2

CH_2

O_2

$O(^3P)$

$O(^1D)$

$O(^3P)$

$O(T)$

$O(^1D)$

$O(^1D)$

$O(^1D)$

$O(^1S)$

e

$N(T)$

$N(T)$

O_2

$N_2O_2^+$

O_2^+

O_2

N_2

N_4^+

C_2H_4

e

ΔT

C_2H_4

$C_2H_4^+$

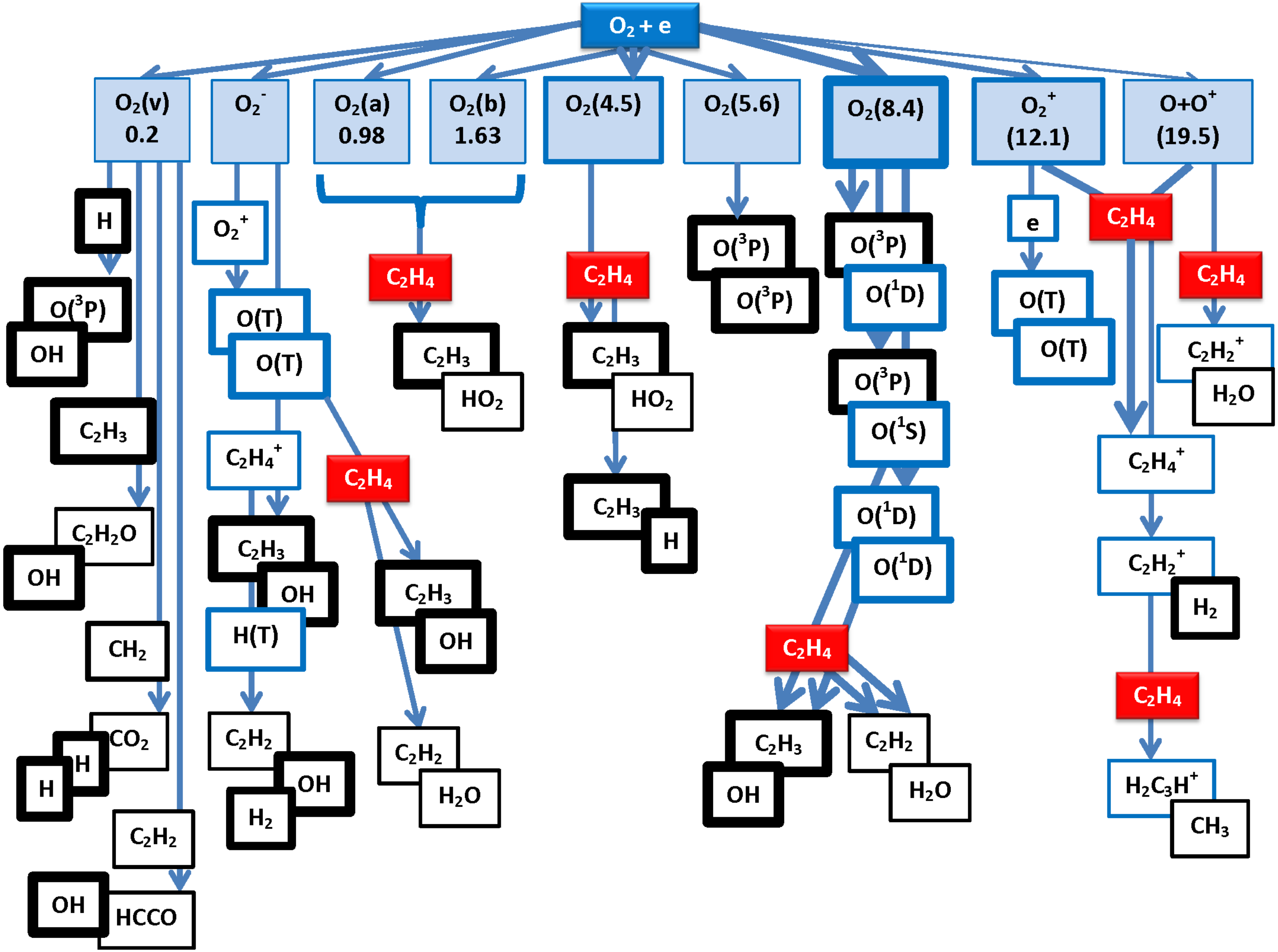
$C_2H_2^+$

H_2

$C_2H_3^+$

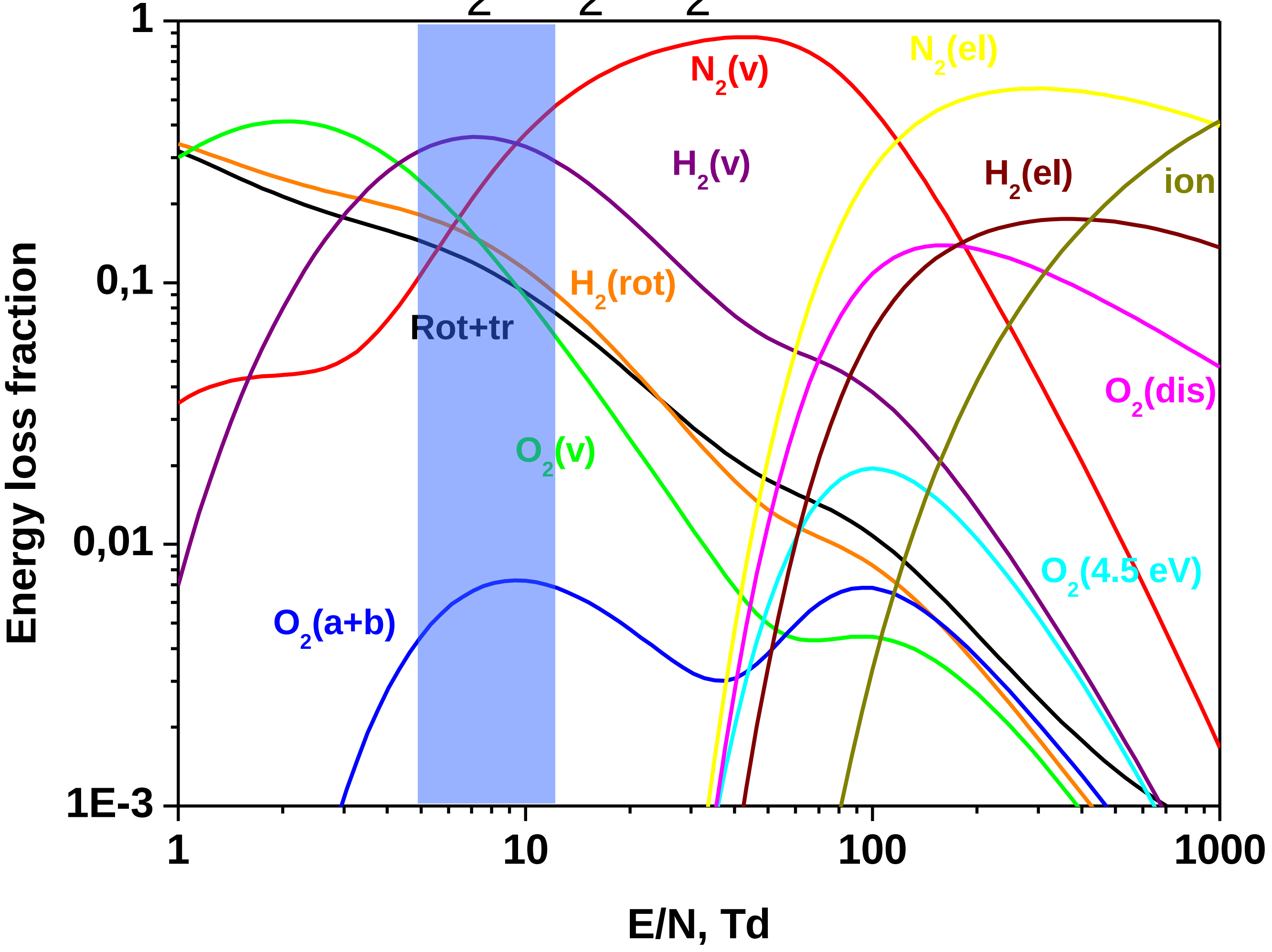
H

PAC Pathways: C_2H_4-air

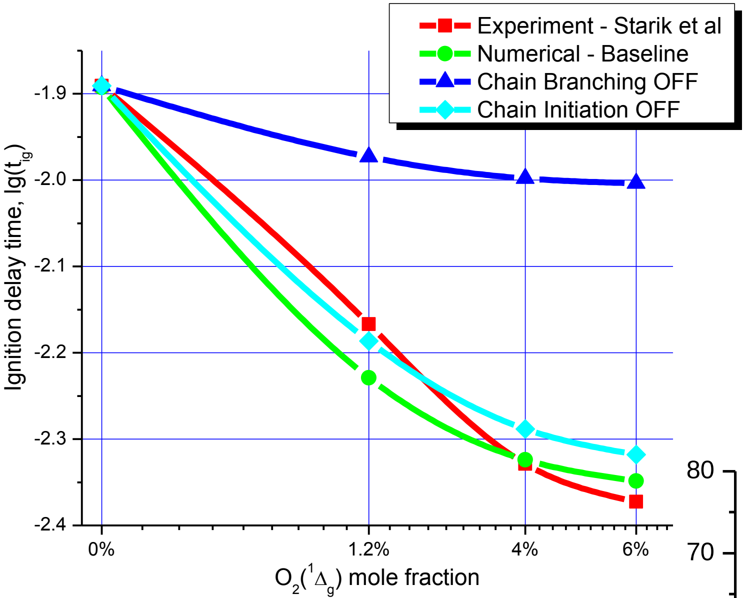


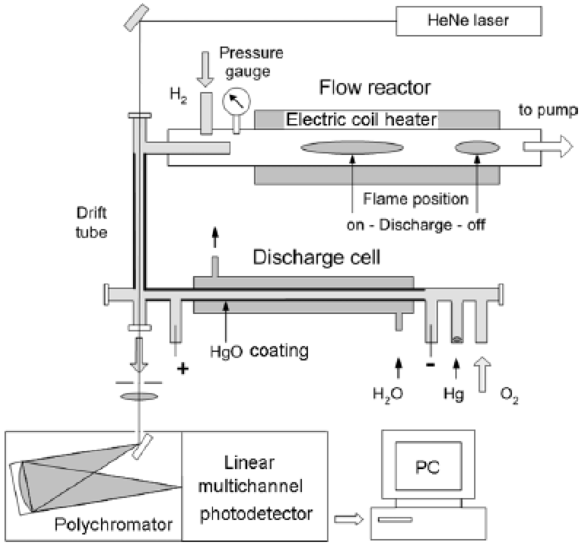
Electron Energy Distribution in Discharge Plasmas

$N_2:O_2:H_2 = 4:1:2$



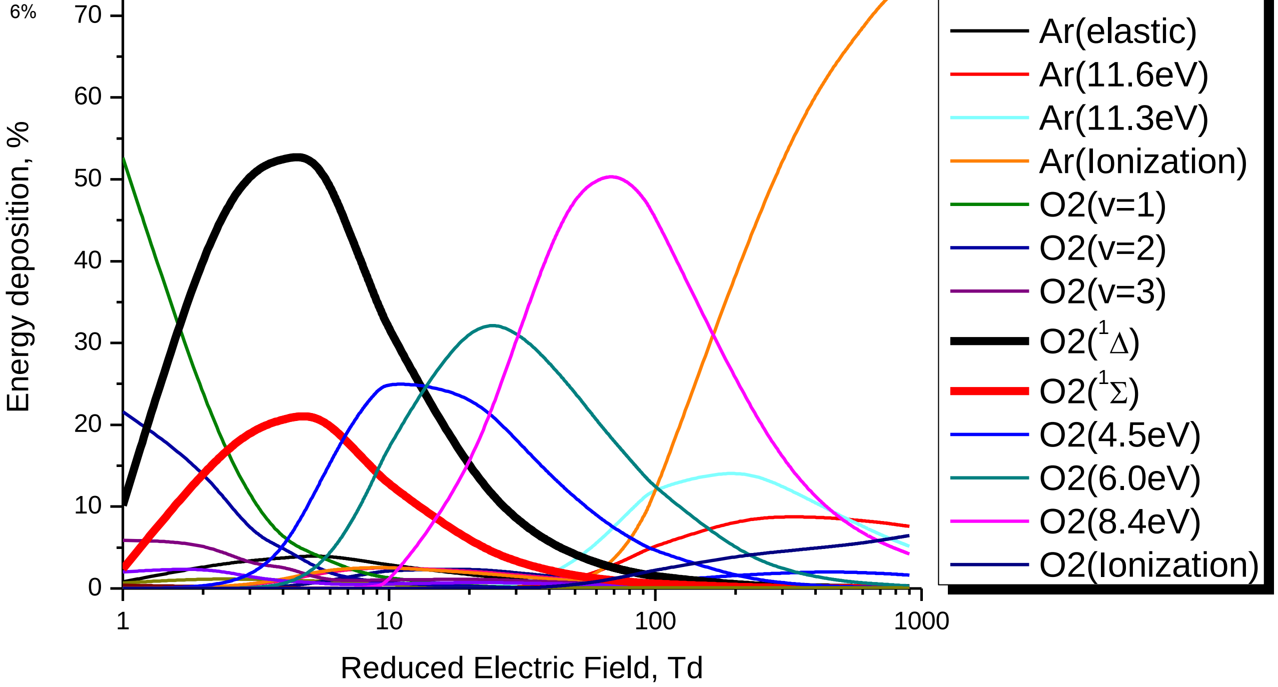
Plasma Assisted Ignition at Low E/n



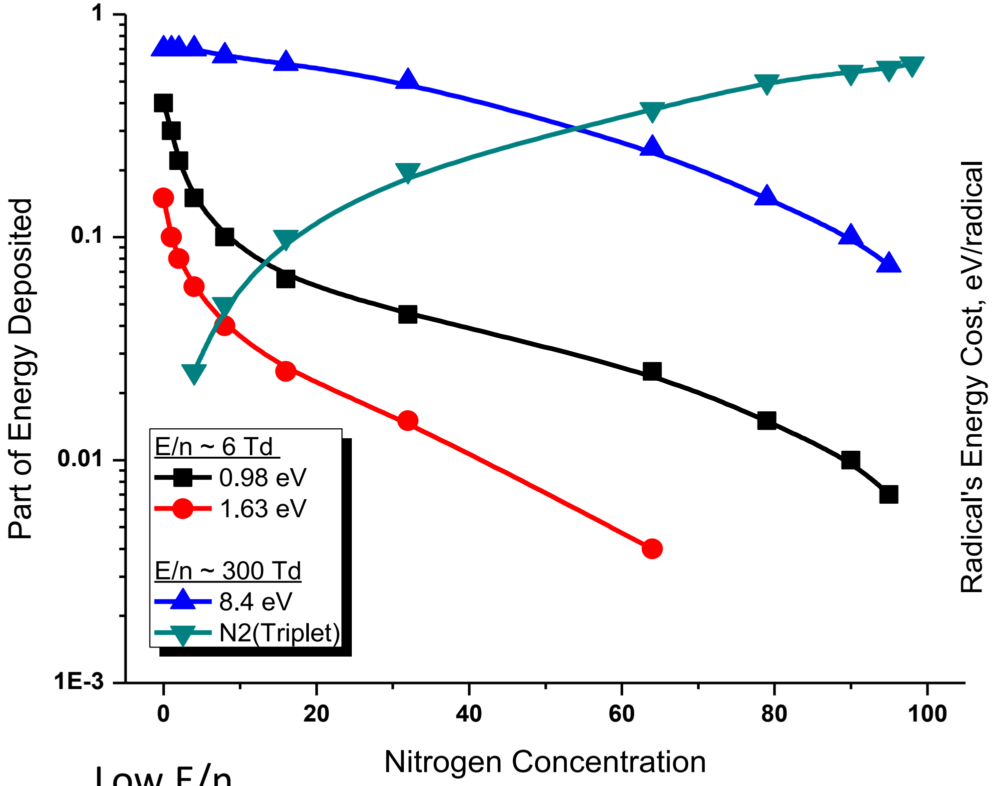


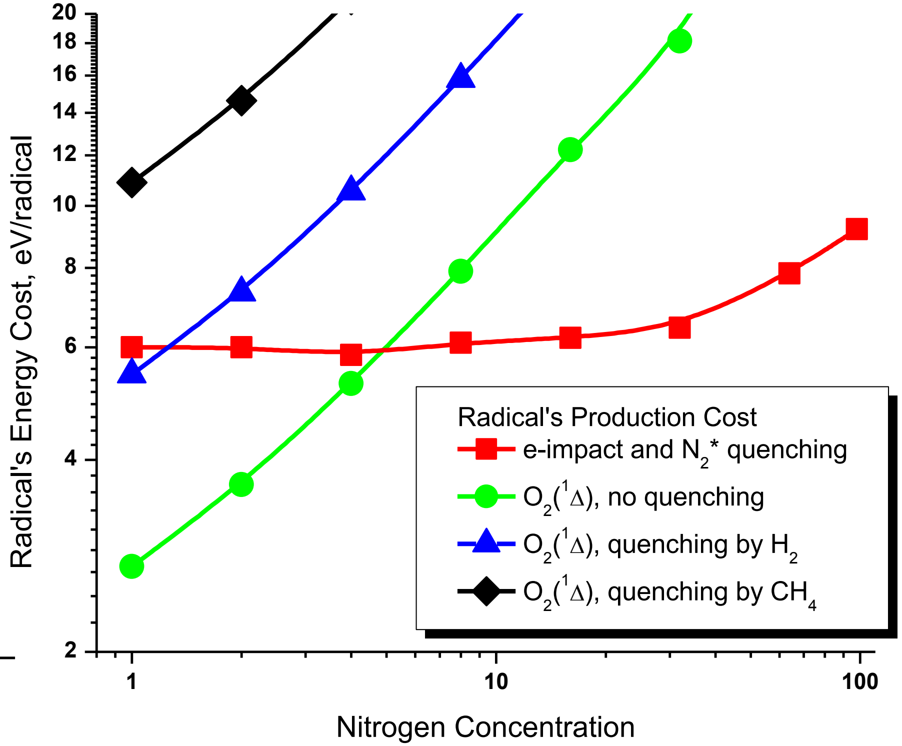
V V Smirnov, O M Stelmakh, V I Fabelinsky, D N Kozlov,
A M Starik and N S Titova,
J. Phys. D: Appl. Phys. **41** (2008)

Chain Branching:
$O_2(^1\Delta)+H=OH+O$



Energy Cost of Radicals Production at Different Nitrogen Concentrations





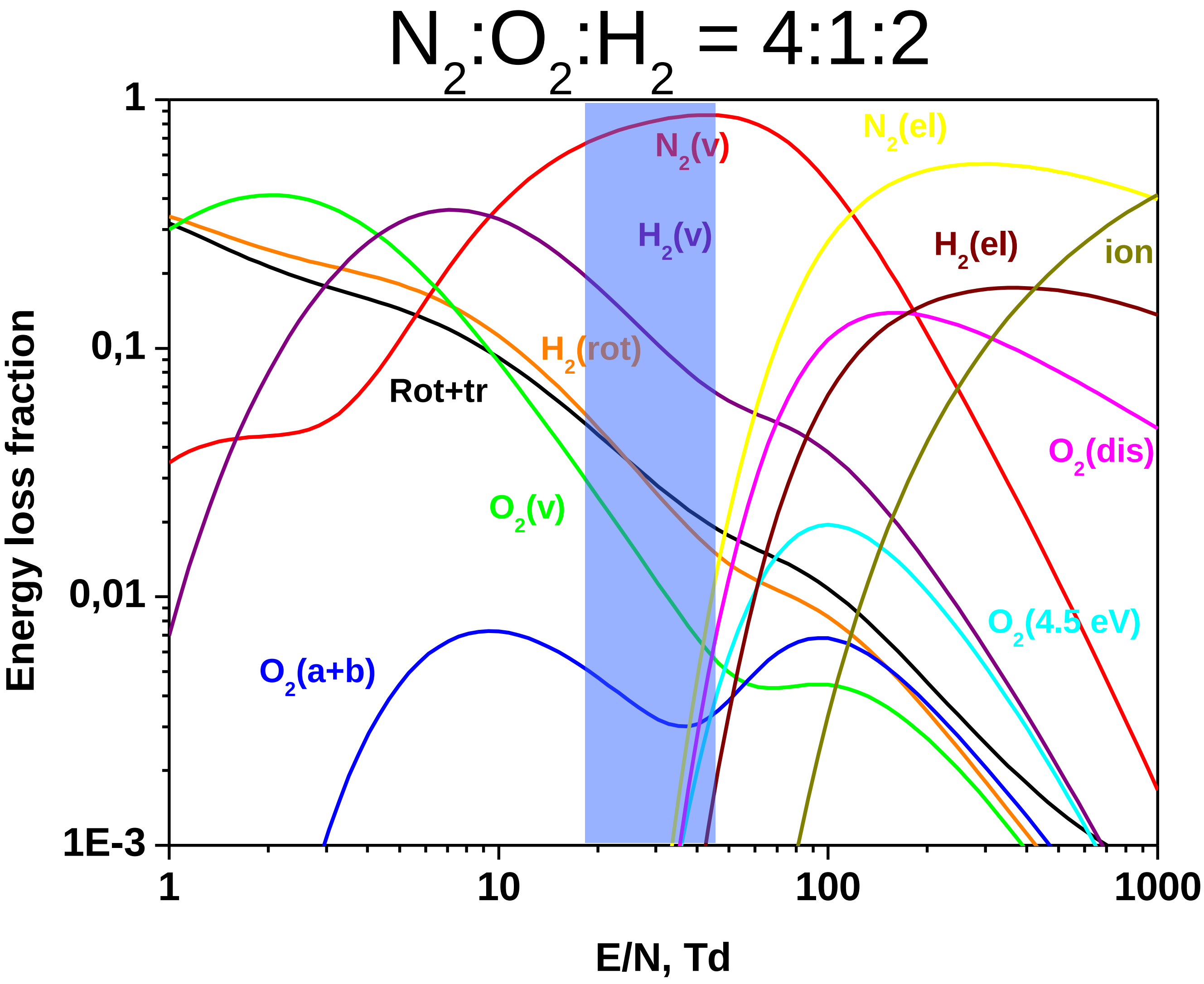
Low E/n

O2(1D) + H = OH + O
O2(1D) + H = O2 + H
O2(1D) + H2 = O2 + H2

High E/n

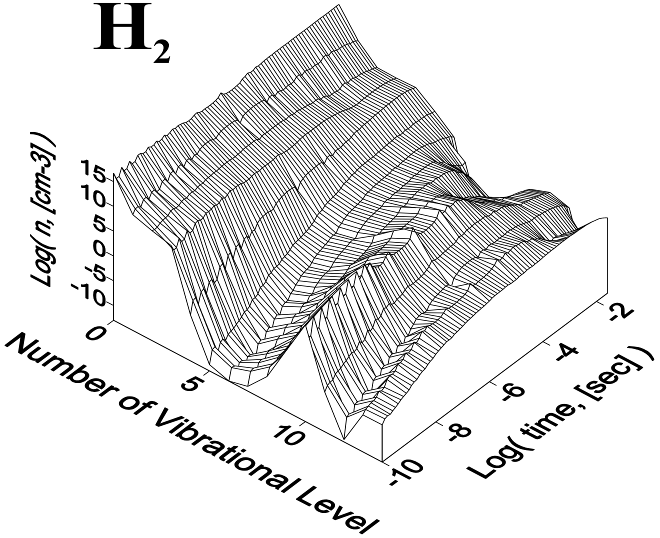
O2 + e = O + O + e
O2 + N2(A,B,C..) = O + O + N2

Electron Energy Distribution in Discharge Plasmas

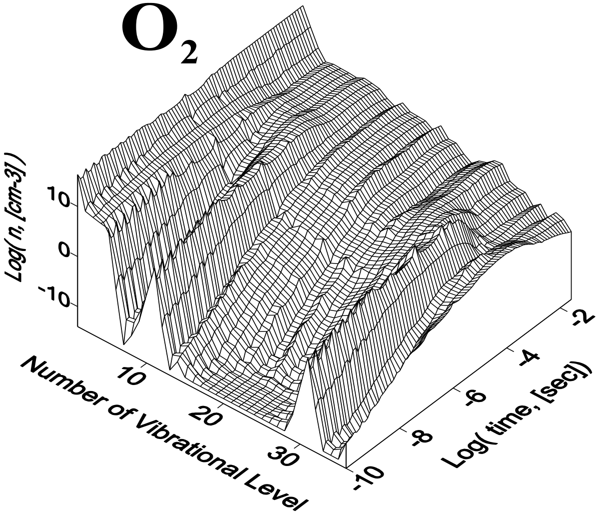


Vibrational Energy Distribution

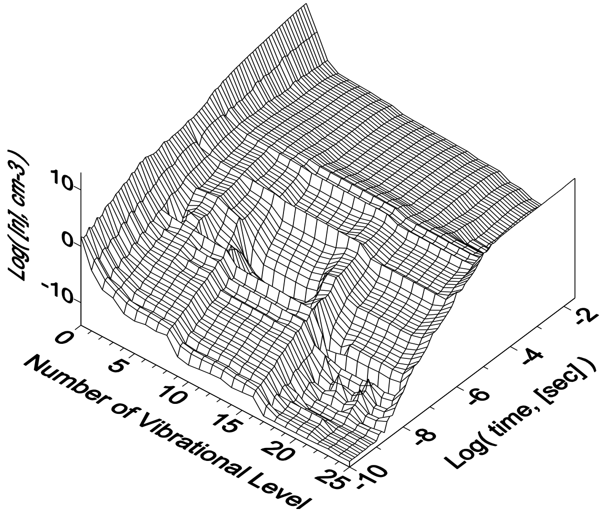
H_2



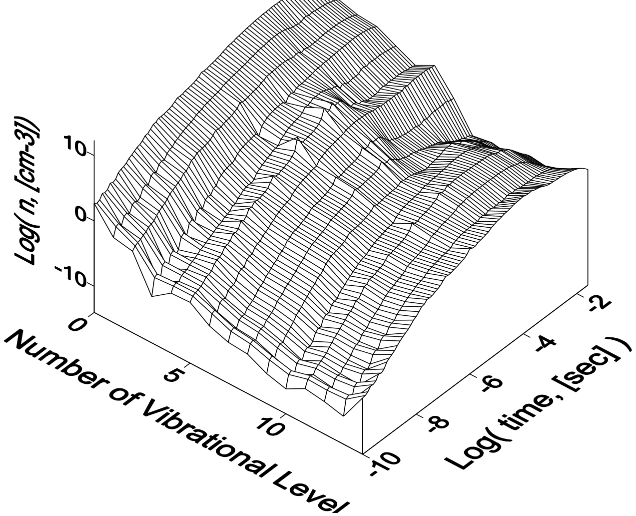
O_2



H_2O (defomational mode)

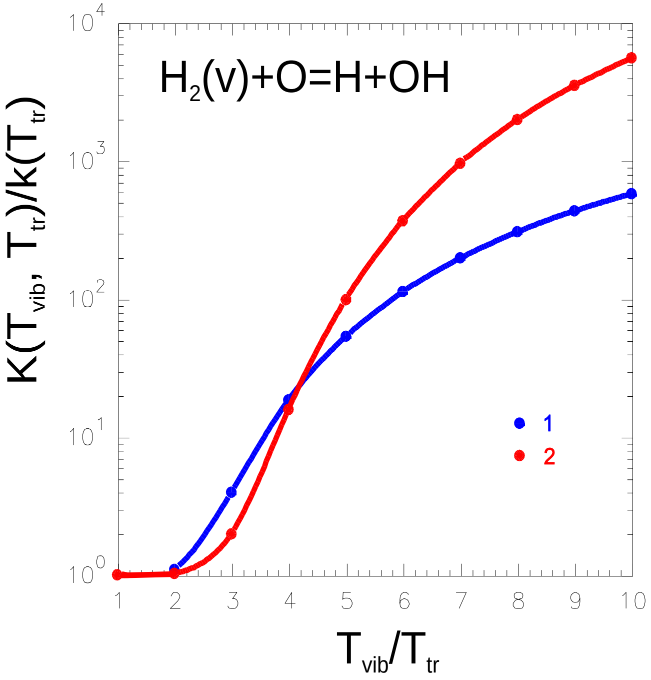


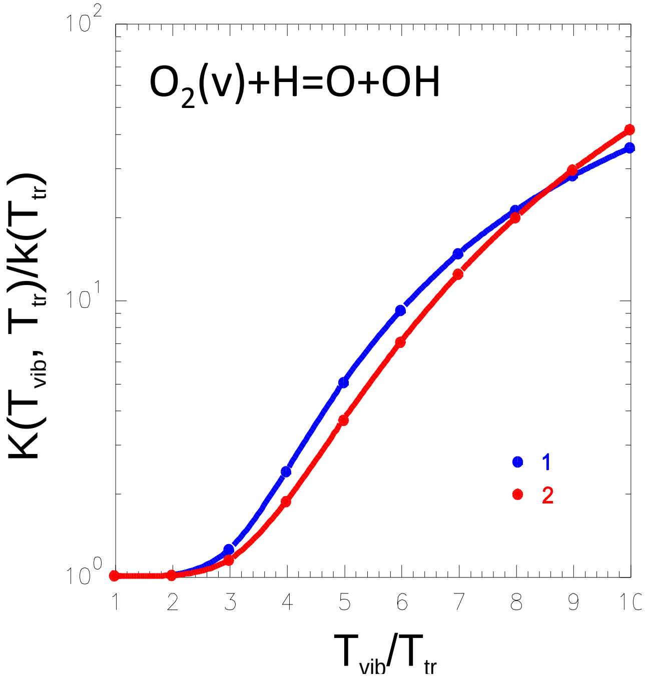
OH



Chemical Reactions with Excited Reagents

AB(v)+C = A +BC(w)
Rate constant from
modified α-model
(Starikovskii, Lashin 1996)



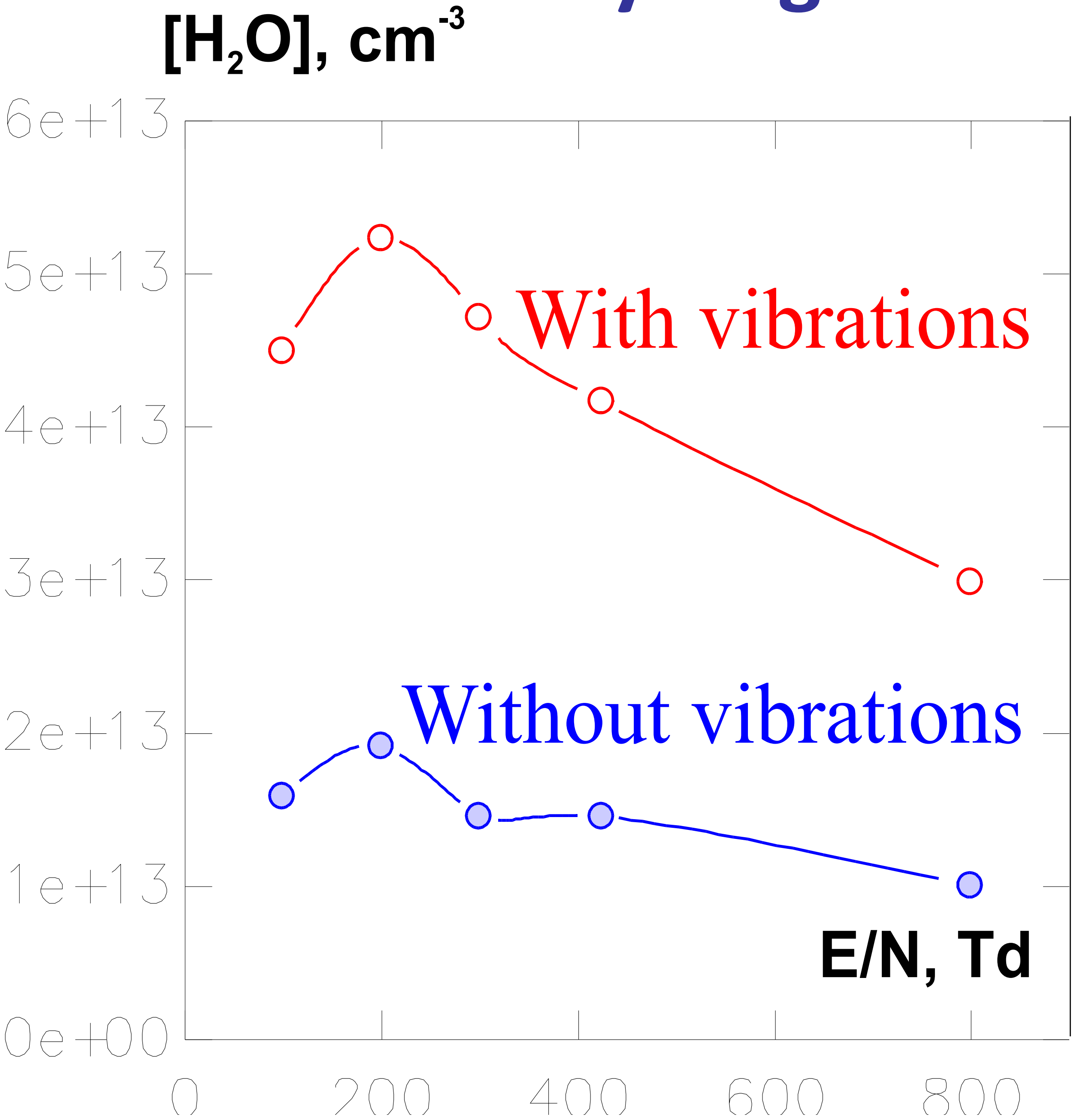


$$H_2(v=1) + O = OH(w=1) + H \qquad (R1)$$

$$H_2(v=0) + O = OH(w=0) + H \qquad (R2)$$

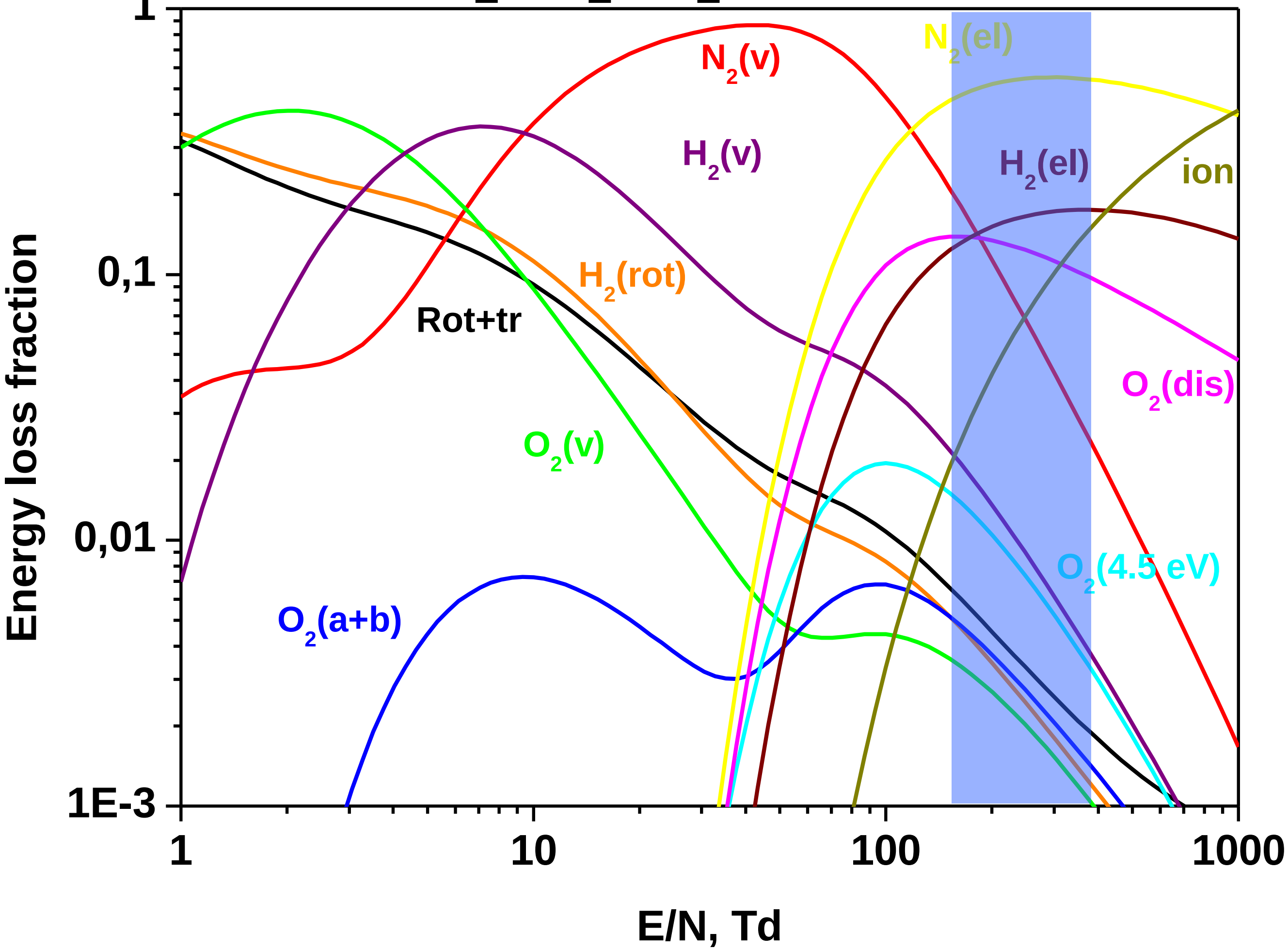
$(k_{R1}/k_{R2})_{exp}$ = 2600 (O'Neal, Benson 1973); $(k_{R1}/k_{R2})_{theor}$ = 2750

Hydrogen Oxidation Rate



Electron Energy Distribution in Discharge Plasmas

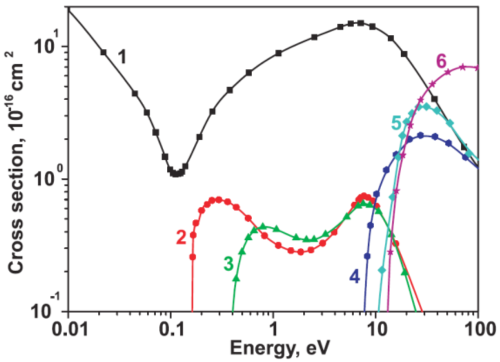
$N_2:O_2:H_2 = 4:1:2$



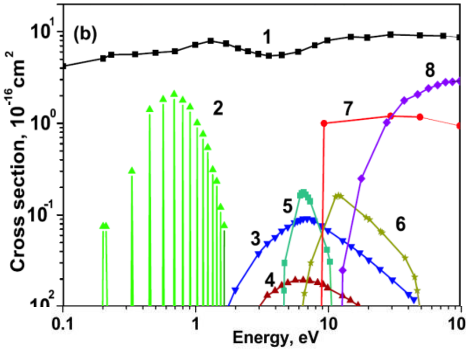
Pulse Current Dynamics – Shock Tube

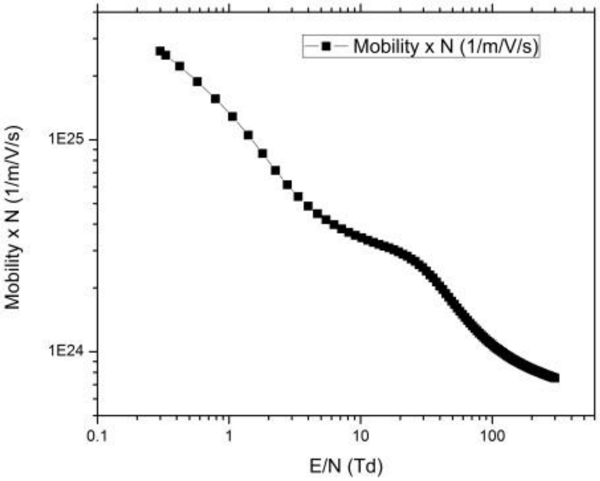
$C_2H_6:O_2:N_2:Ar = 2:7:28:63$

Ethane. Hayashi 1987

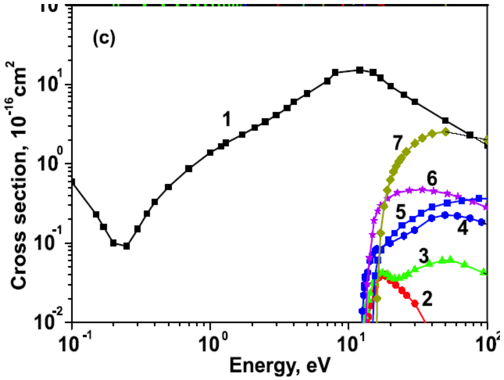


Oxygen. Ionin 2007

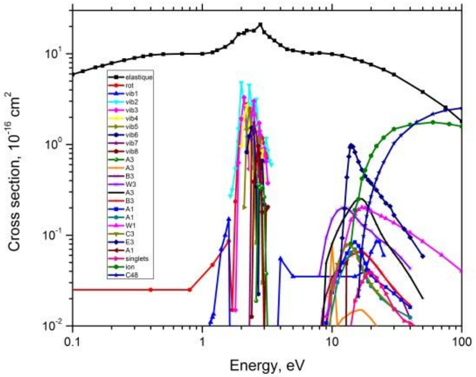


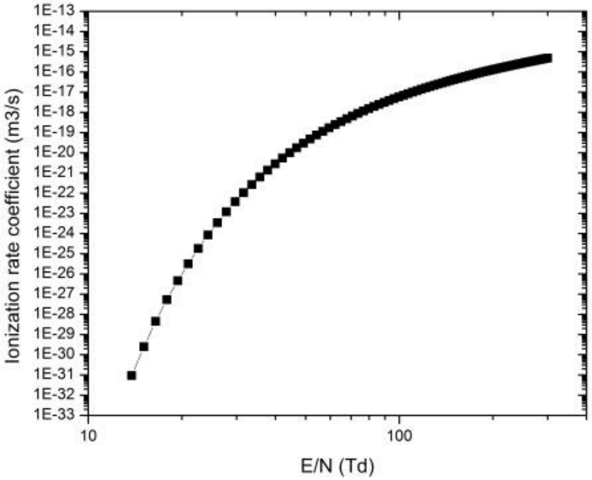


Argon. Tachibana 1989



N_2. Phelps 1994





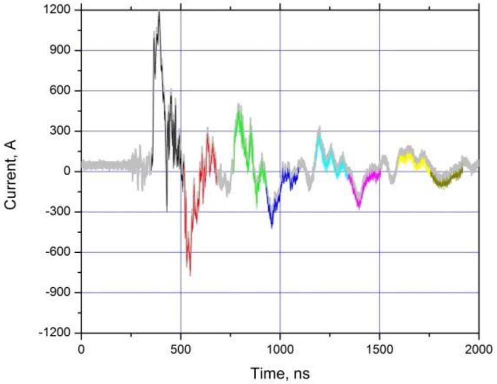
$$\frac{\partial(nf)}{\partial t}+\mathbf{v}\nabla(nf)+\frac{Ze}{m}\{\mathbf{E}+\tfrac{1}{c}[\mathbf{v}\times\mathbf{H}]\}\nabla_v(nf)=S(nf)$$

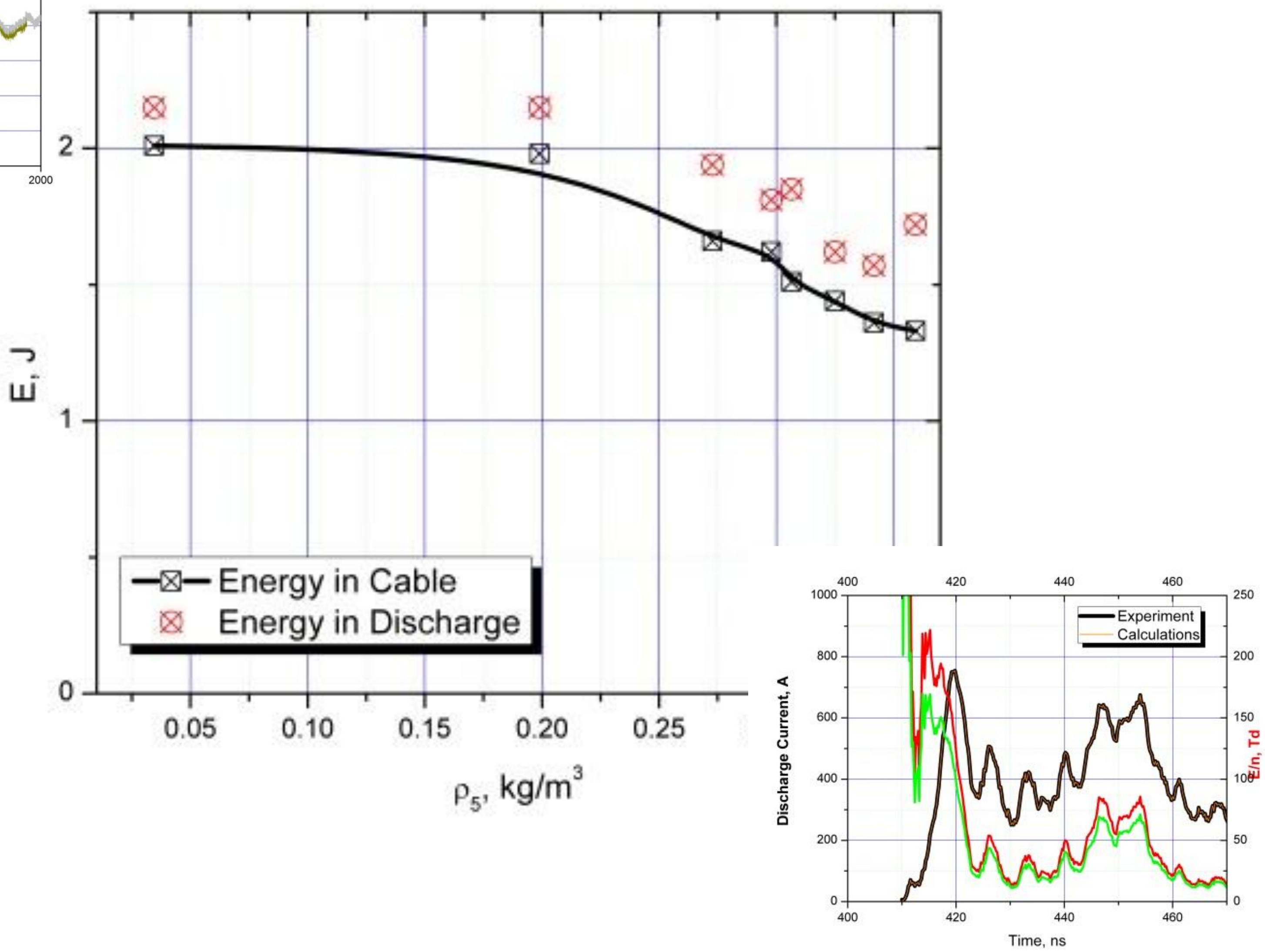
$$f(v,\theta)=\sum_{l=0}^{\infty} f_l(v)P_l(\cos\theta)\approx f_0(v)+f_1(v)\cos\theta$$

$$\nu_\varepsilon/\nu_m \ll 1$$

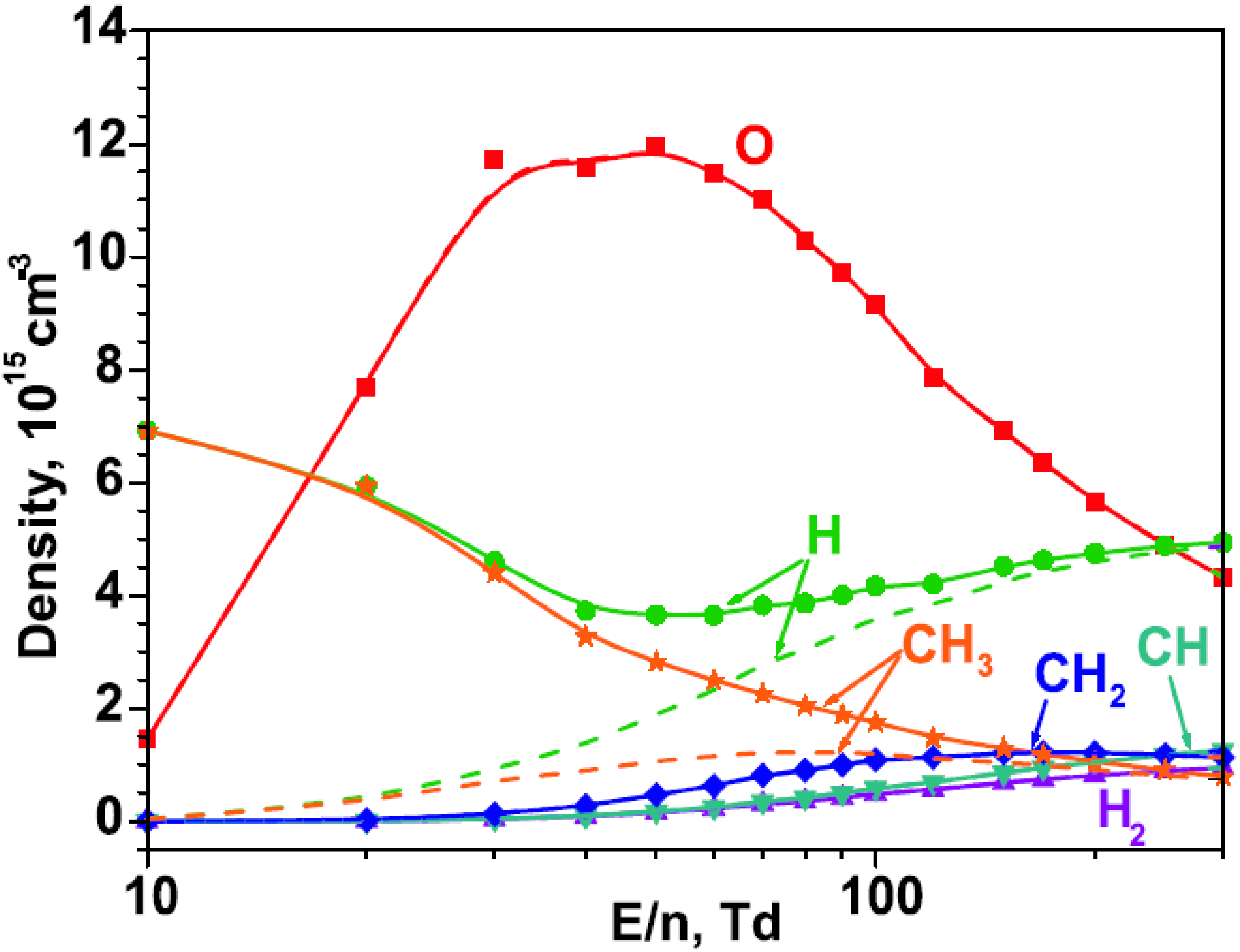
Discharge Energy Comparison

$C_2H_6:O_2:N_2:Ar = 2:7:28:63$

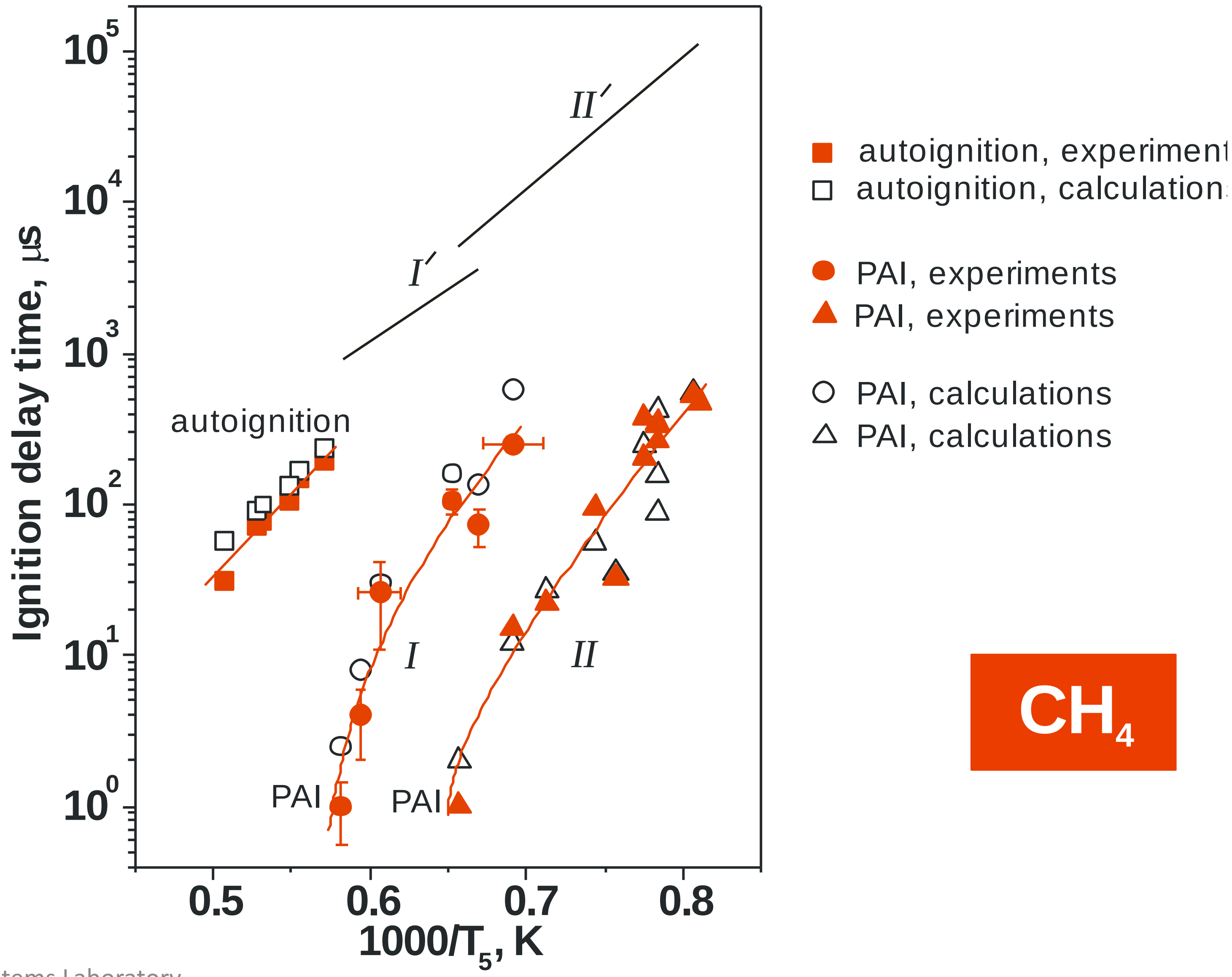




Radicals Production in Discharge CH_4-O_2-Ar mixture

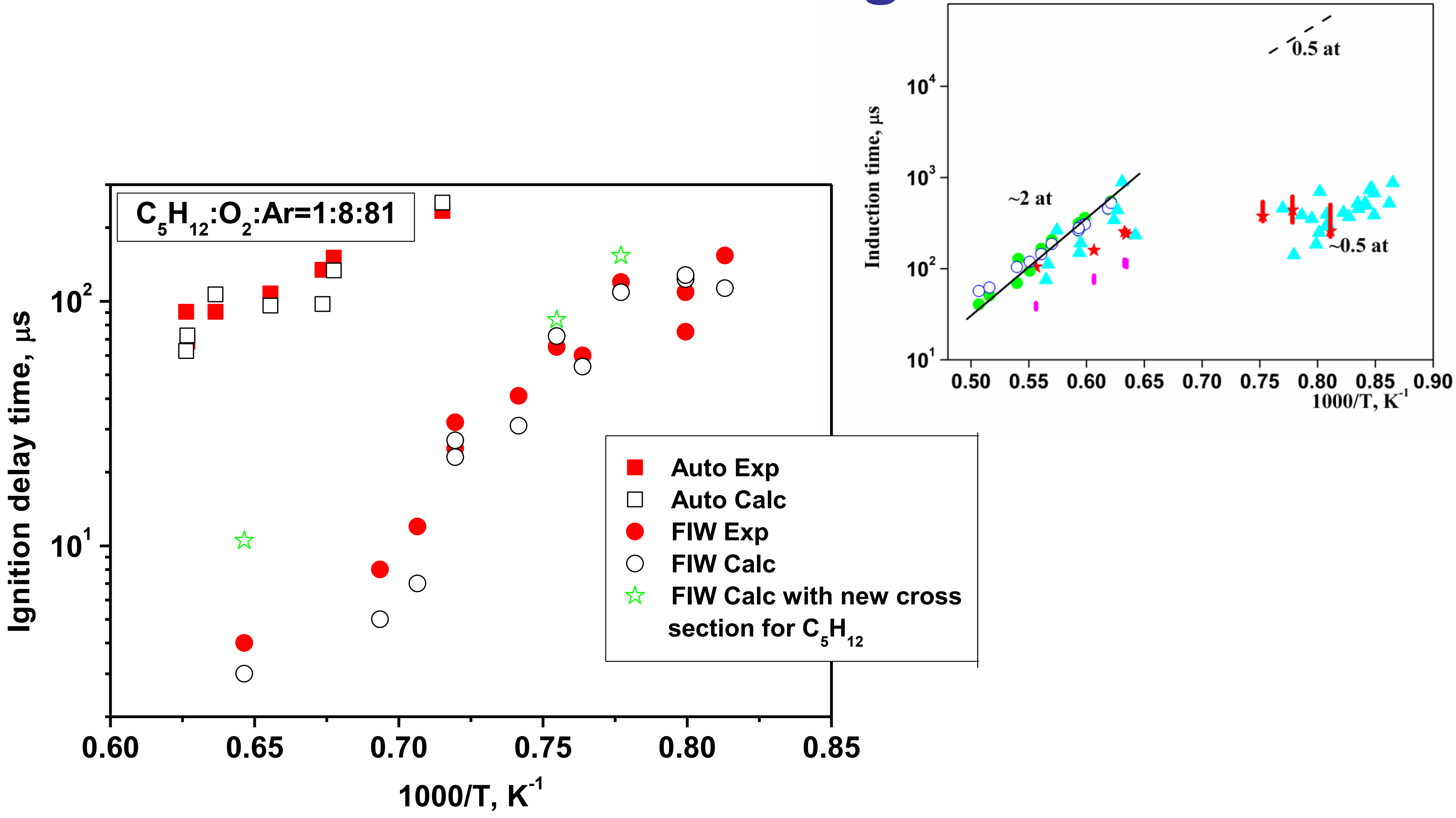


Ignition Delay Time: Methane-Containing Mixture

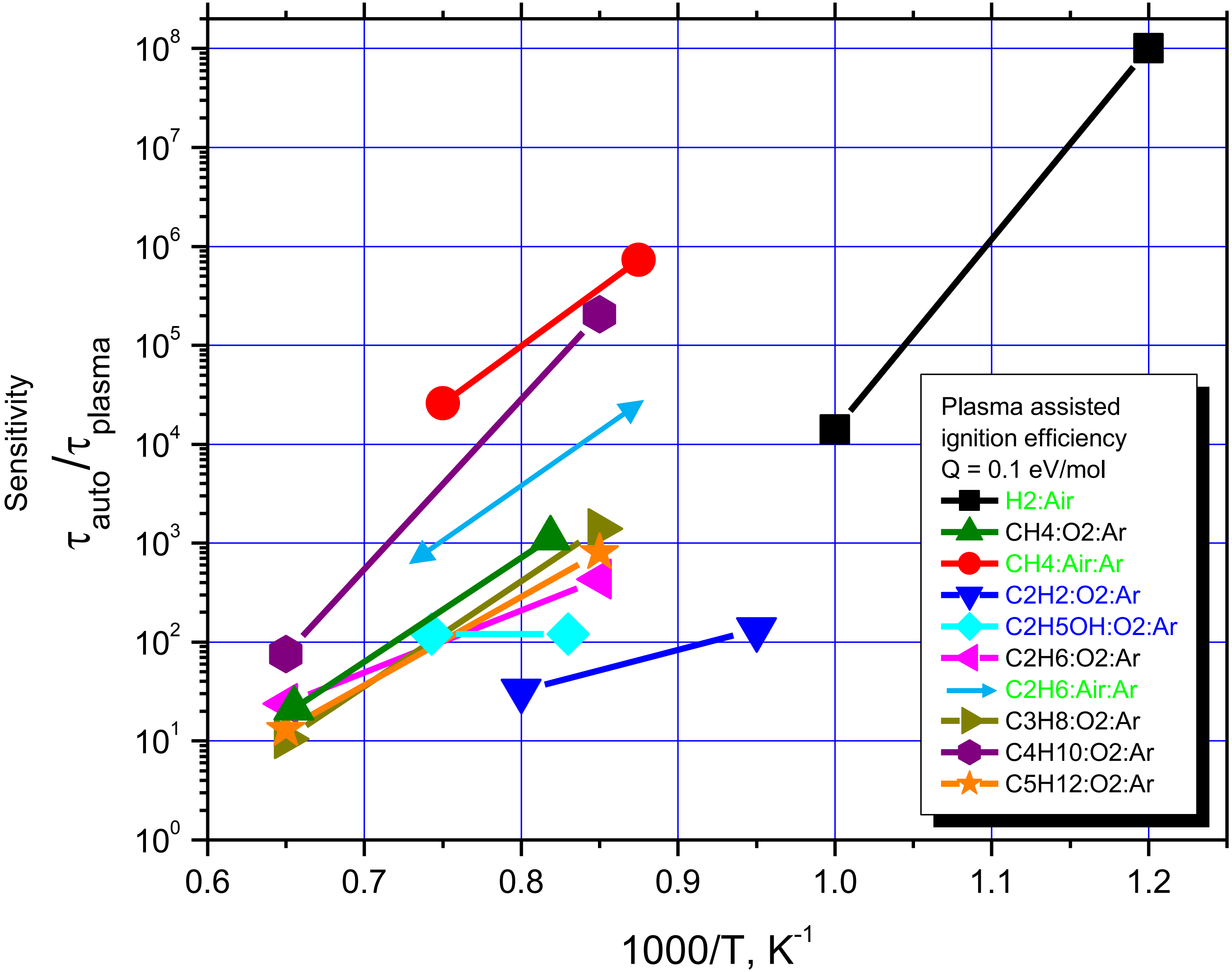


CH$_4$

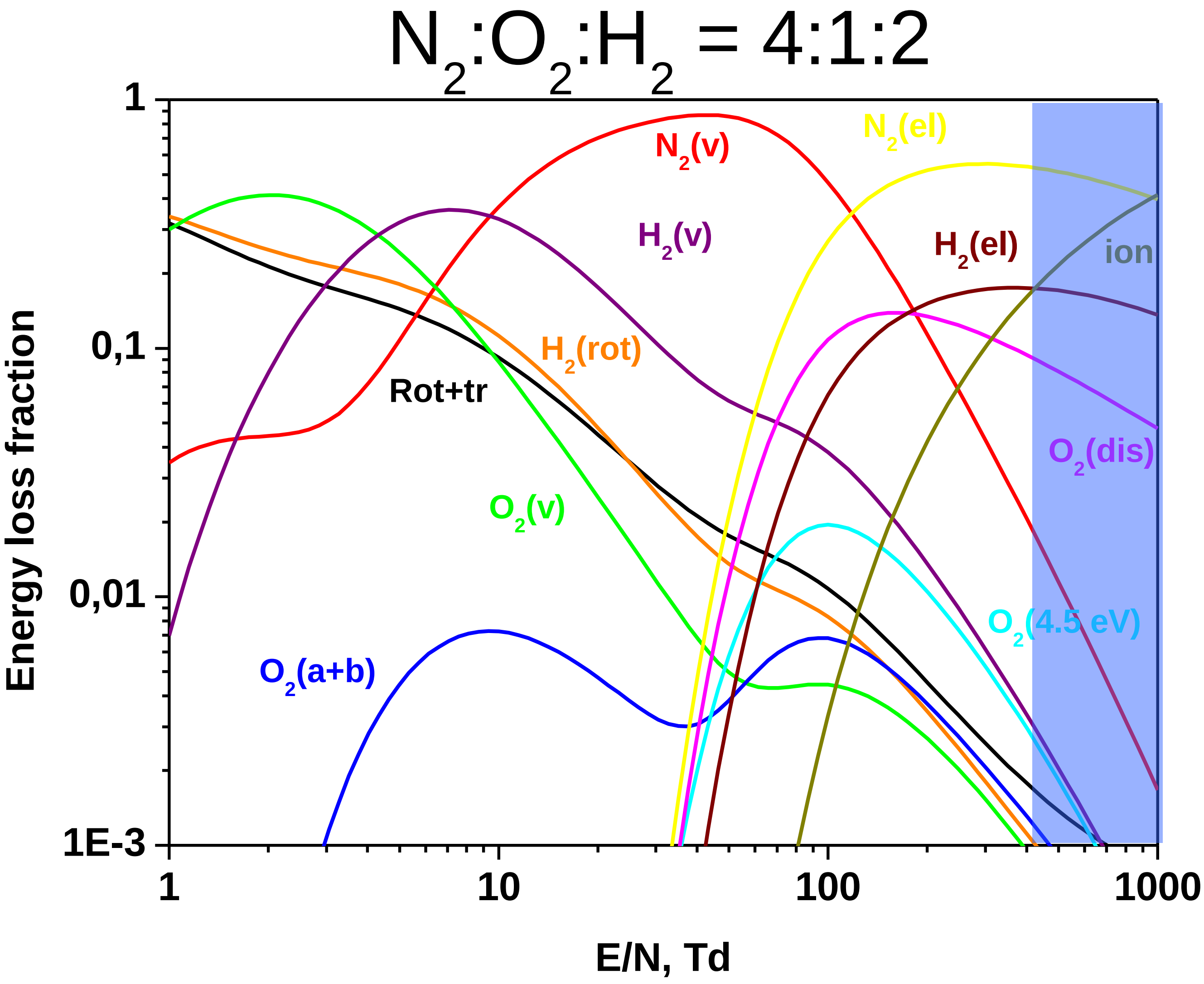
Pentane-Oxygen and Methane-Air Plasma Assisted Ignition



Plasma Ignition Sensitivity
0.1 eV/mol



Electron Energy Distribution in Discharge Plasmas



Ionic Oxidation Mechanisms: Low Energy Thresholds

$$O_2 + e^- + M \rightarrow O_2^- + M$$

$$H_2 + O_2^- \rightarrow OH^- + OH \qquad k = 0.4\text{x}10^{-10}$$

$$OH + H_2 \rightarrow H_2O + H$$

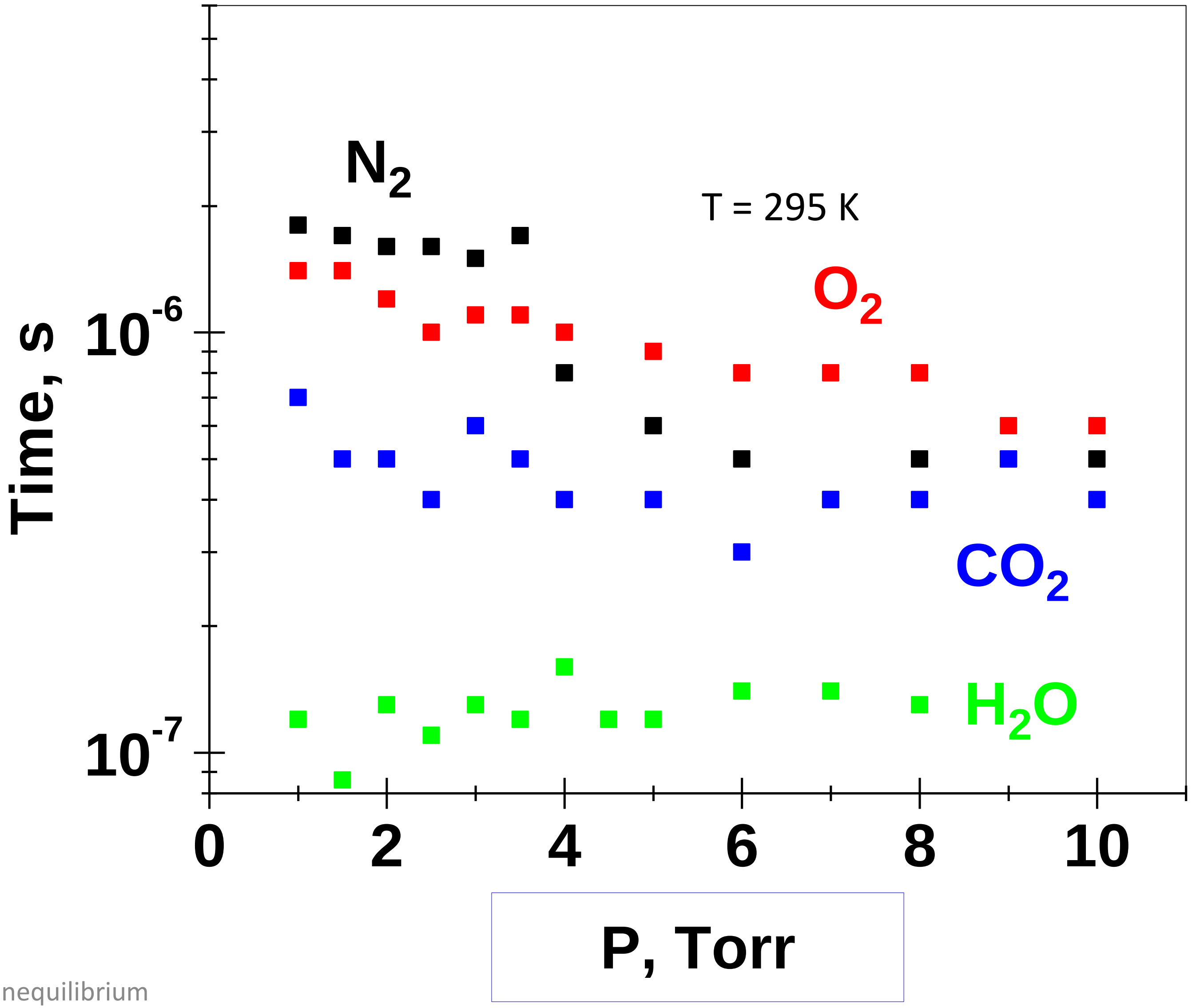
$$OH^- + H \rightarrow H_2O + e^- \qquad k = 1.4\text{x}10^{-9}$$

$$H + O_2 + M \rightarrow HO_2 + M$$

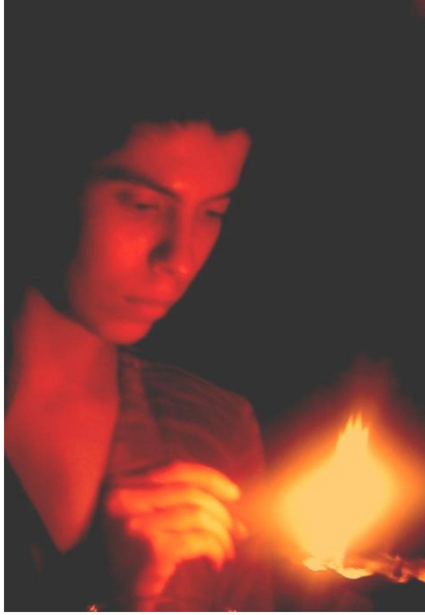
$$OH^- + HO_2 \rightarrow H_2O + O_2 + e^- \qquad k = 1.0\text{x}10^{-9}$$

I.N.Kosarev, A.Yu.Starikovskii. Mechanism for Electric Breakdown in a Chemically Nonequilibrium System and the Influence of the Chain Oxidation Reaction in an H2–Air Mixture on the Breakdown Threshold. Plasma Physics Reports, 2000. V.26. N.8. P.701.

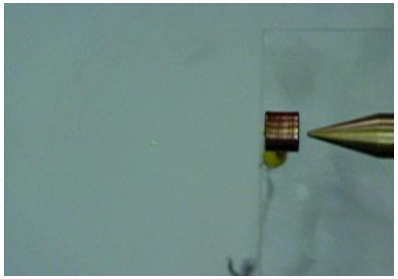
Plasma Decay Time at T = 295 K



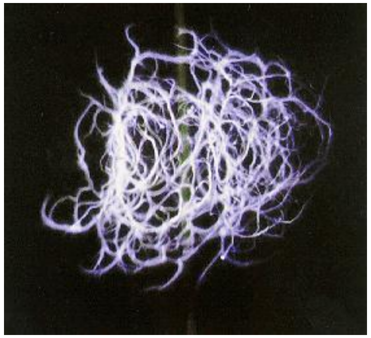
Mechanisms of Plasma/Flame Interaction



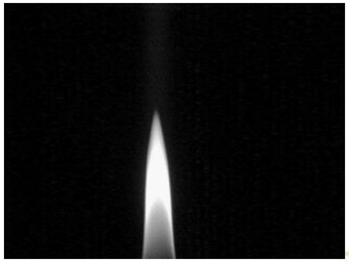
1. Heating



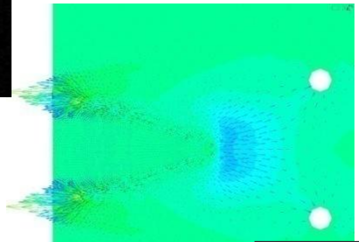
2. Turbulization



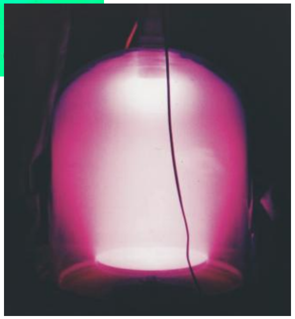
3. Momentum Transfer



4. Electrons/Ions Diffusion/Drift



5. Excitation, Dissociation, Ionization



SDBD Discharge and Fast Heating

Gate = 0.5 ns

Time shift between frames is 1 ns

The movie duration is 41 ns

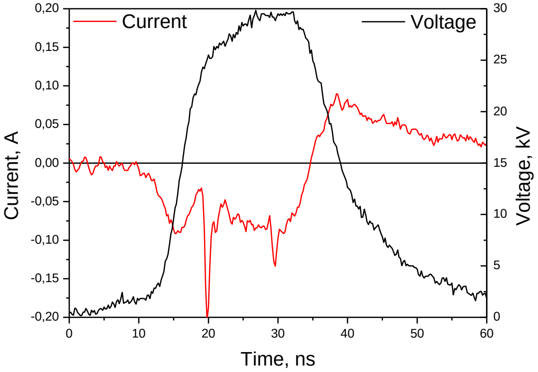
Impulse Parameters

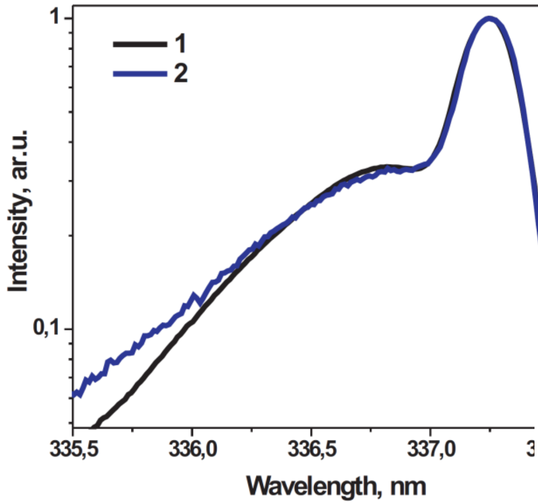
V = 14 kV

$t_{1/2}$ = 20 ns

Frequency = 1 kHz

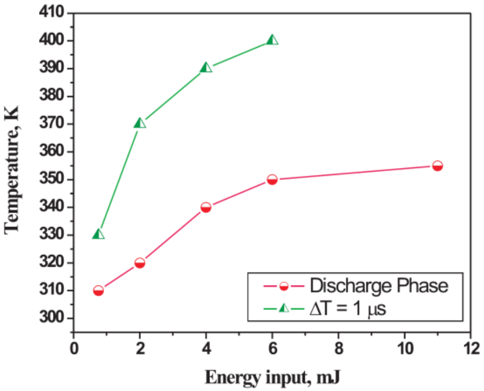
Velocity = 0.4 mm/ns





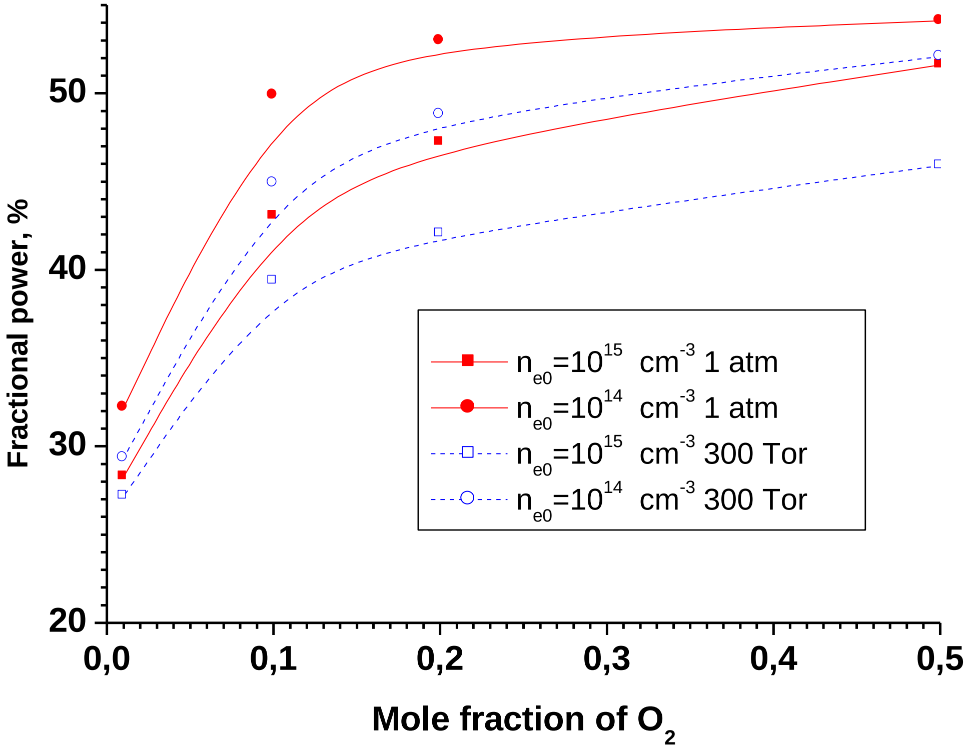
1- 0-30 ns

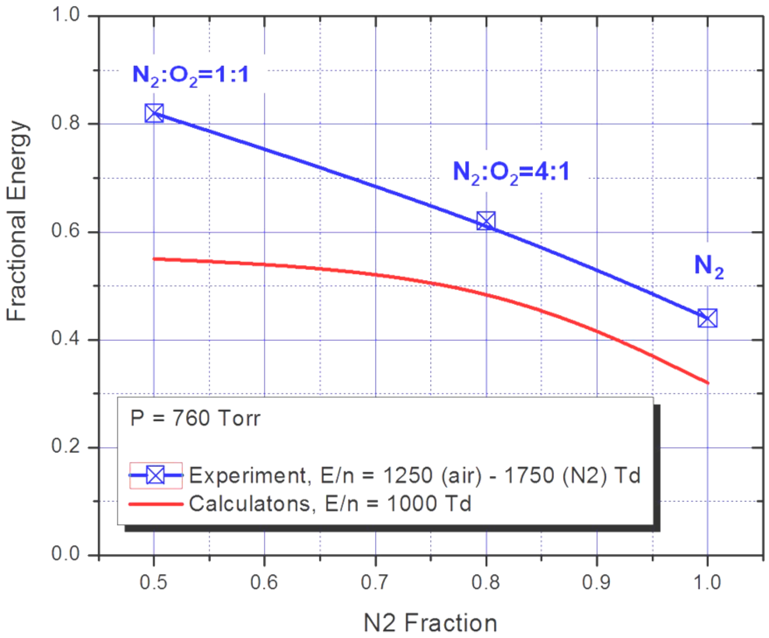
2- 1000-1030 ns



Fractional Electron Power Transferred Into Heat in N_2:O_2 Mixtures

$E/N = 10^3$ Td





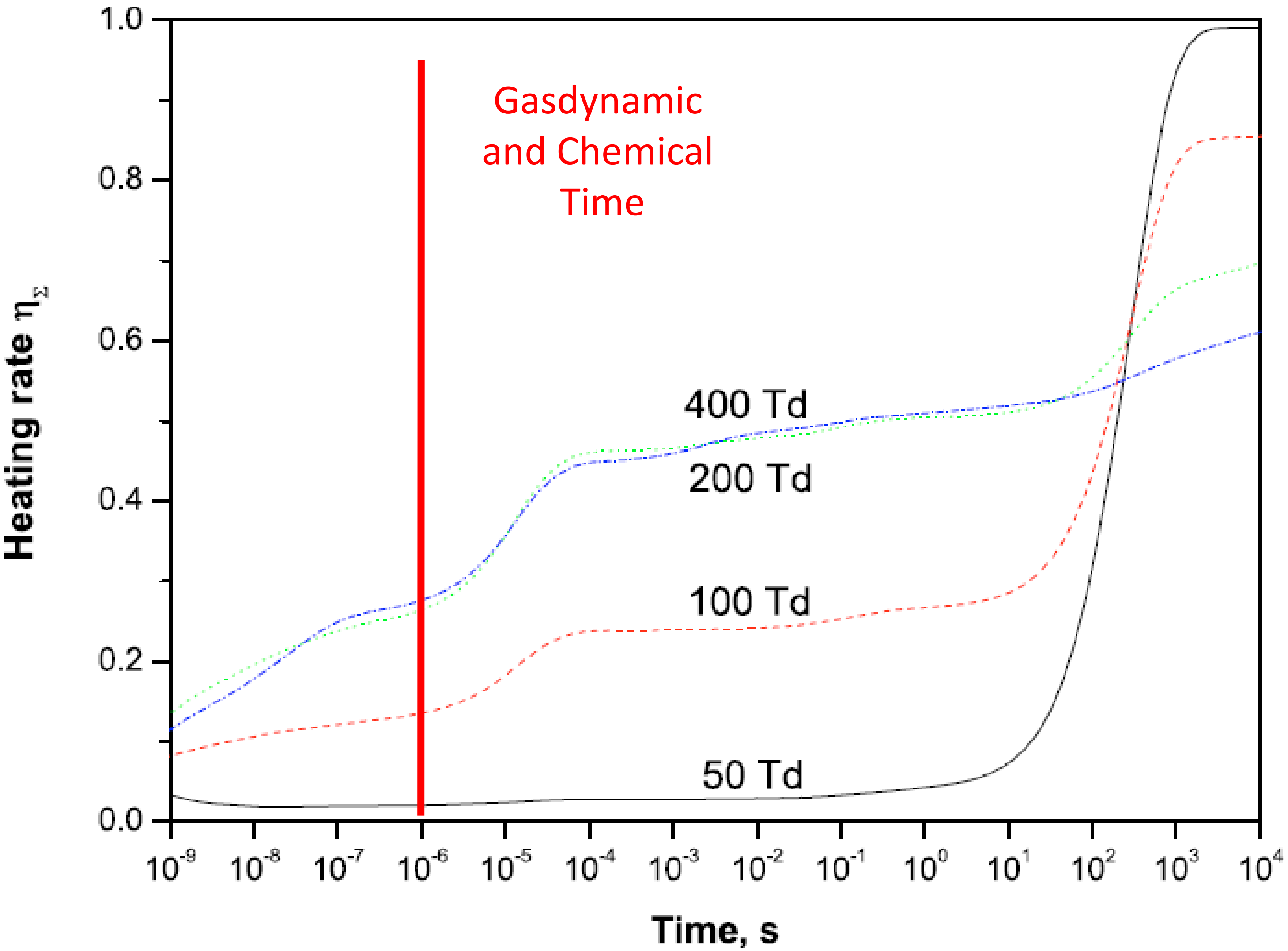
Oxygen is required for efficient fast heating!

$AB^+ + O_2^-$ (+ M) → products + ΔE

N_2(A,B,C,a) + O_2 → e + 2O + ΔE

…

Heating Rate Calculated for Different Electric Fields in Dry Air at Normal Conditions



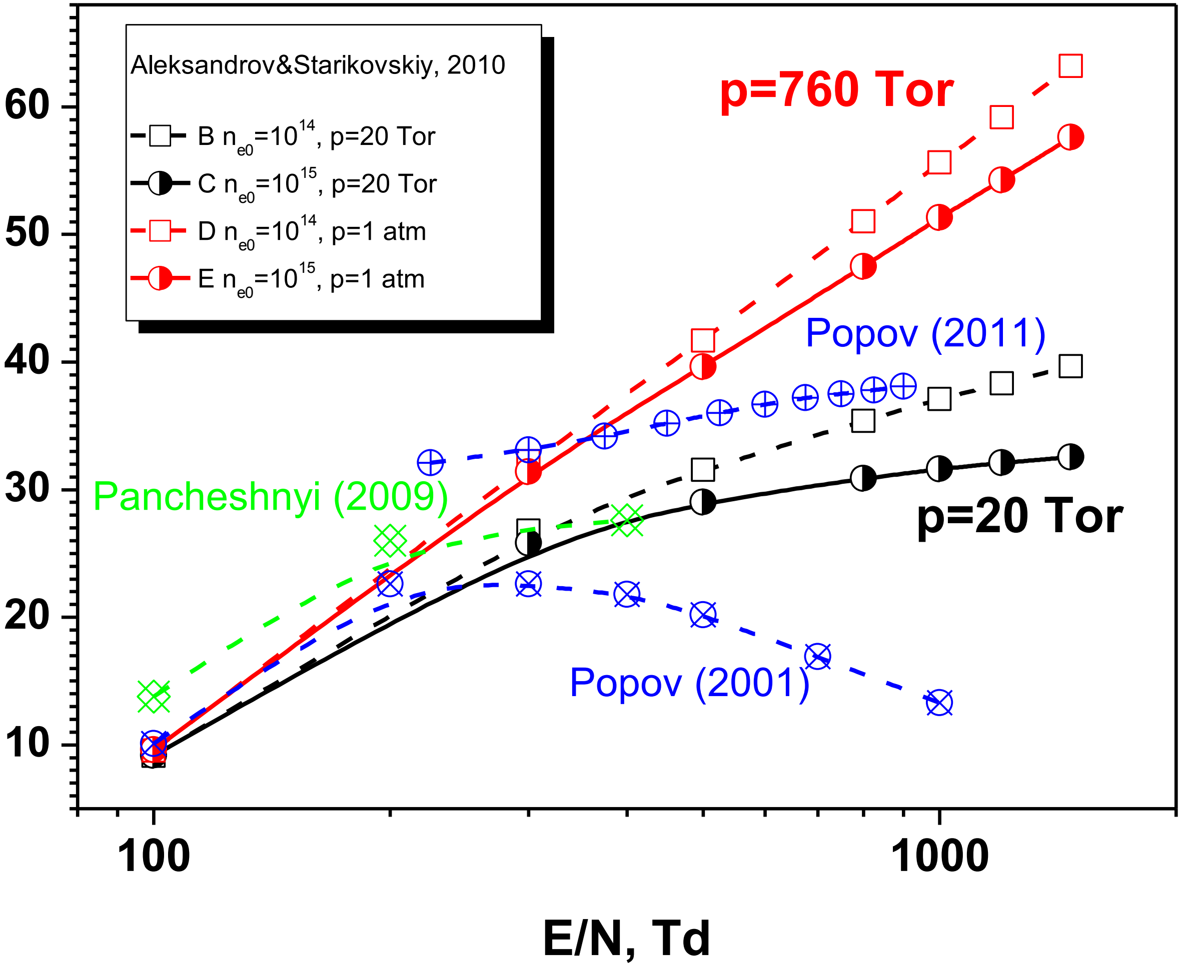
Flitti et al., Eur. Phys. J. Appl. Phys. 45, 21001 (2009)

Mechanism of Fast Heating in Discharge Plasmas (high E/N)

$e + O_2^+ \rightarrow O + O^* + \Delta E$

$O_2^- + O_2^+ \rightarrow O_2 + O_2 + \Delta E$

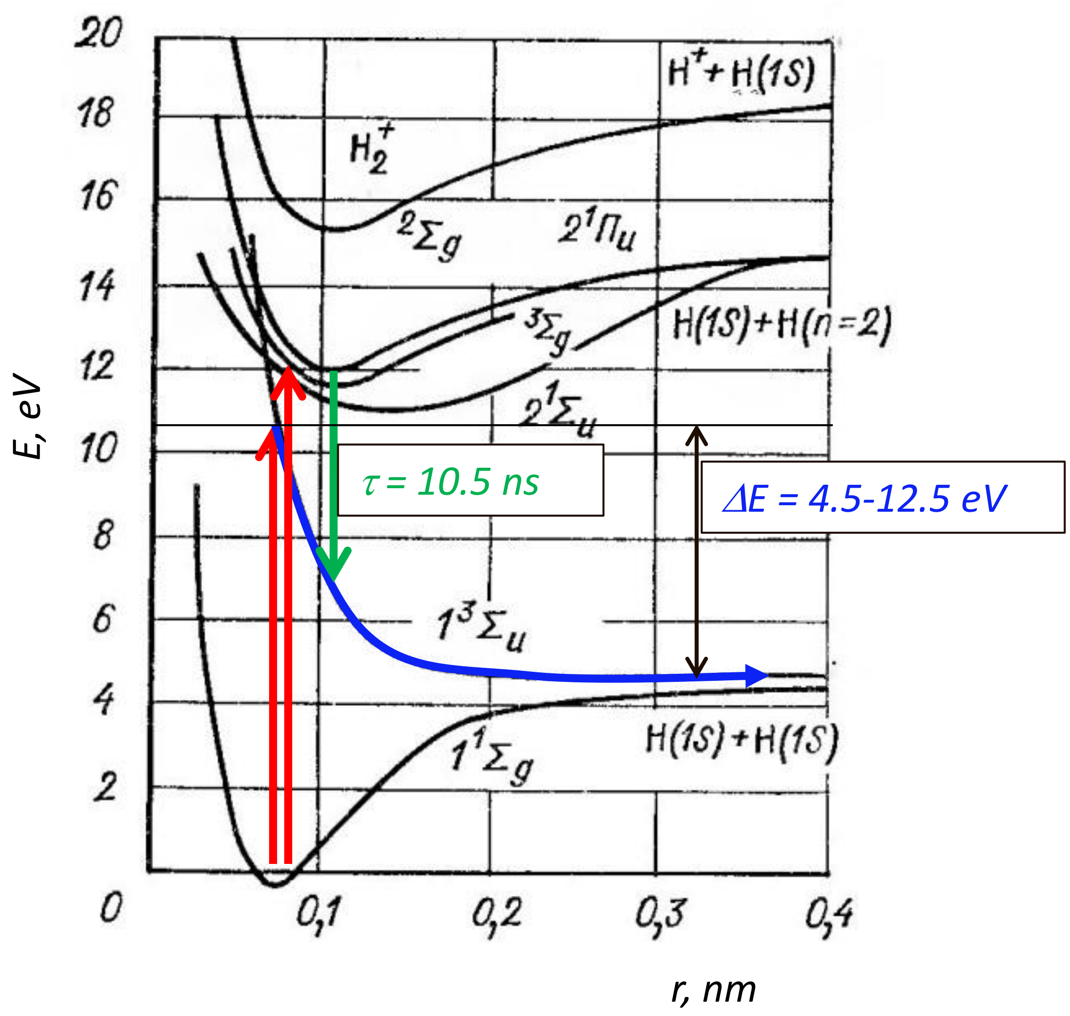
$e + O_4^+ \rightarrow O_2 + O_2 + \Delta E$



High (> 200 Td) E/N:

electron-ion and ion-ion recombination kinetics

Potential Energy Curves of Molecular Hydrogen



τ = 10.5 ns

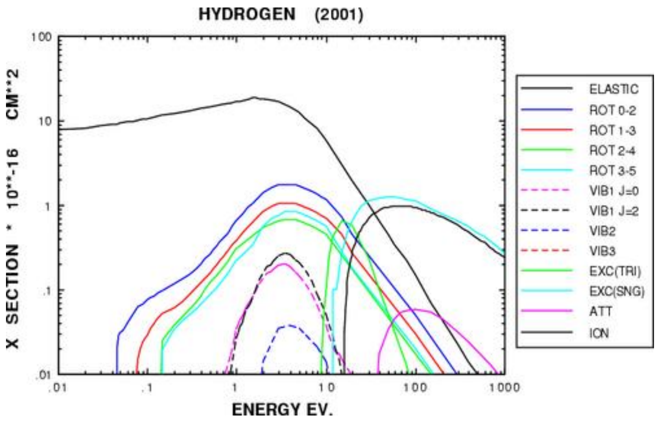
ΔE = 4.5-12.5 eV

$H_2(b^3\Sigma_u)$, 8.9 eV
σ_{max} = 0.33 A^2 (17 eV)

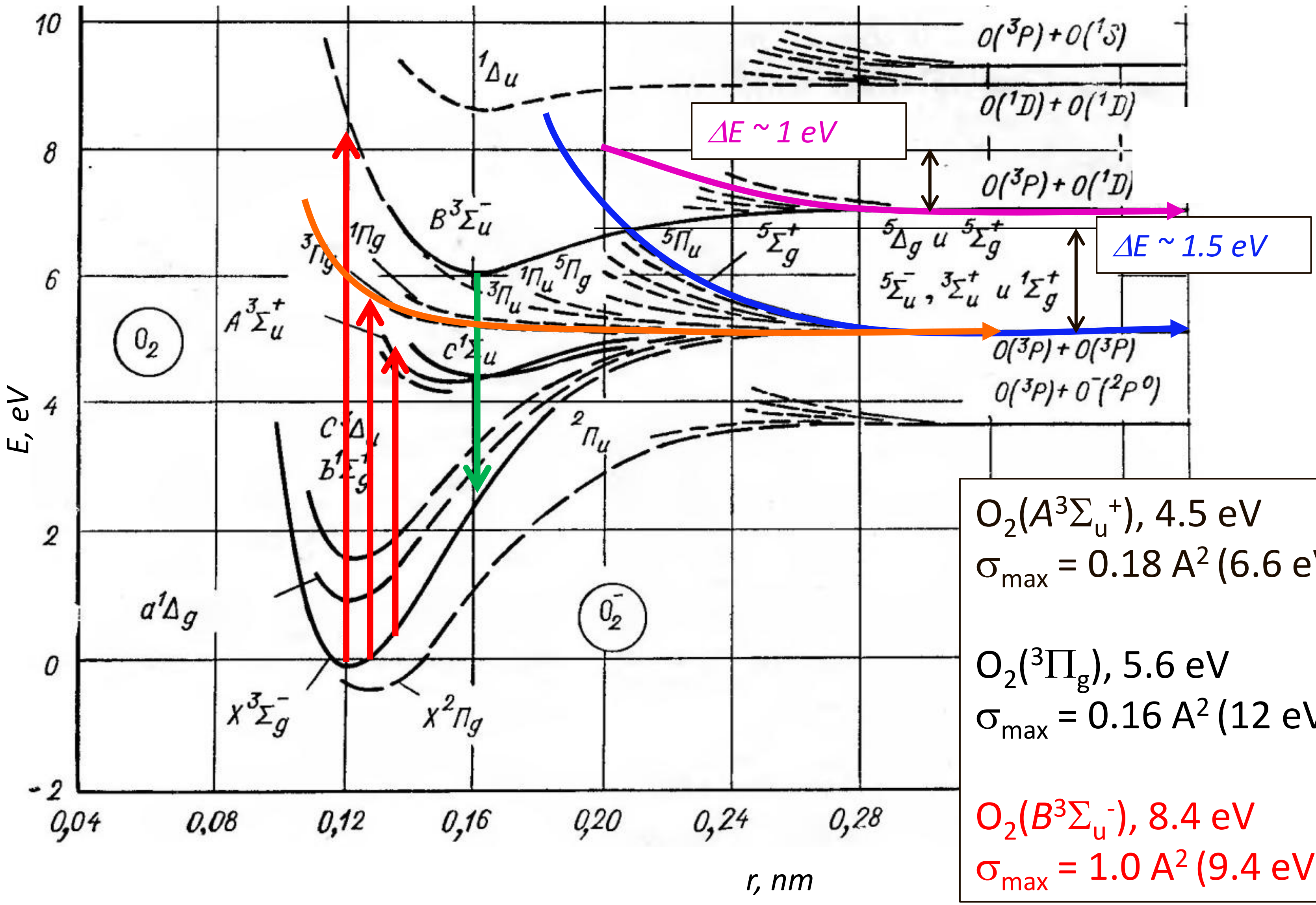
$H_2(a^3\Sigma_g)$, 11.8 eV
σ_{max} = 0.12 A^2 (15 eV)

$H_2(B^1\Sigma_u)$, 11.3 eV
σ_{max} = 0.48 A^2 (40 eV)

$H_2(C^1\Pi_u)$, 12.4 eV
σ_{max} = 0.40 A^2 (40 eV)



Potential Energy Curves of Molecular Oxygen

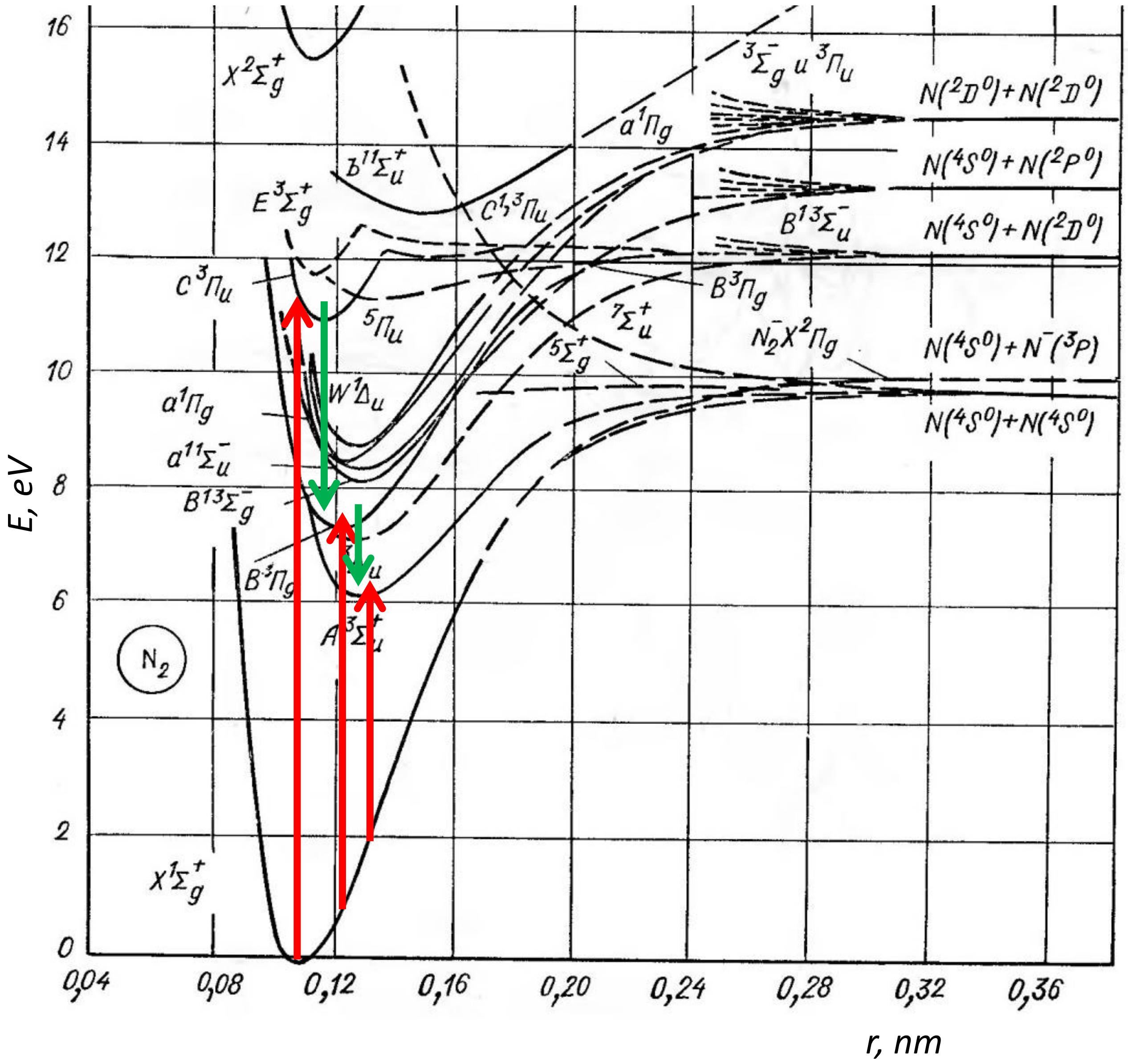


$O_2(A^3\Sigma_u^+)$, 4.5 eV
$\sigma_{max} = 0.18$ A^2 (6.6 eV)

$O_2(^3\Pi_g)$, 5.6 eV
$\sigma_{max} = 0.16$ A^2 (12 eV)

$O_2(B^3\Sigma_u^-)$, 8.4 eV
$\sigma_{max} = 1.0$ A^2 (9.4 eV)

Potential Energy Curves of Molecular Nitrogen



$N_2(A^3\Sigma_u^+)$, 6.2 eV
σ_{max} = 0.08 A^2 (10 eV)

$N_2(B^3\Pi_g)$, 7.35 eV
σ_{max} = 0.20 A^2 (12 eV)

$N_2(C^3\Pi_u)$, 11.03 eV
σ_{max} = 0.98 A^2 (14 eV)

Mechanisms of production of “hot” atoms in discharge plasmas

A.Yu. Starikovskiy, “Hydrogen plasma assisted ignition by NS discharge behind reflected shock wave” ,45th AIAA Plasmadynamics and Lasers Conference, Paper AIAA 2014-2245 (2014)

Direct electron-impact dissociation

$e + O_2 \rightarrow e + O_2^*$ $O_2^* \rightarrow 2O(^3P,^1D) + 1.3$ eV

$e + H_2 \rightarrow e + H_2^*$ $H_2^* \rightarrow 2H(^1S) + 4.4$ eV

$e + CH_4 \rightarrow e + CH_4^*$ $CH_4^* \rightarrow CH_3 + H + 3.5$ eV

Dissociation via N_2 excitation

$e + N_2 \rightarrow e + N_2(C)$

$N_2(C) + O_2 \rightarrow N_2 + 2O(^3P,^1D) + 3.9$ eV

$N_2(C) + H_2 \rightarrow N_2 + 2H(^1S) + 6.5$ eV

HI UV absorption. Okabe, 1984

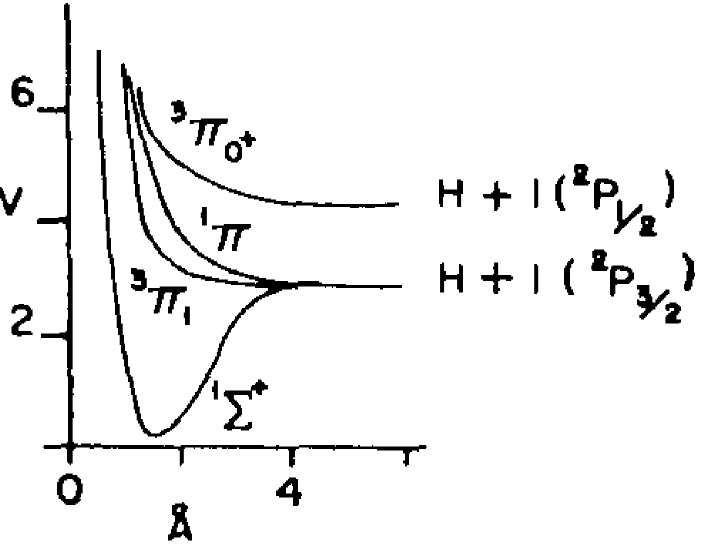


Fig. V–6. Potential energy curves of HI. From Wilson and Armstrong (1051). Originally from Mulliken, *Phy. Rev.* 51, 310 (1937). Reprinted by permission. Copyright 1937 by the American Physical Society.

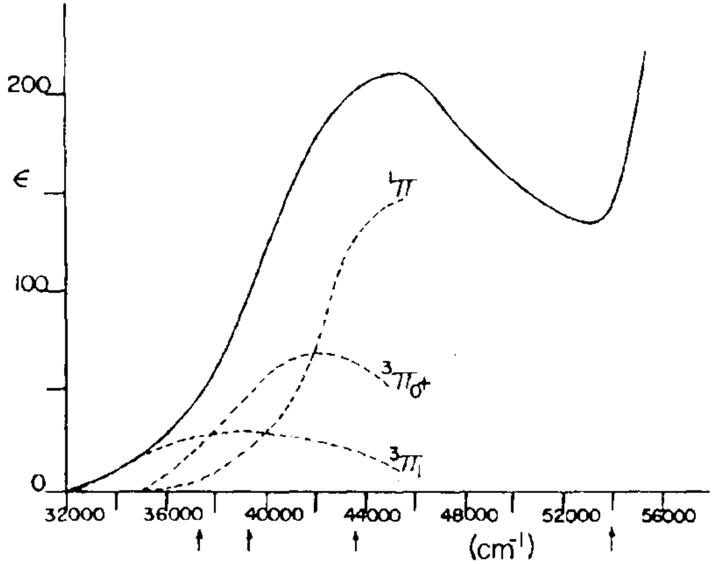


Fig. V–5. Absorption coefficients of HI and contribution of the transitions to the absorption continuum in the ultraviolet region. Solid curve, absorption coefficients ε of HI in units of l mol^{-1} cm^{-1} base 10 at room temperature. Reprinted with permission from B. J. Huebert and R. M. Martin, *J. Phys.* Chem. 72, 3046 (1968). Copyright by the American Chemical Society. Dashed curves, absorption coefficients of the transitions $^3\Pi_1-^1\Sigma^+$, $^3\Pi_0^+-^1\Sigma^+$, and $^1\Pi-^1\Sigma^+$. The $^3\Pi_1$ and $^1\Pi$ states dissociate into H + I($^2P_{3/2}$), while the $^3\Pi_0^+$ state dissociates into H + I($^2P_{1/2}$). The arrows indicate four incident wavelengths (2662, 2537, 2281, and 1850 Å) at which the ratios of I($^2P_{1/2}$) to I($^2P_{3/2}$) are obtained. From Clear et al. (219) reprinted by permission. Copyright 1975 by the American Institute of Physics.

$$\mathrm{HI} \xrightarrow{h\nu} \mathrm{H} + \mathrm{I} \qquad \text{(V-8)}$$

$$\mathrm{H} + \mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I} \qquad \text{(V-9)}$$

$$2\mathrm{I} + \mathrm{M} \rightarrow \mathrm{I_2} + \mathrm{M} \qquad \text{(V-10)}$$

The excess energy beyond that required to break the H—I bond is 3.65 eV at 1849 Å. This excess energy appears primarily as the kinetic energy of H

The effect of “hot” atoms on chemical reactions

$H + O_2 \rightarrow O + OH$

$k_{eq}(T = 300\text{K}) = 2.5\times10^{-21}\ \text{cm}^3/\text{s}$

$k_h = 1.6\times10^{-10}\ \text{cm}^3/\text{s}$

$O + H_2 \rightarrow H + OH$

$k_{eq}(T = 300\text{K}) = 9.3\times10^{-18}\ \text{cm}^3/\text{s}$

$k_h = 1.5\times10^{-10}\ \text{cm}^3/\text{s}$

The effect is important only when energy degradation of “hot” atoms is slow!

Monte Carlo simulation of energy degradation of “hot” atoms

Simultaneous consideration of

- “cooling” of “hot” atoms in elastic collisions

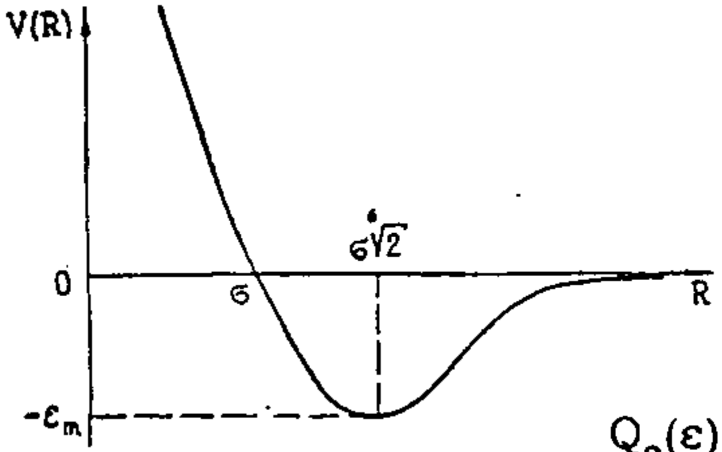
and

-chemical reactions.

Other inelastic processes were neglected

Determination of cross sections for scattering of “hot” atoms

Elastic collisions: **calculations in quasi-classical approach using Lennard-Jones interaction potential**



$$V(R) = 4\varepsilon_m\left[\left(\frac{\sigma}{R}\right)^{12}-\left(\frac{\sigma}{R}\right)^{6}\right]$$

$$Q_0(\varepsilon) = \pi\sigma^2 Q^*(x)$$

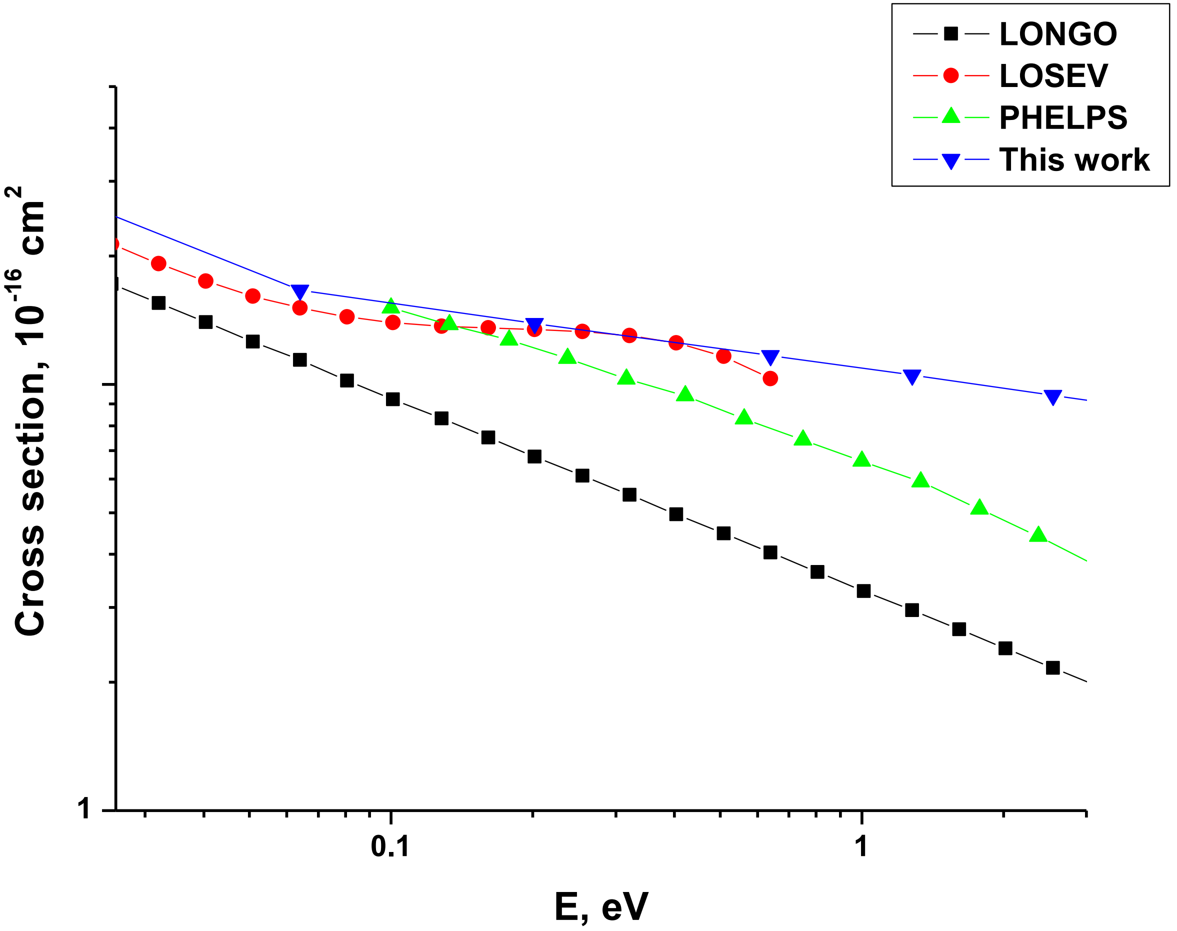
$$Q^*(x) = -0{,}17x^4 + 0{,}259x^3 + 1{,}02x^2 - 2{,}57x + 2{,}24$$

$$x = \lg(\varepsilon/\varepsilon_m)$$

$$\sigma(i,j) = [\sigma(i,i)+\sigma(j,j)]/2 \qquad \varepsilon_m(i,j) = \{\varepsilon_m(i,i)\cdot\varepsilon_m(j,j)\}^{1/2}$$

Determination of cross sections for scattering of “hot” atoms

Elastic collisions: **calculations in quasi-classical approach using Lennard-Jones interaction potential**

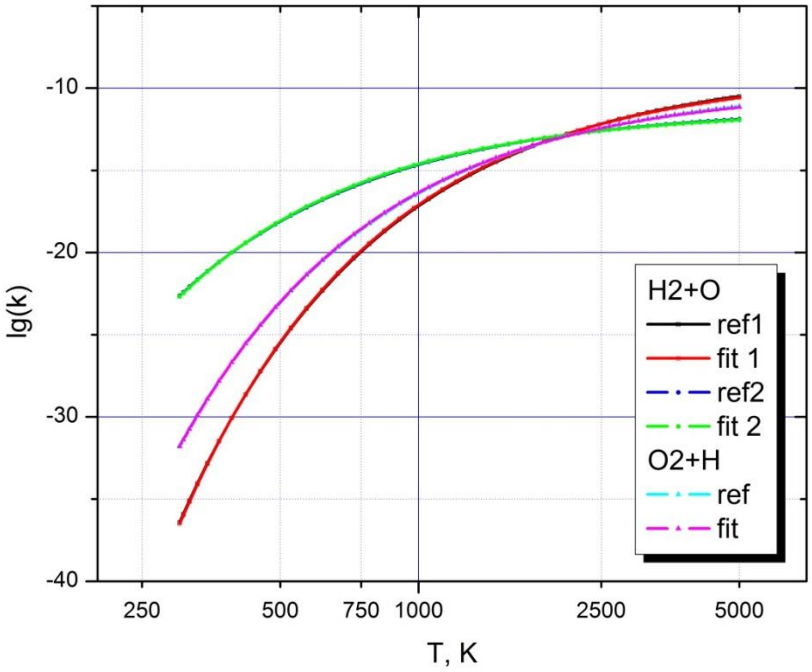


Determination of cross sections for scattering of “hot” atoms

Chemical reactions: **adjustment of cross sections to fit available data for rate constants in a wide range of gas temperatures**

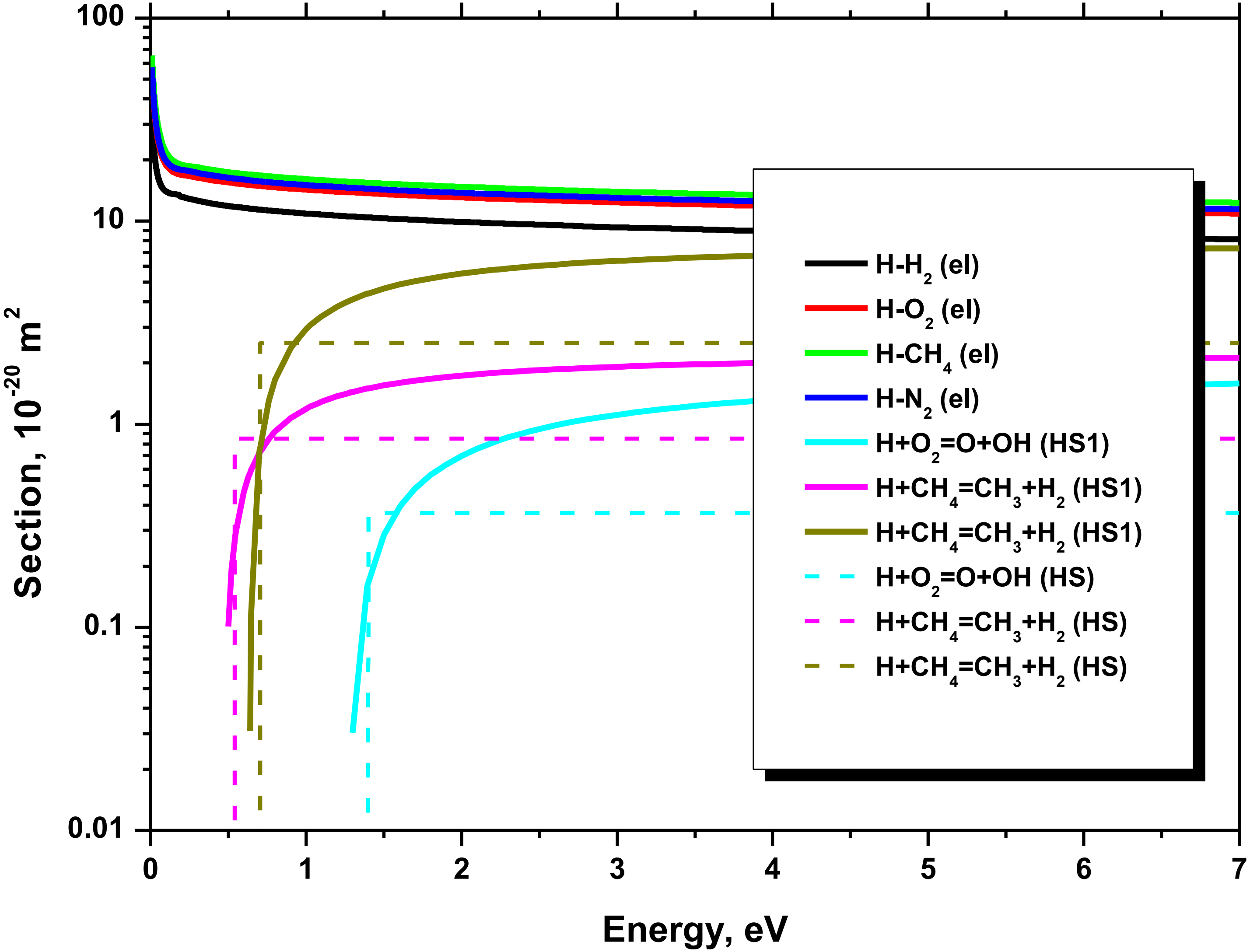
$$\sigma(\varepsilon) = \begin{cases} 0, \varepsilon \le E_0 \\ \pi R_0^2 \left(1 - \dfrac{E_0}{\varepsilon}\right), \varepsilon > E_0 \end{cases}$$

“Hard Sphere Model”

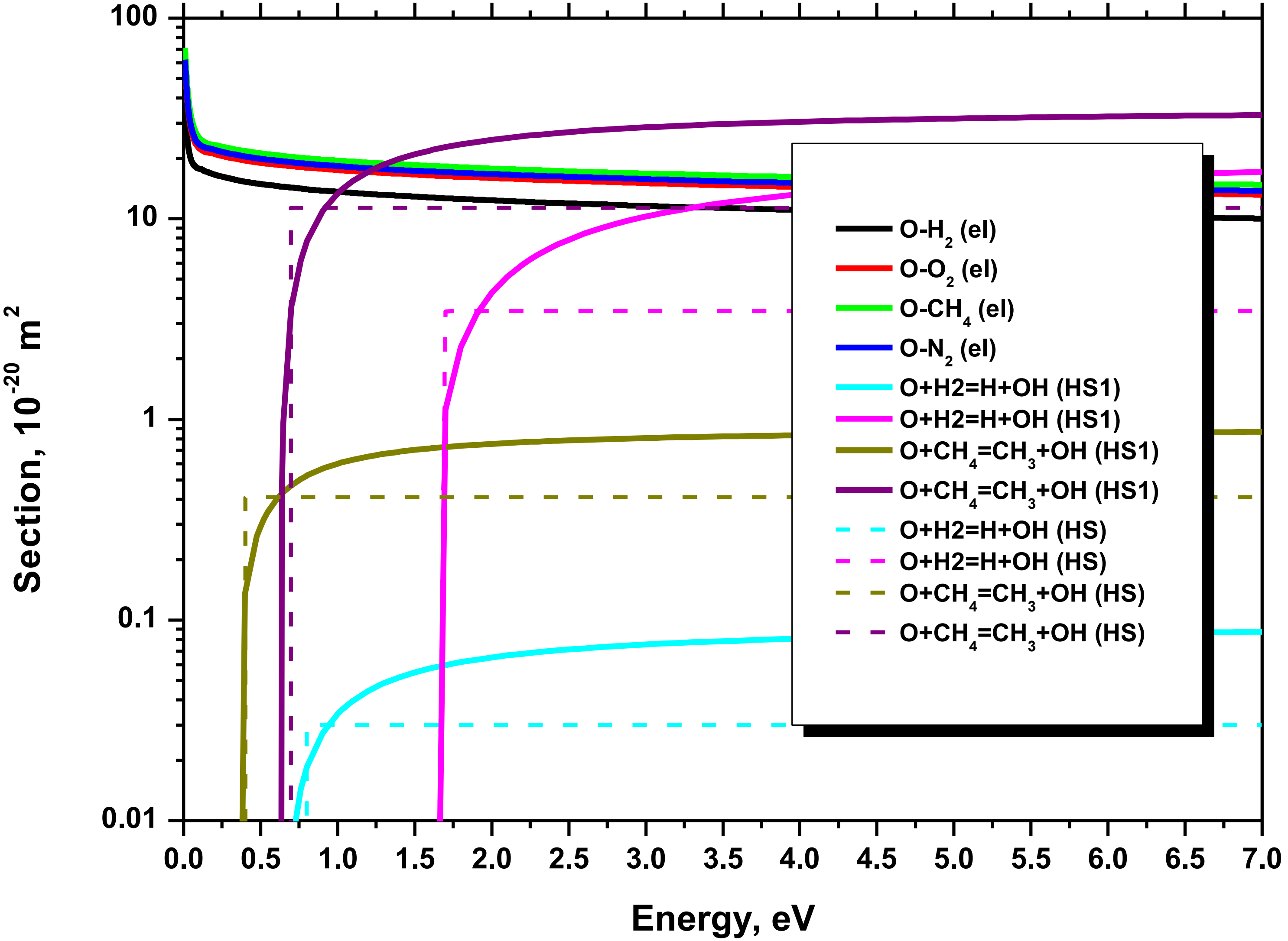


$$k(T) = \left(\frac{8\pi kT}{\mu}\right)^{1/2} R_0^2 \, exp(-E_0/kT)$$

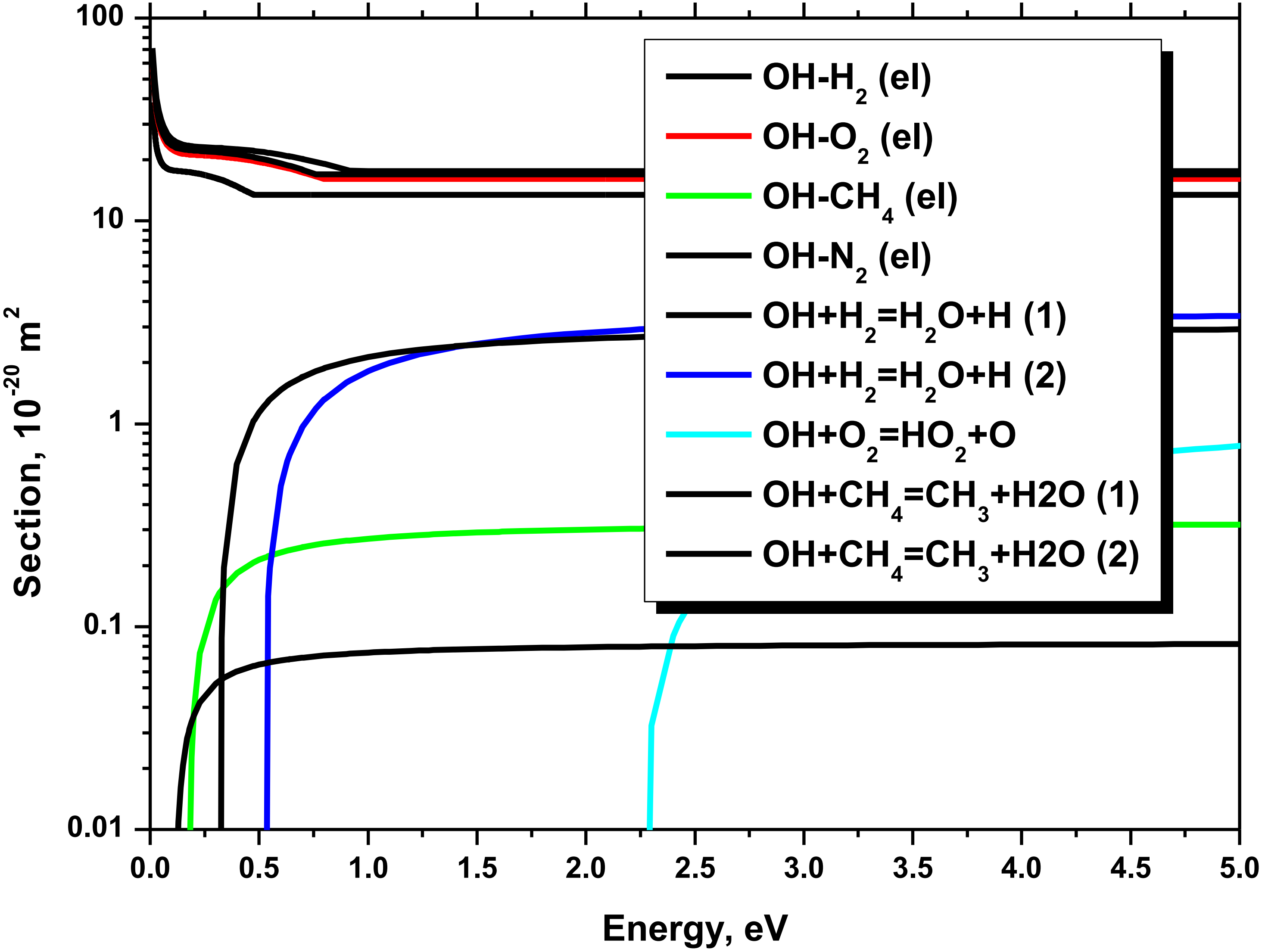
Cross sections for H atom scattering



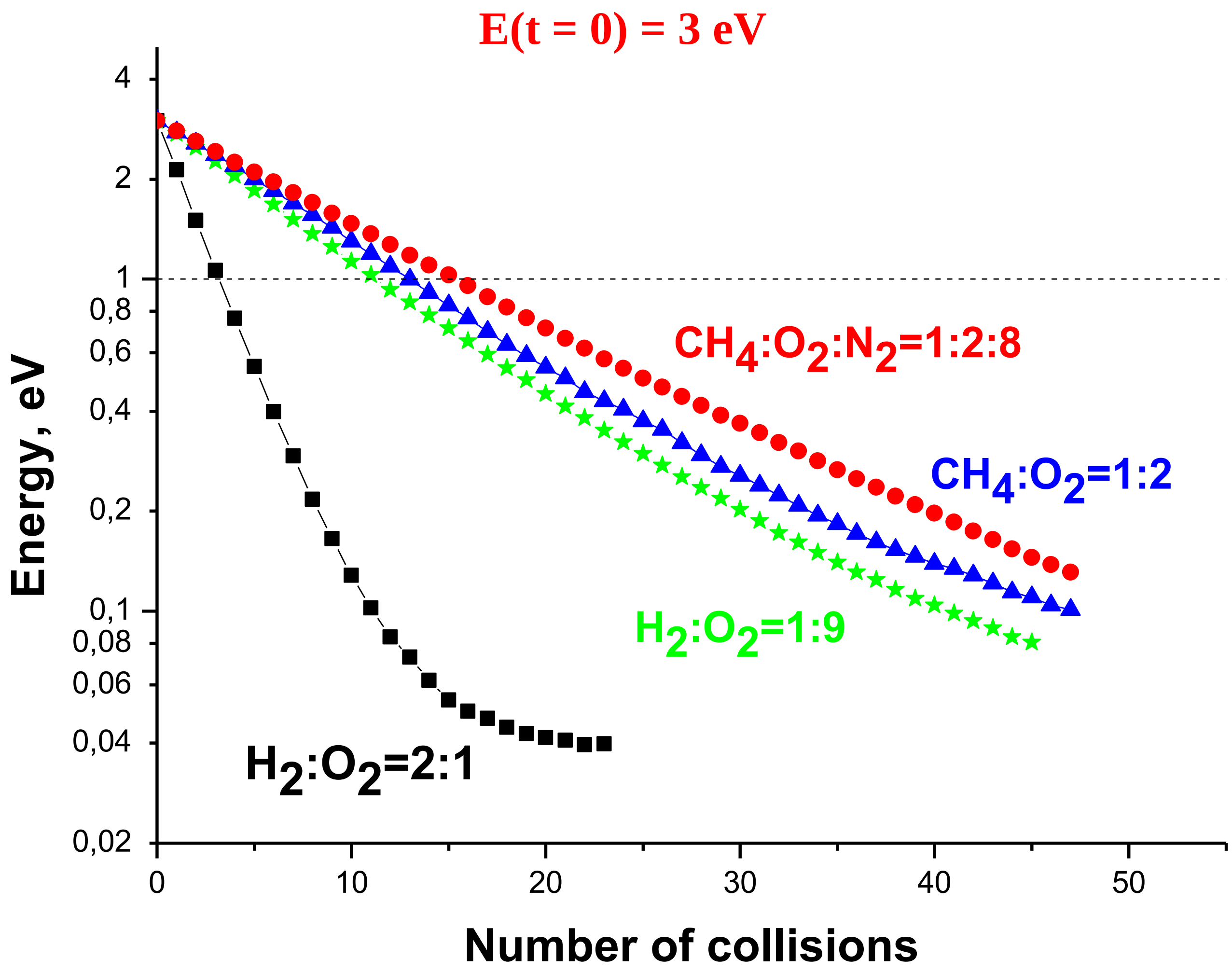
Cross sections for O atom scattering



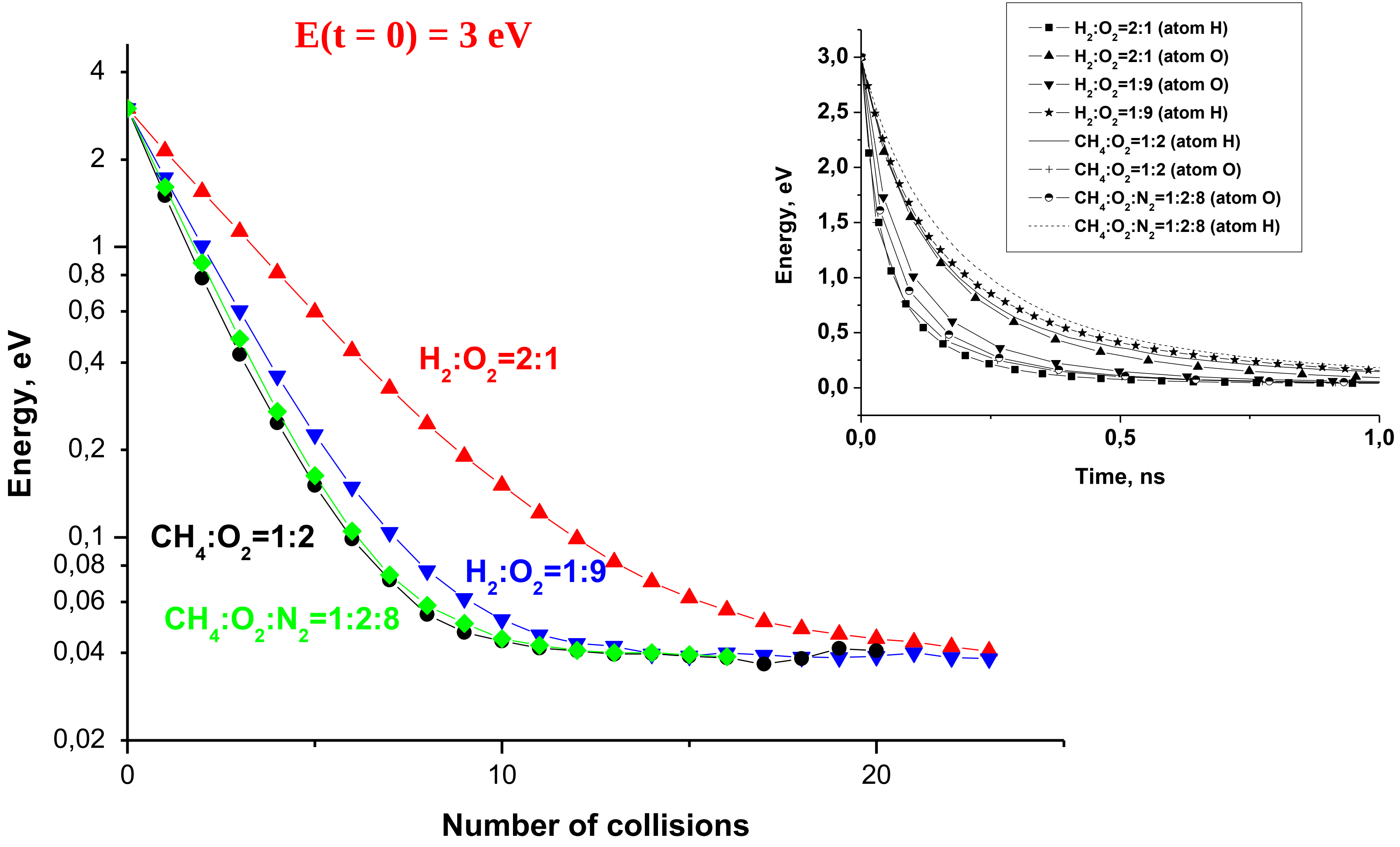
Cross sections for OH scattering



Energy degradation of “hot” H atoms

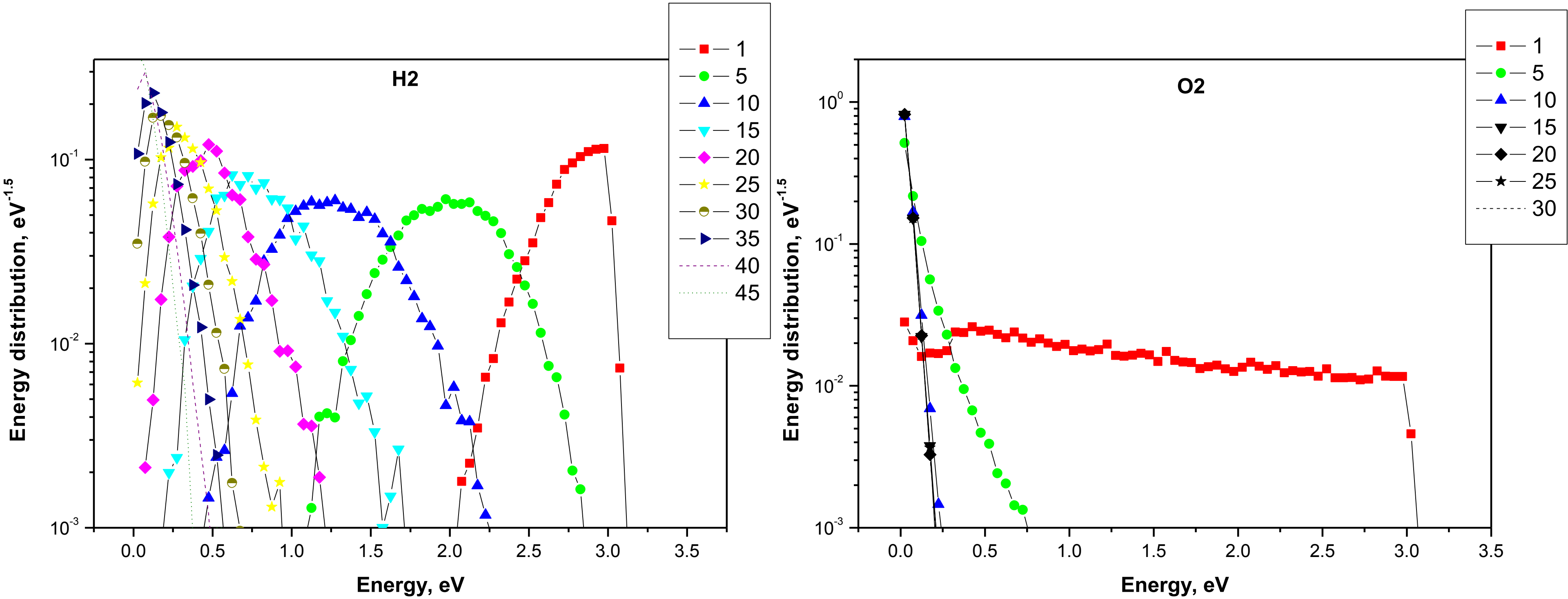


Energy degradation of “hot” O atoms



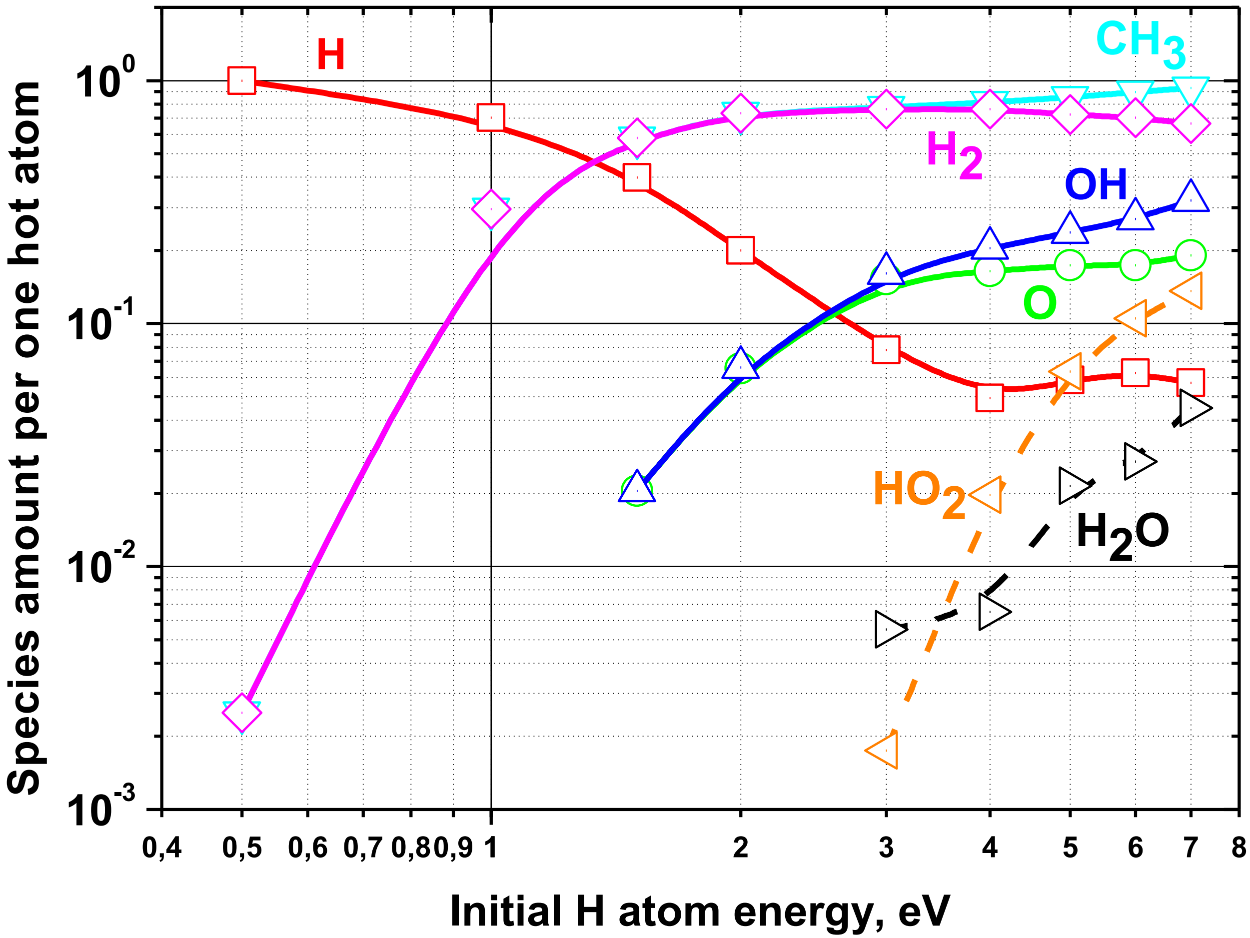
E(t = 0) = 3 eV

Energy distributions for H and O atoms

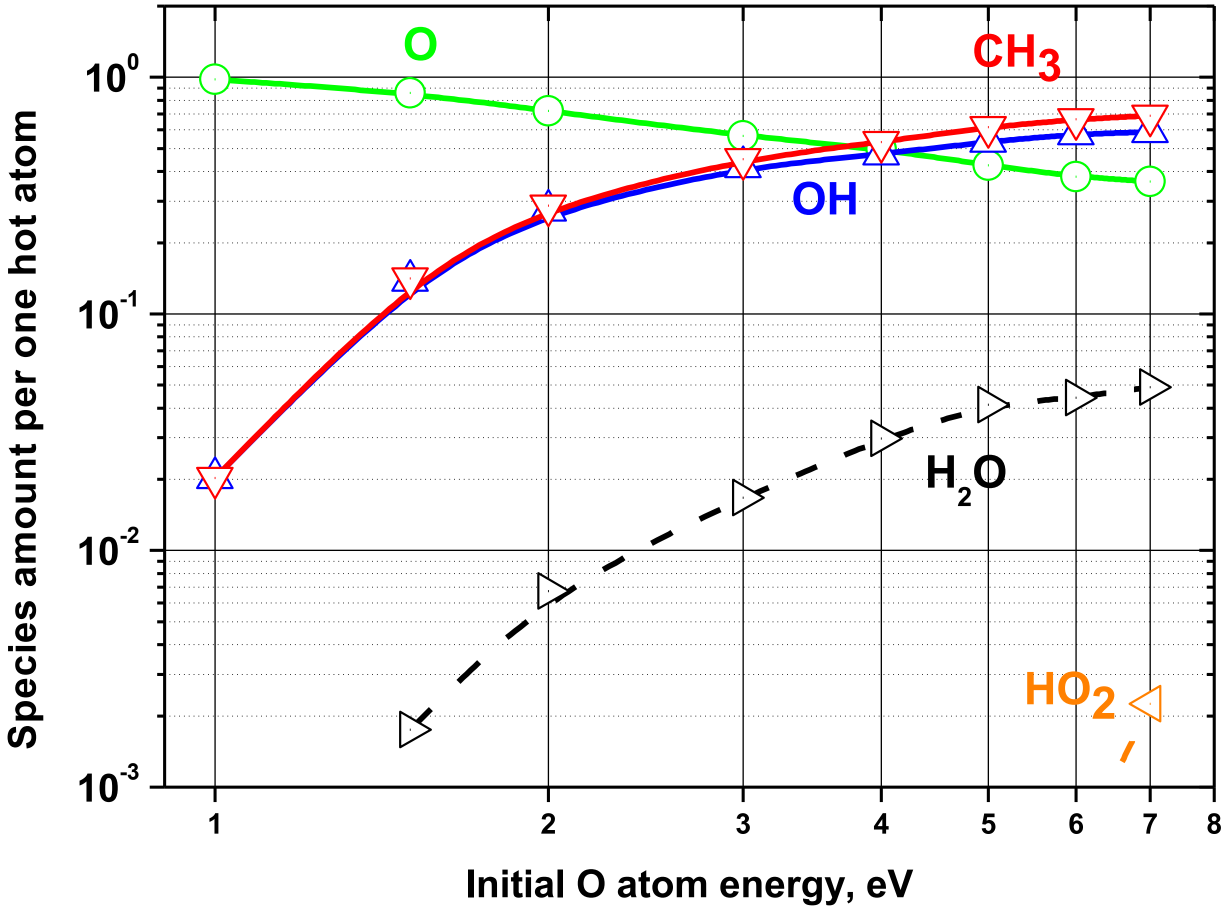


Stoichiometric CH_4:O_2 = 1:2 mixture. Initial energy of H and O atoms is 3 eV.

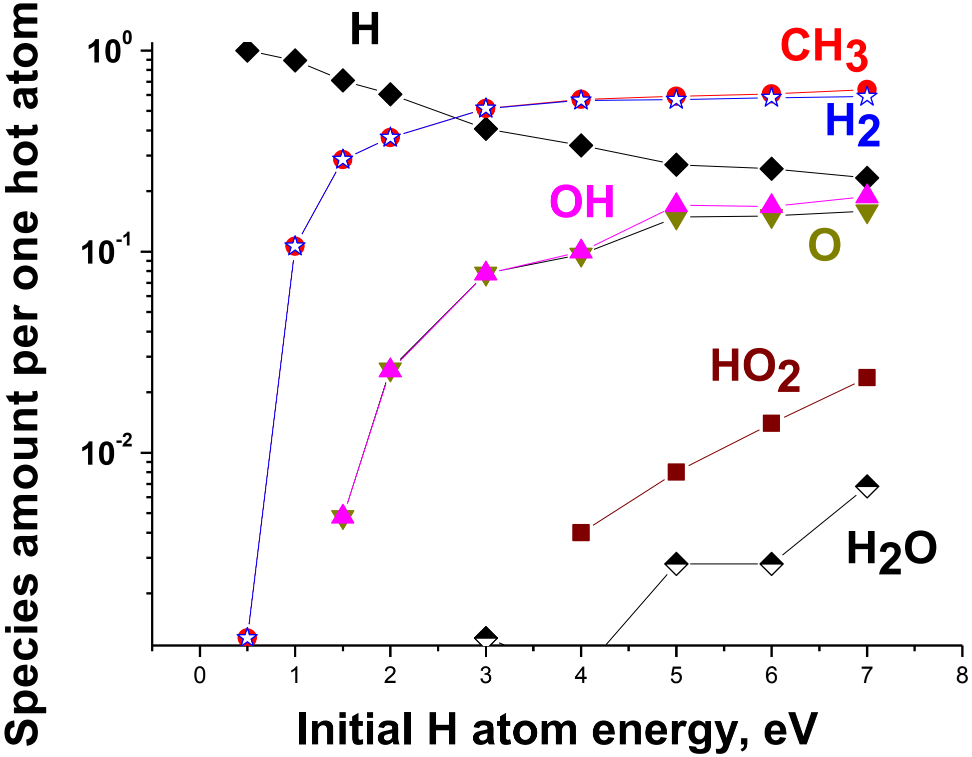
Amount of active species generated by hot H atoms in CH_4:O_2 mixture (φ = 1)

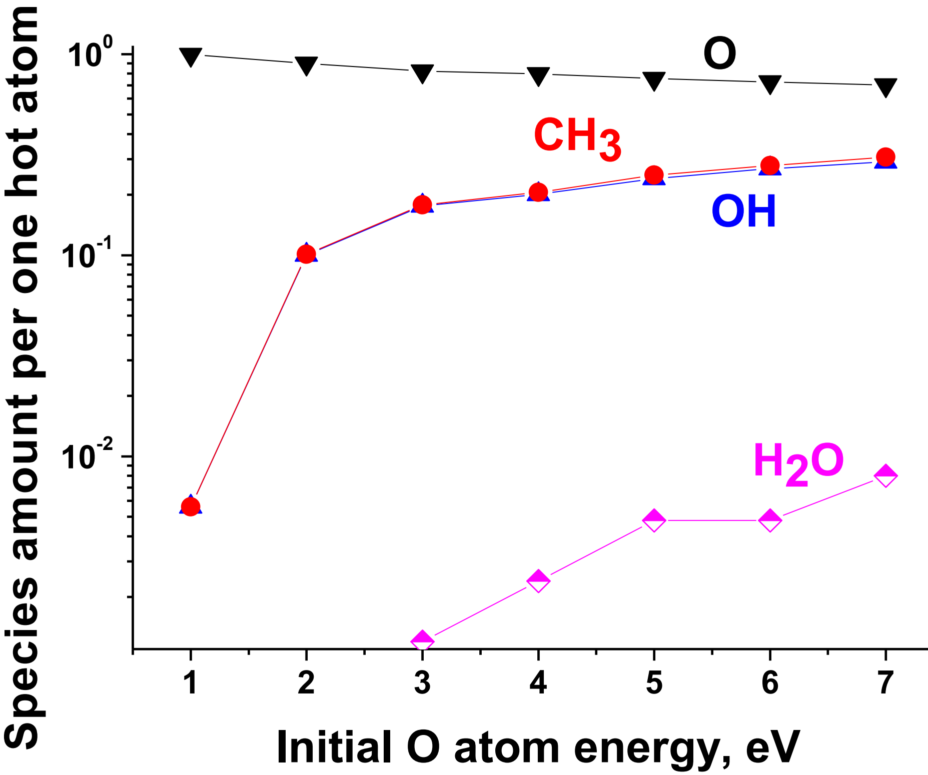


Amount of active species generated by hot O atoms in CH_4:O_2 mixture ($\phi = 1$)

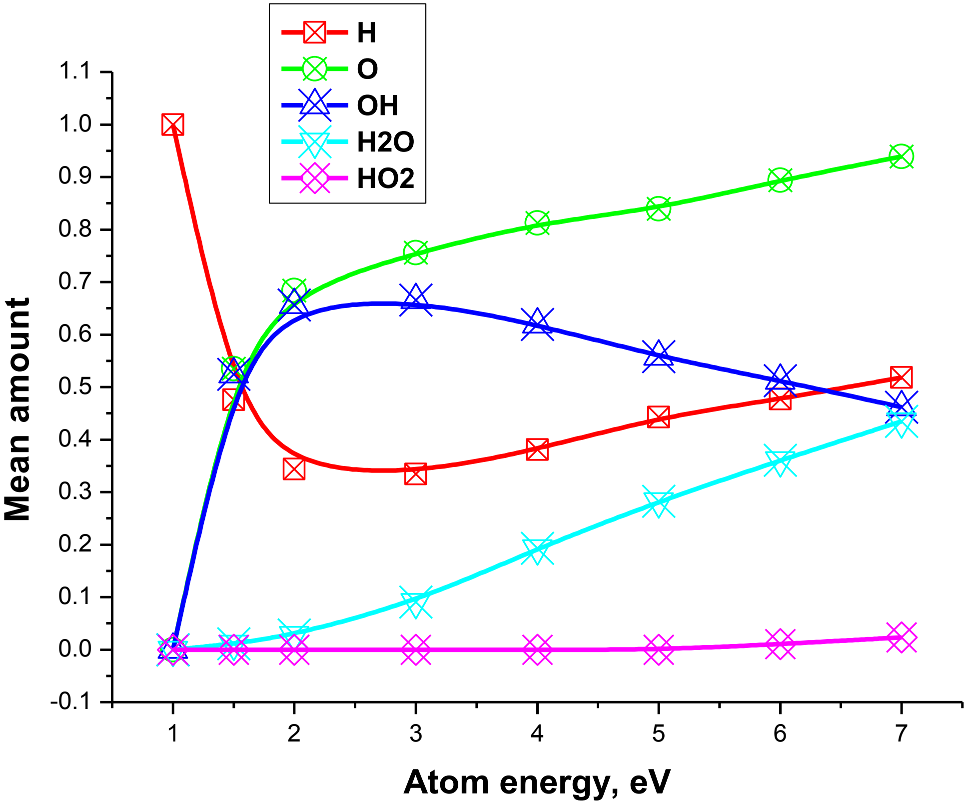


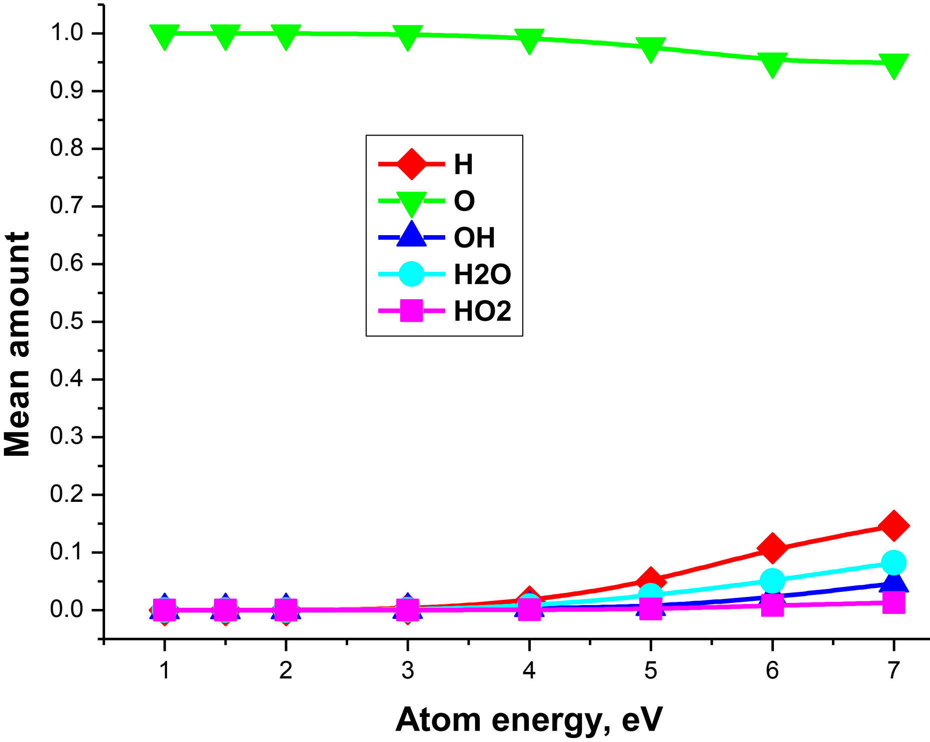
Amount of active species generated by hot O and H atoms in CH_4:air mixture ($\phi = 1$)



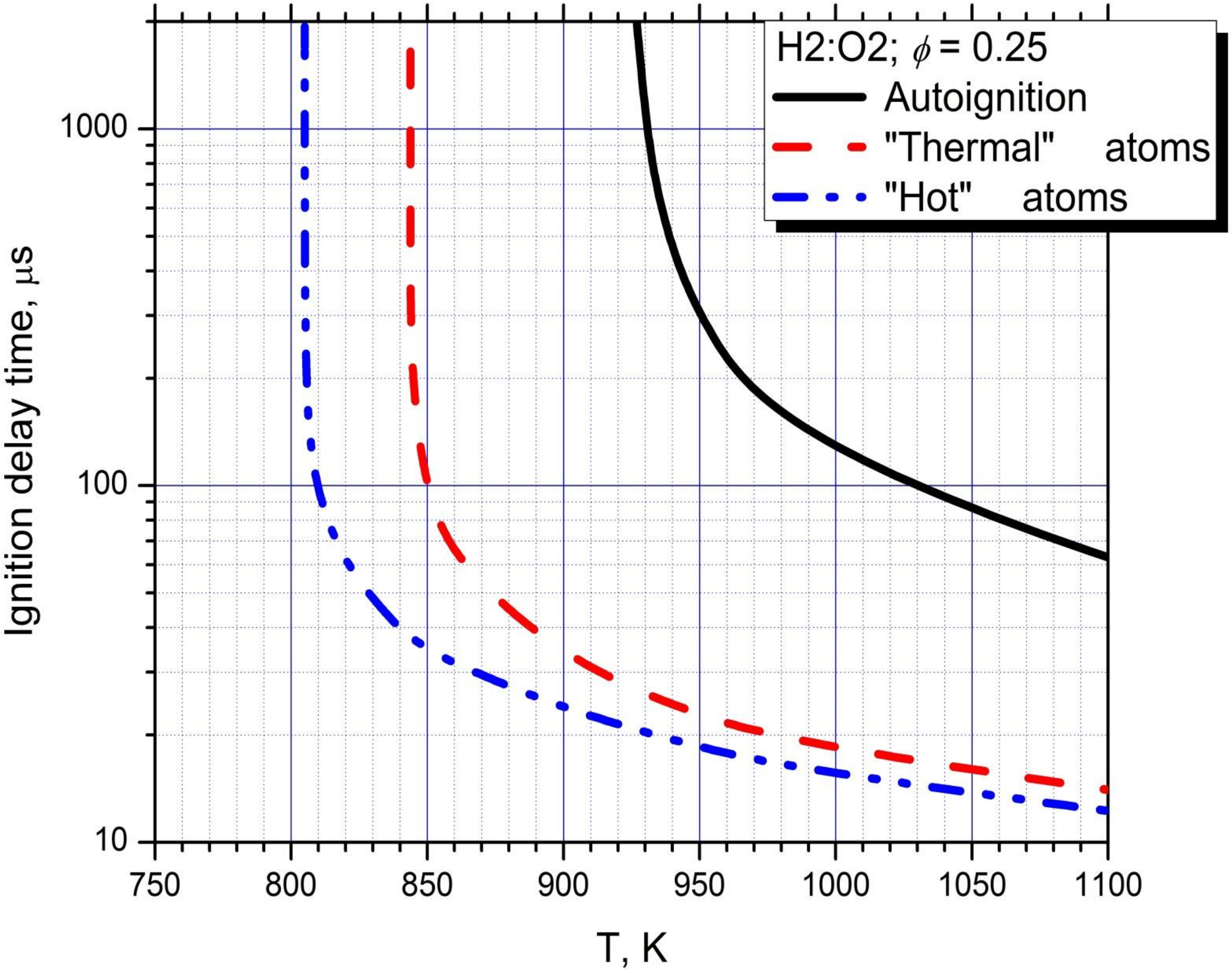


Amount of active species generated by hot O and H atoms in stoichiometric H_2:O_2 mixture at 300 K as a function of their initial energy

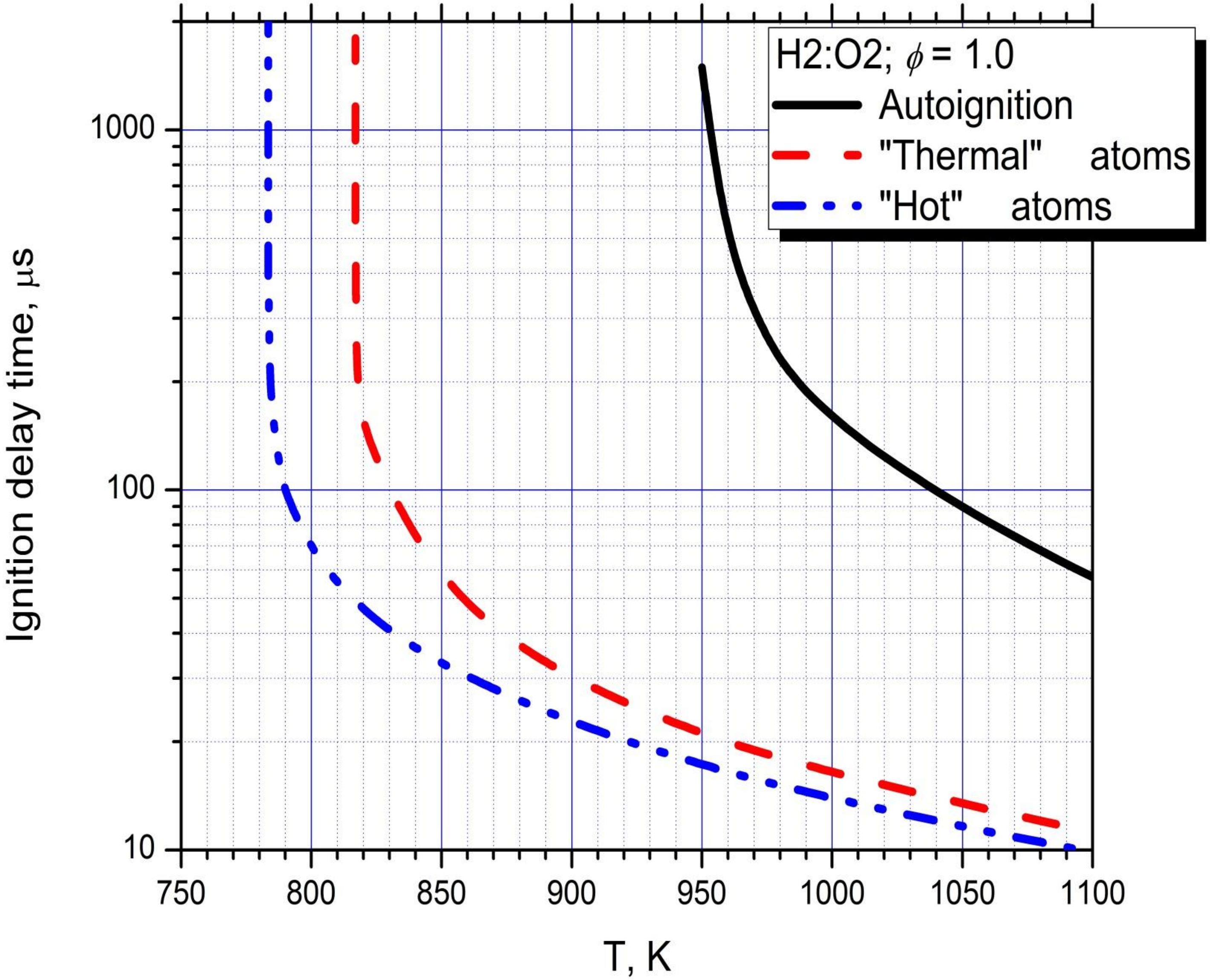




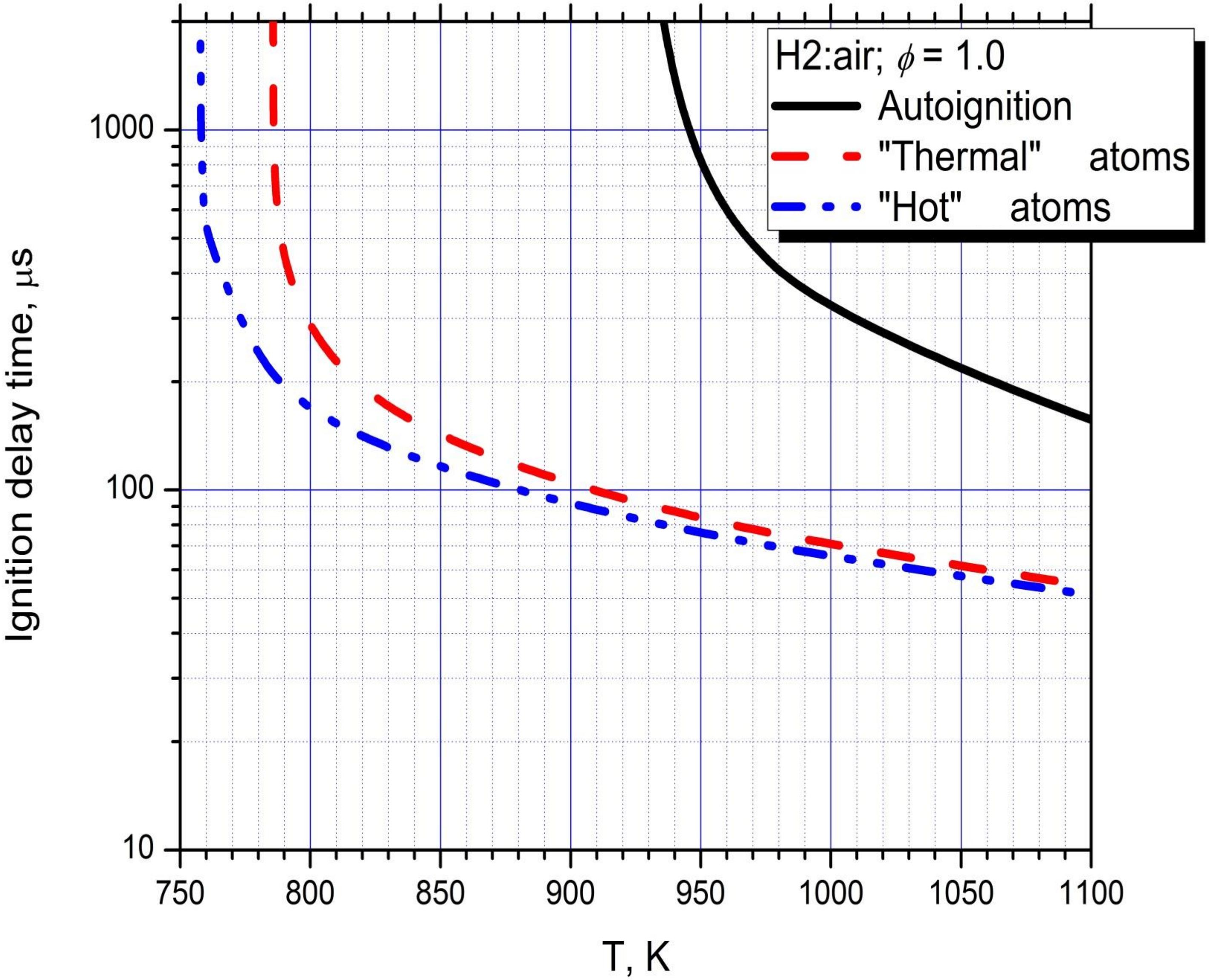
Role of translationally-hot H atoms in ignition of lean H_2-O_2 mixture. P = 1 atm.



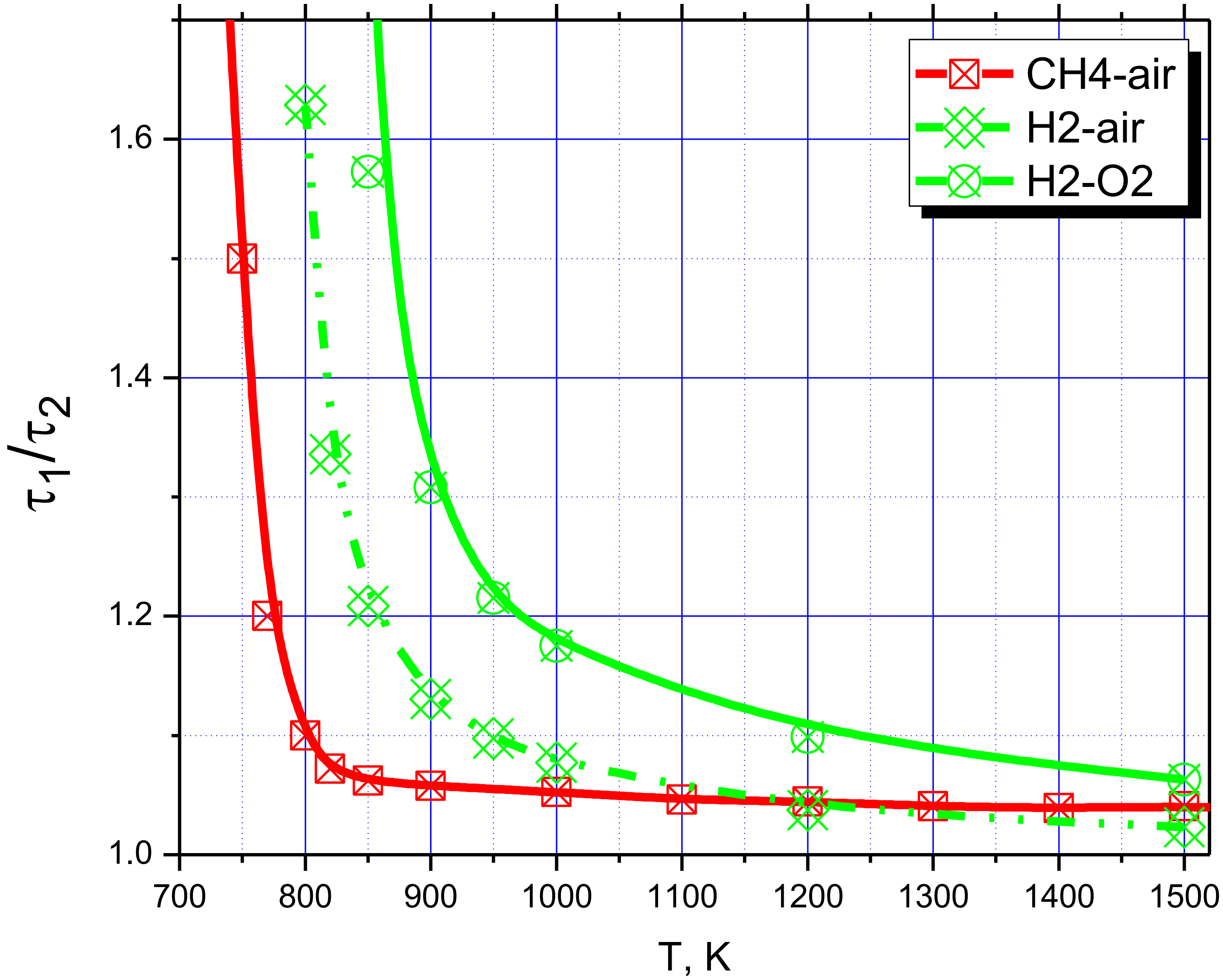
Role of translationally-hot H atoms in ignition of stoichiometric H_2-O_2 mixture. P = 1 atm.



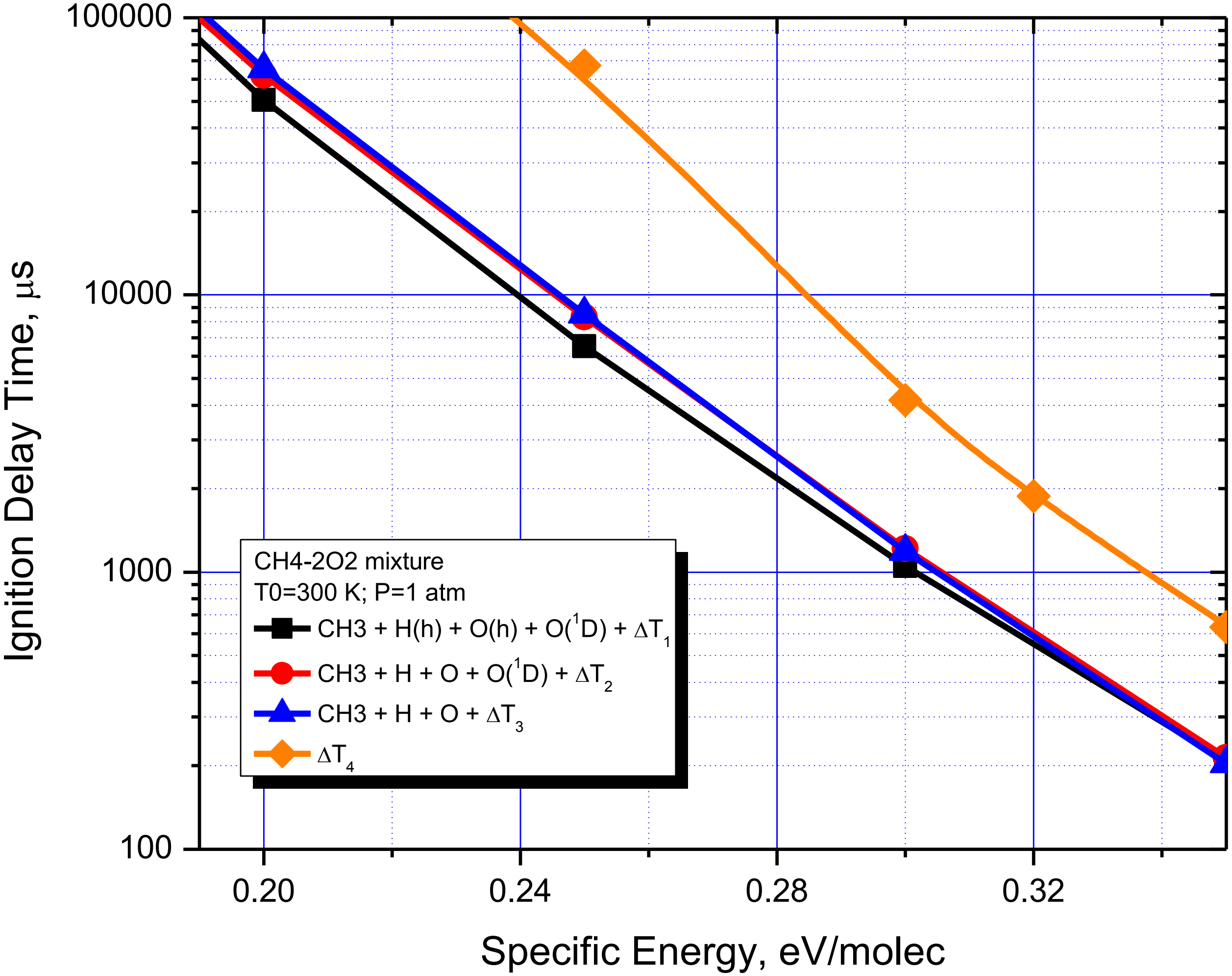
Role of translationally-hot H atoms in ignition of stoichiometric H_2-air mixture. P = 1 atm.



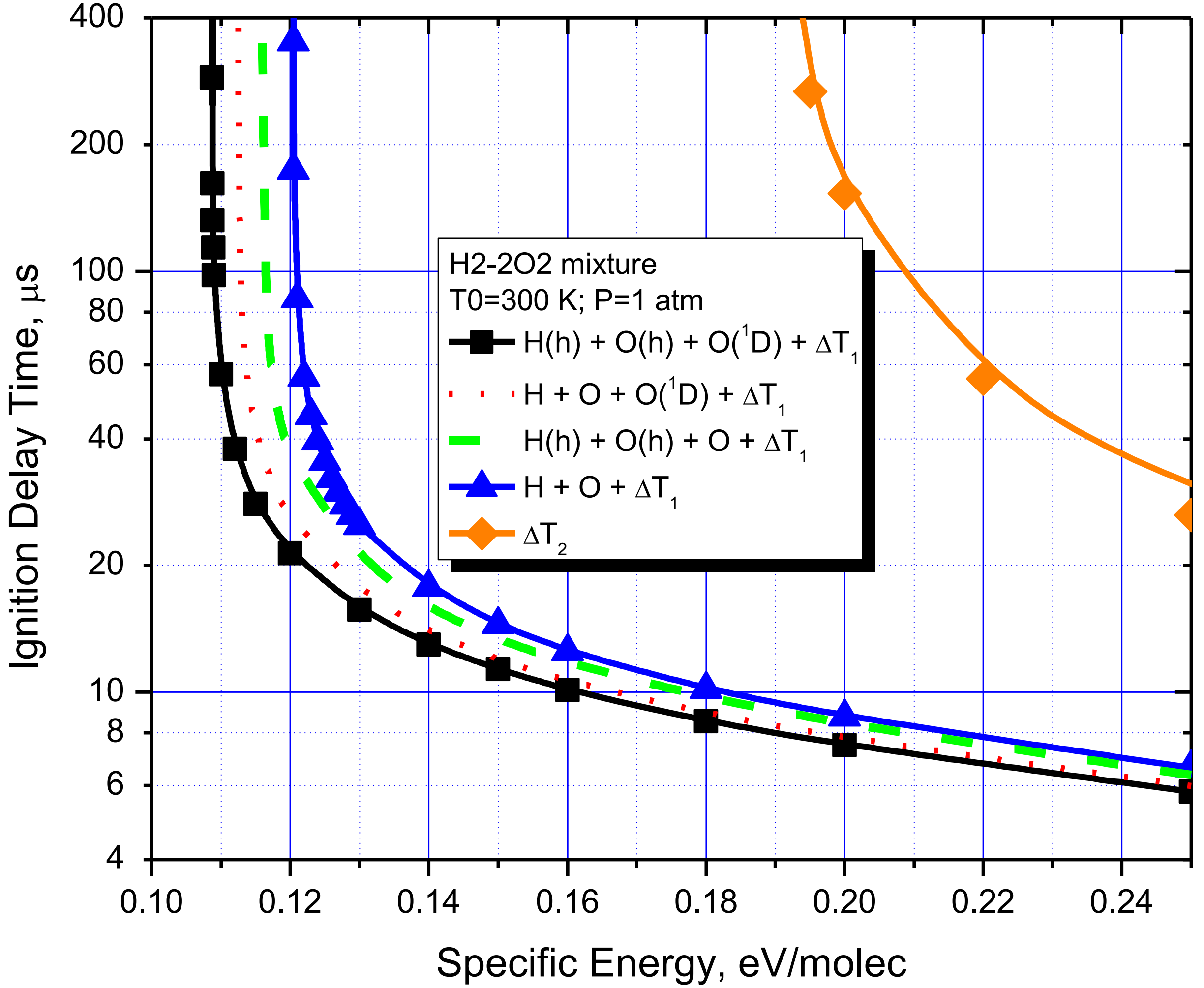
Role of translationally-hot atoms in ignition of stoichiometric methane-air mixture. P = 1 atm.



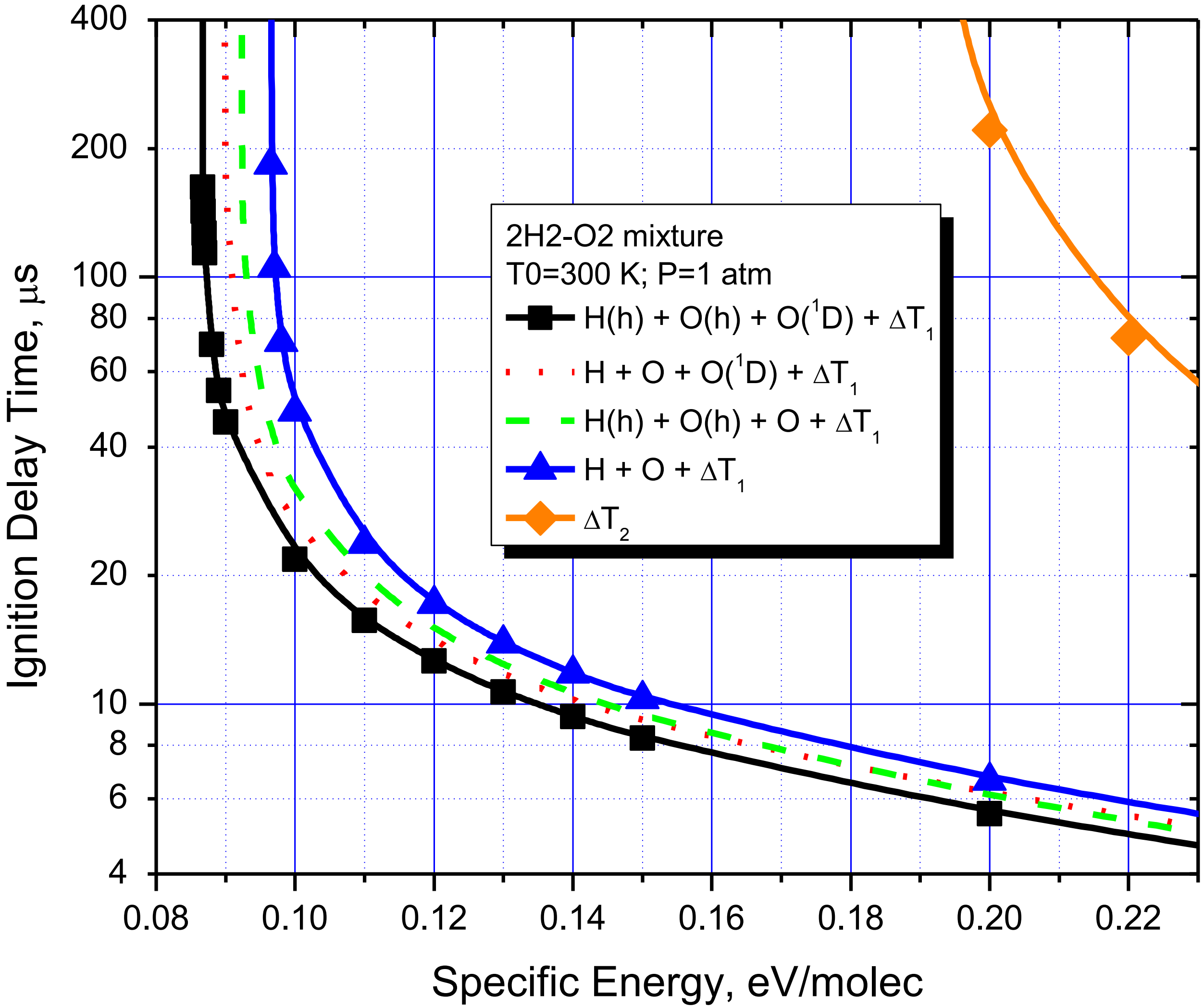
Low-temperature Ignition



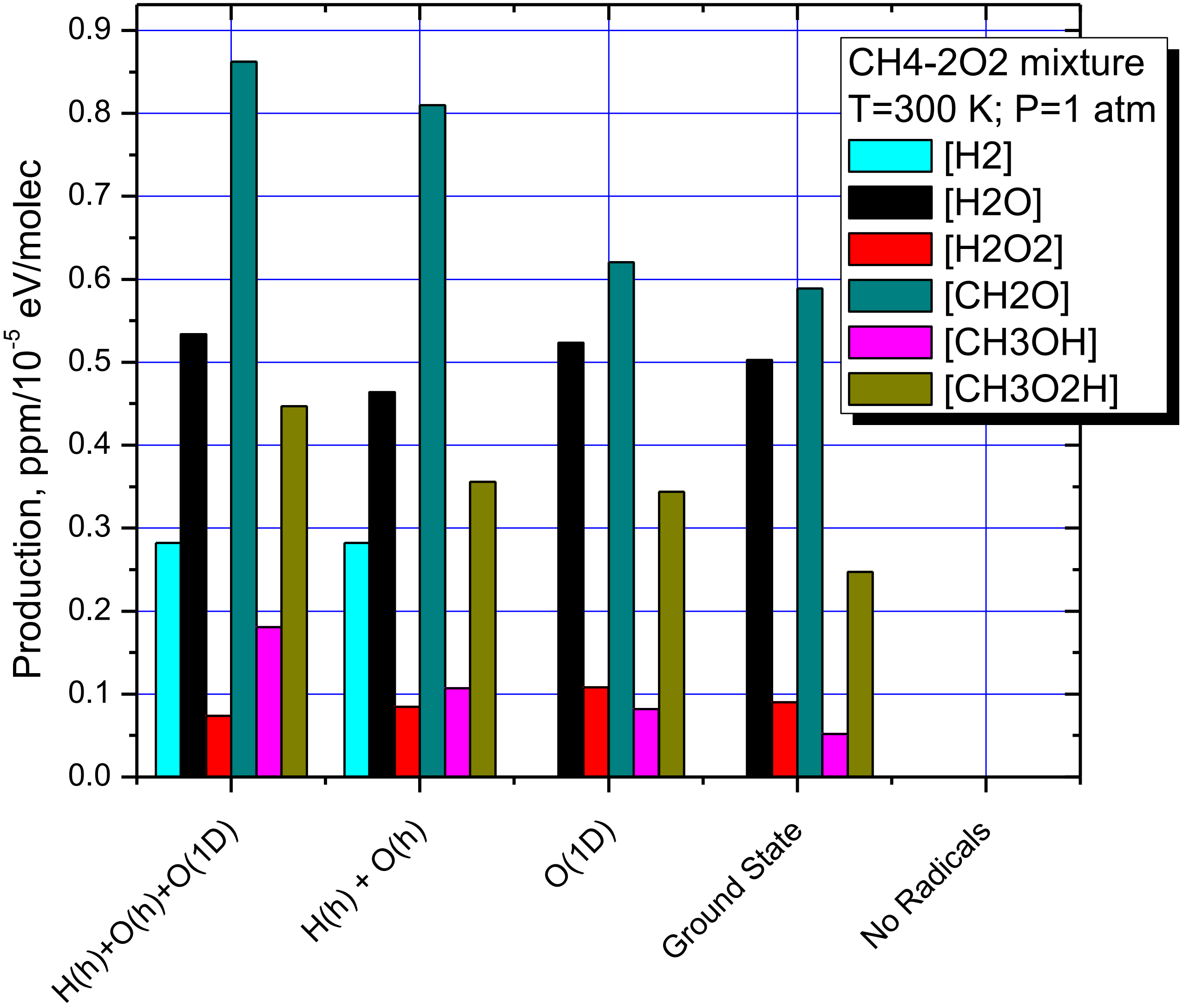
Low-temperature Ignition



Low-temperature Ignition

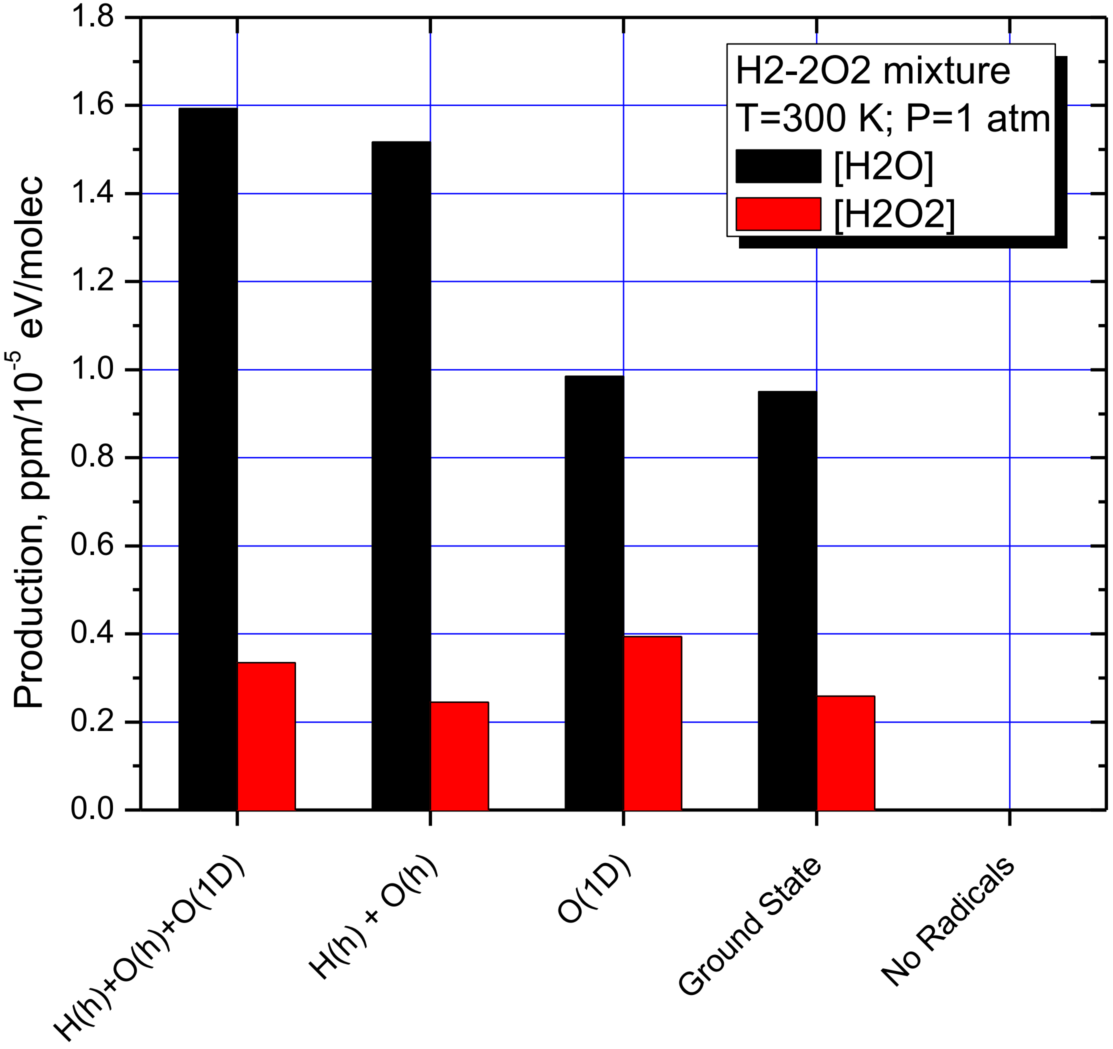


Low-temperature Oxidation

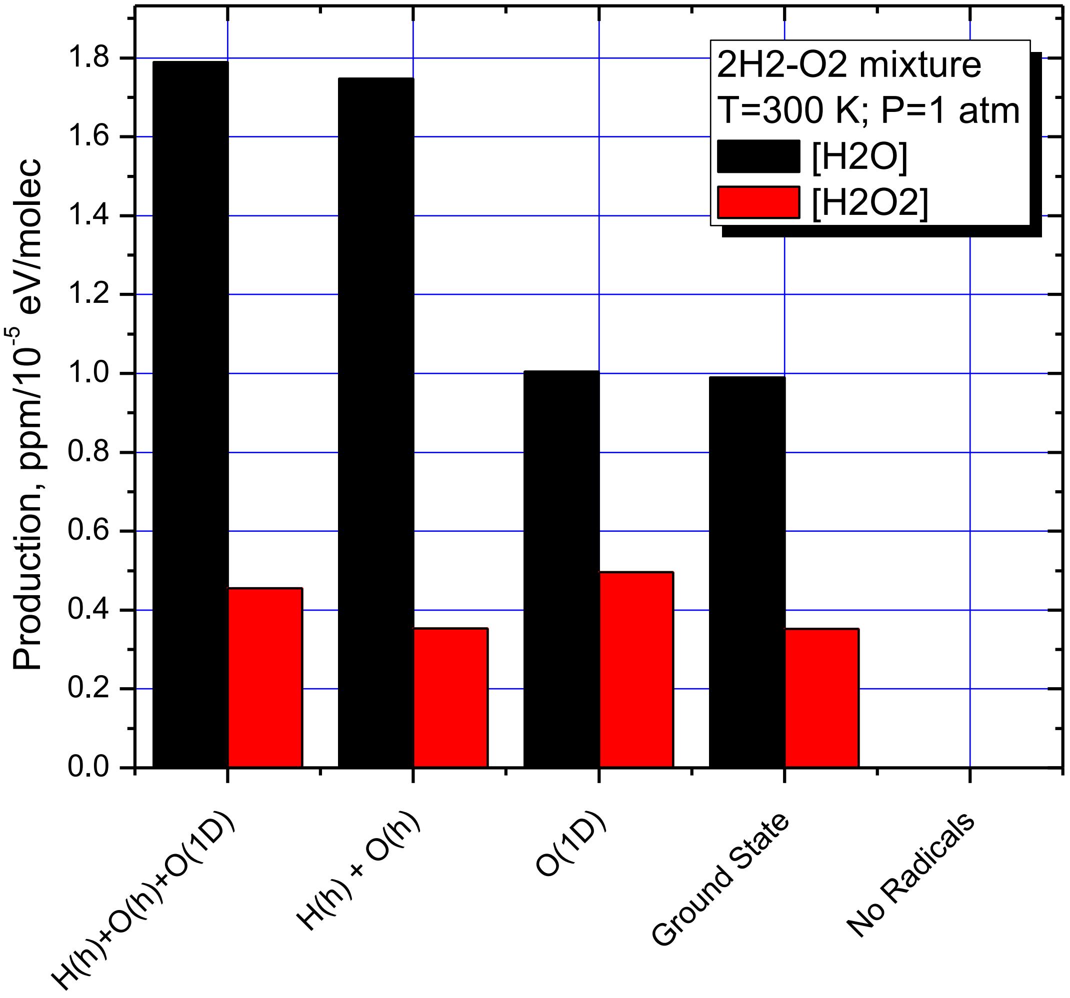


Formaldehyde
Hydrogen
Methanol

Low-temperature Oxidation



Low-temperature Oxidation



Conclusions

- Using Monte Carlo simulation, energy degradation of “hot” H and O atoms in H_2:O_2, CH_4:O_2 and CH_4:air mixtures at room gas temperature was studied taking into account elastic collisions and chemical reactions.

- Energy degradation is longer for H atoms in CH_4-containing mixtures and in lean H_2:O_2 mixtures, whereas degradation time of O atoms is much shorter.

- When energy degradation of “hot” atoms is long, the amount of active species produced in a high-voltage discharge can be increased and active species composition is changed. This can lead to a noticeable decrease in the threshold temperature of plasma-assisted ignition.