Plasma Assisted Combustion Mechanism for Small Hydrocarbons

Andrey Starikovskiy

Nickolay Aleksandrov

PRINCETON
University

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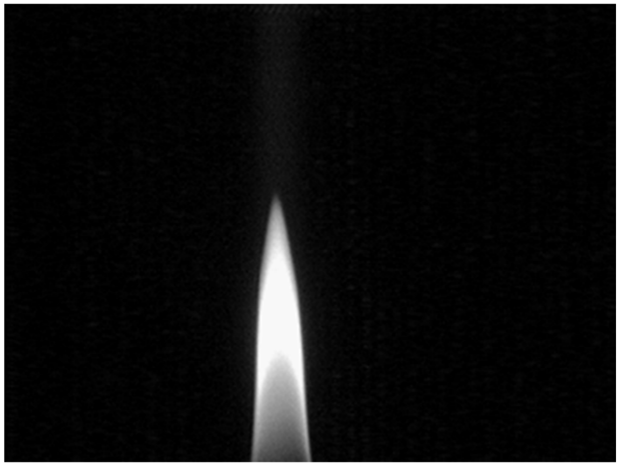
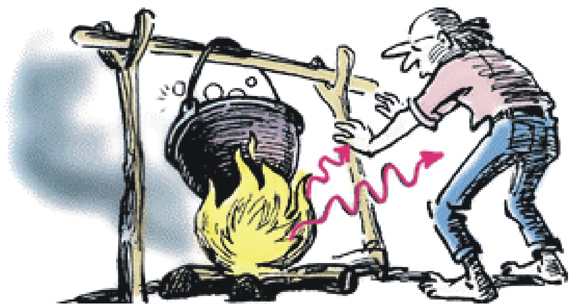
Prescribed by ANSI Std Z39-18

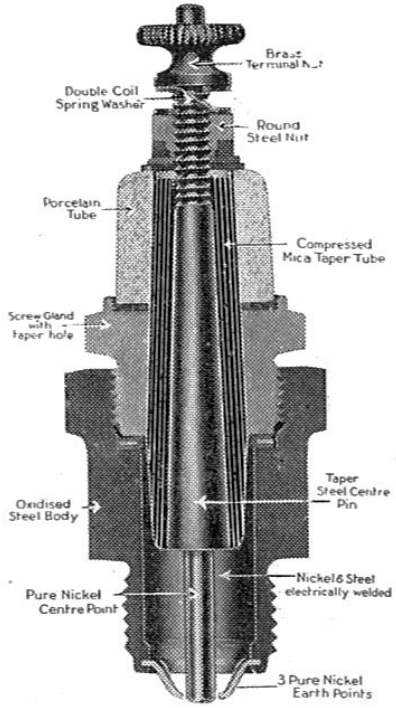
Ignition, Combustion and Flame Control by Nonequilibrium Plasma



1814 – Brande. Flame/Field Interaction

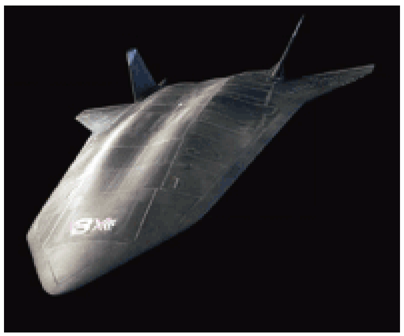
W.T. Brande. Phil.Trans.Roy.Soc., 1814,104, 51.





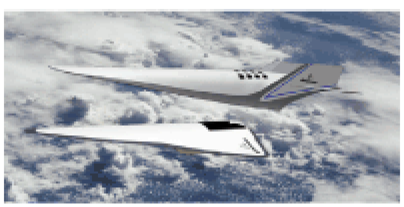
In 1860 Étienne Lenoir used an electric spark plug in his gas engine, the first internal combustion piston engine and is generally credited with the invention of the spark plug

Propulsion Efficiency and Operating Regimes for Variety of Flight Systems



(a)

(b)



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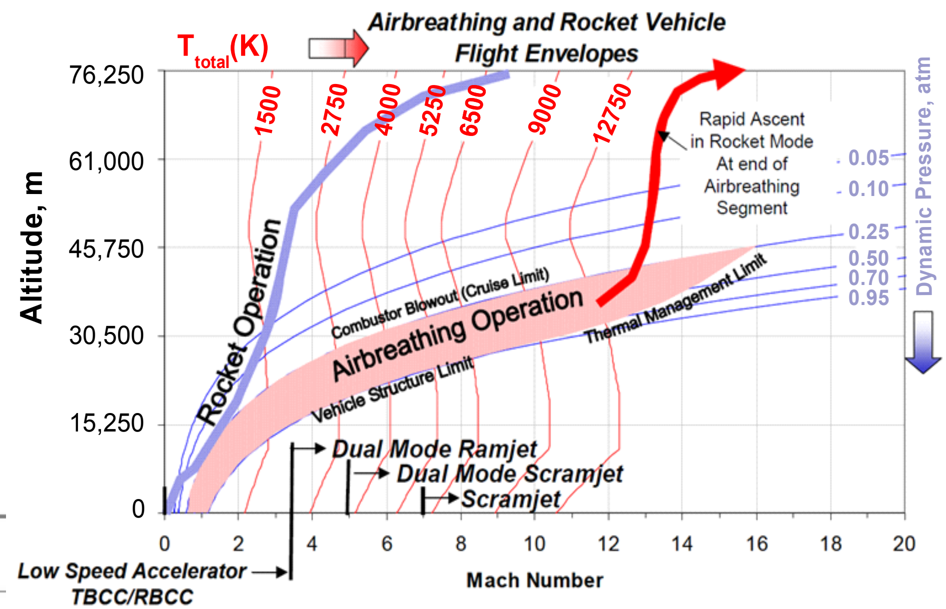
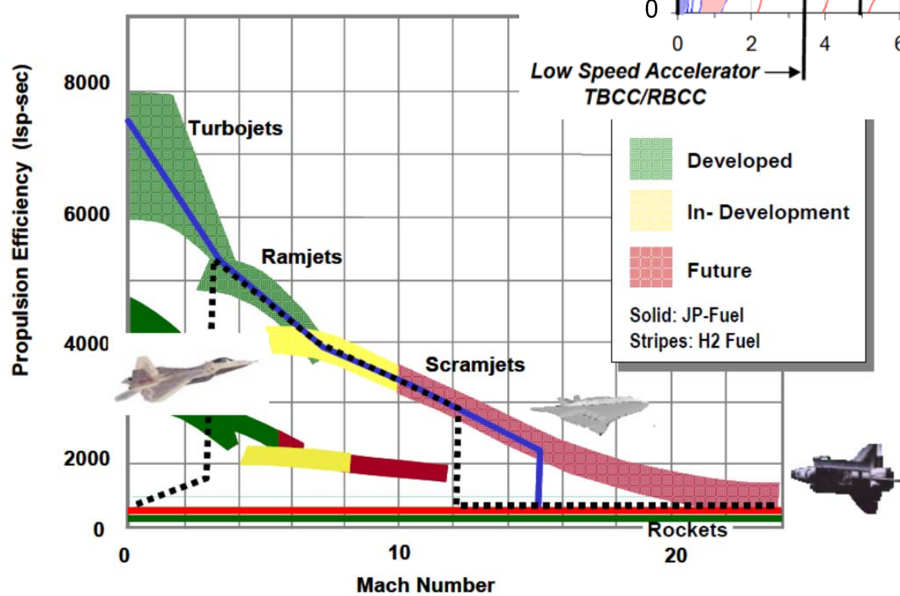
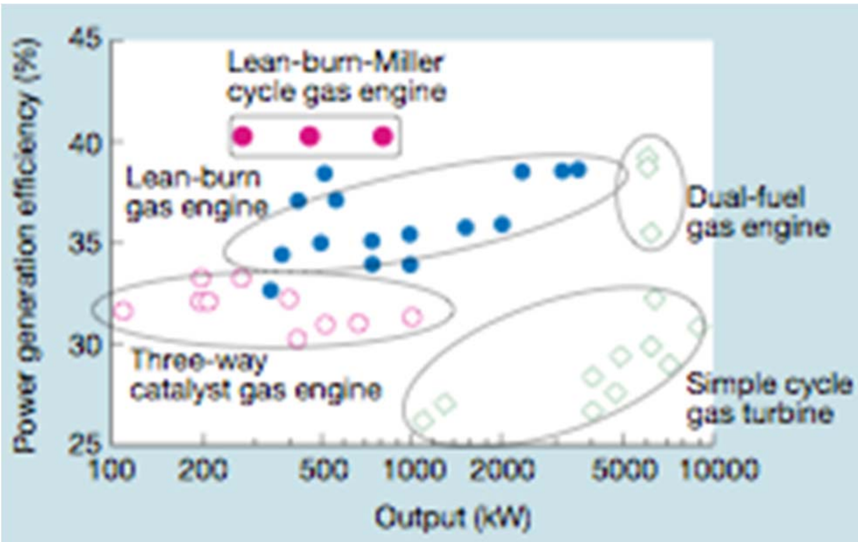
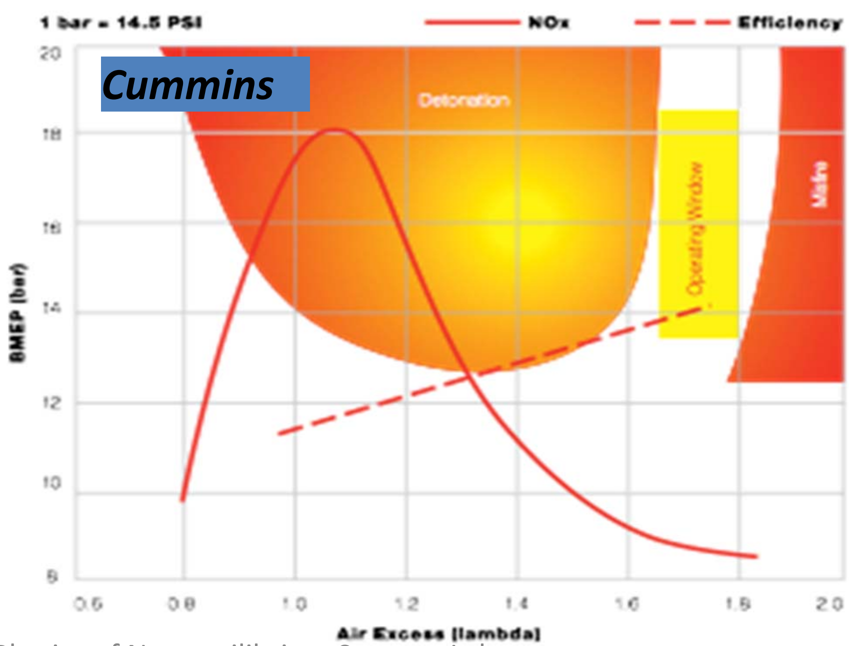


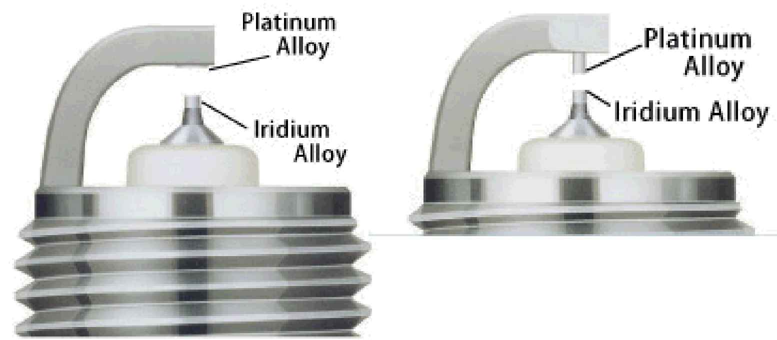


Lean Ignition for Gas IC Engines

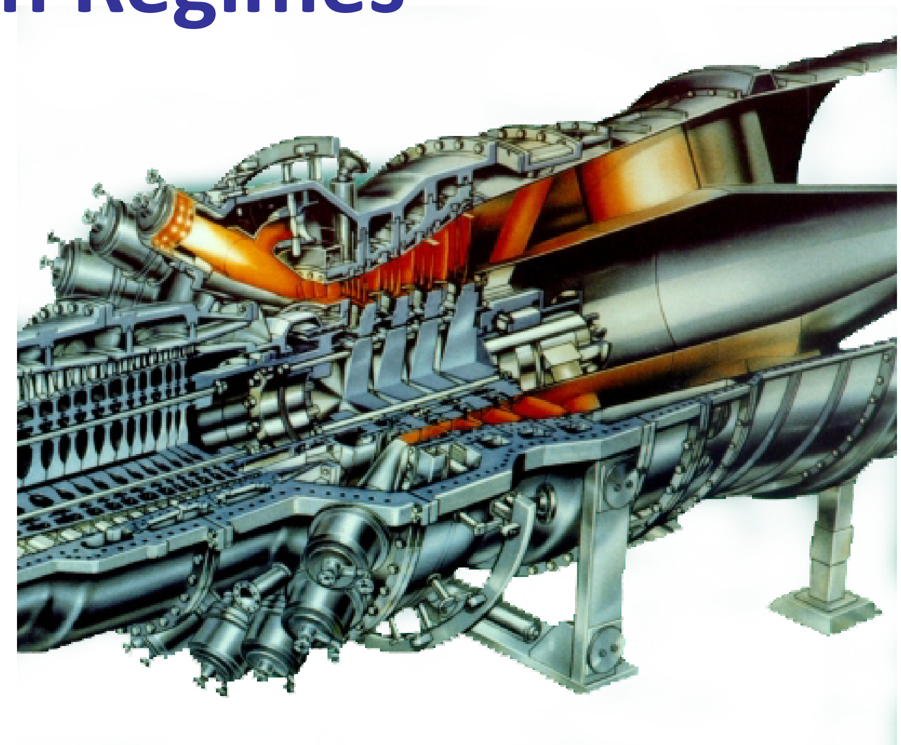


- Regular spark plugs **λ < 1.4**
- Regular spark plugs with thin (Iridium/Platinum) electrodes **λ < 1.6**
- RF, "plasma", etc. plugs **λ < 1.8**





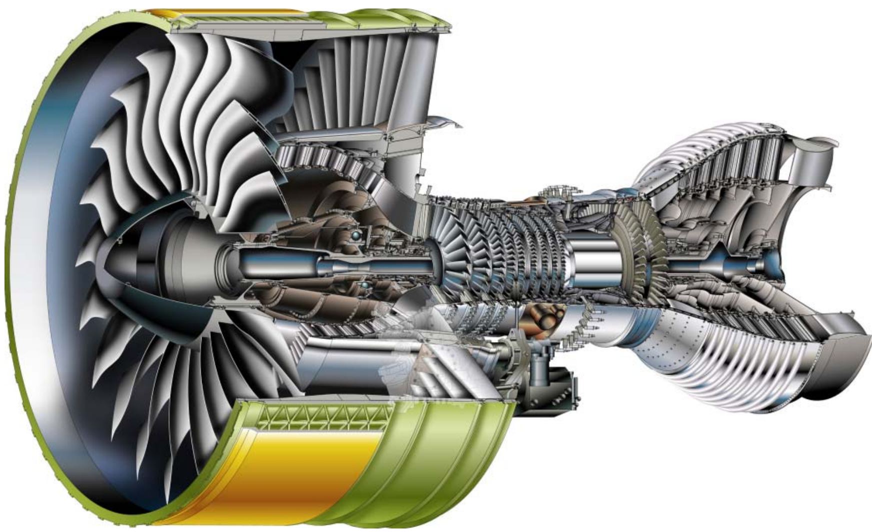
GTE Lean Regimes



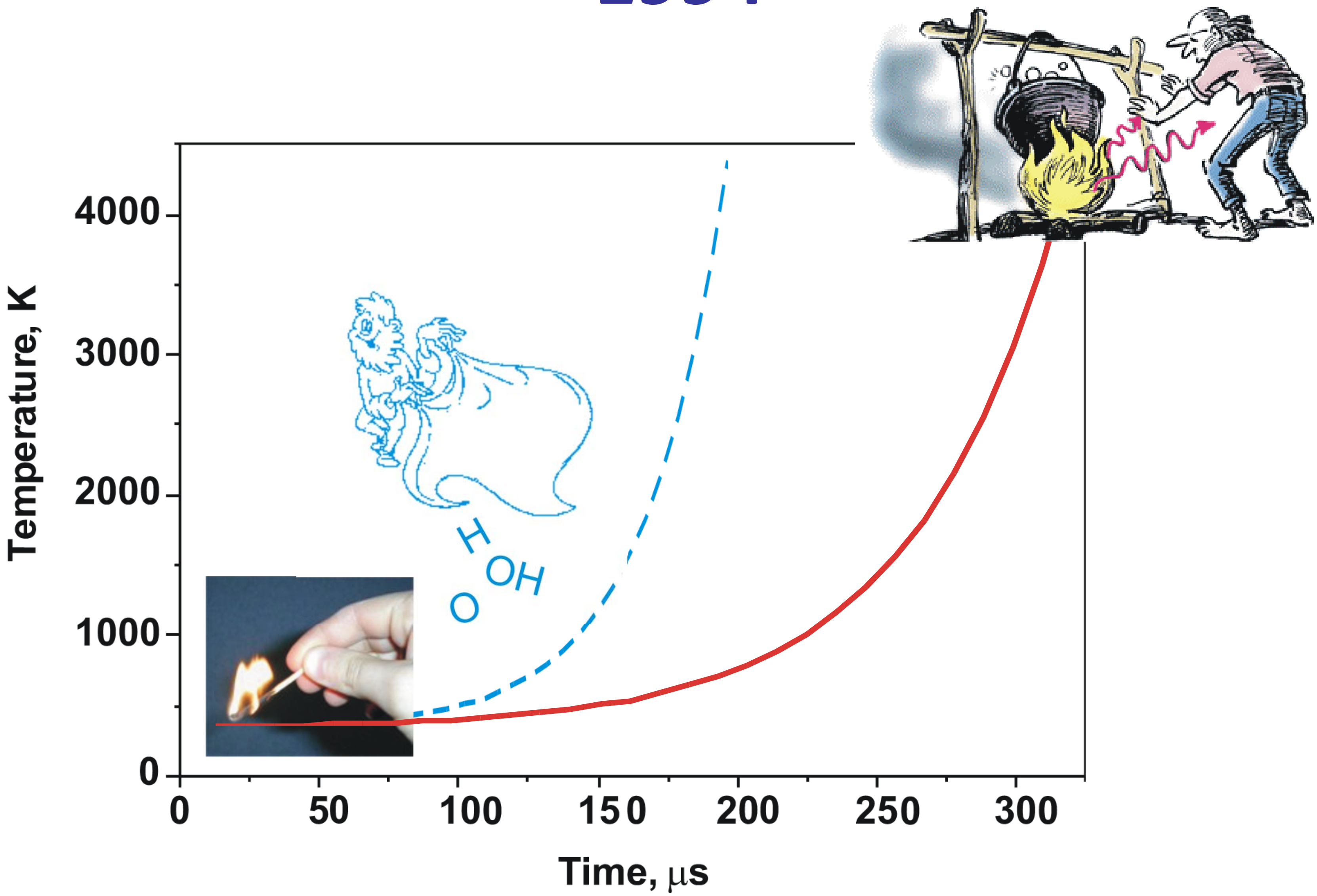
T = 700 – 1300 K

P = 20 – 30 atm

W = 10 – 1000 MW



Decreasing of Ignition Delay Time - 1994



Kinetic Model: Previous Versions

D.V.Zatsepin, S.M.Starikovskaia, A.Yu.Starikovskii *Hydrogen oxidation in a stoichiometric hydrogen-air mixtures in the fast ionization wave*. Combust. Theory Modeling, 2001. V.5 pp.97-129.

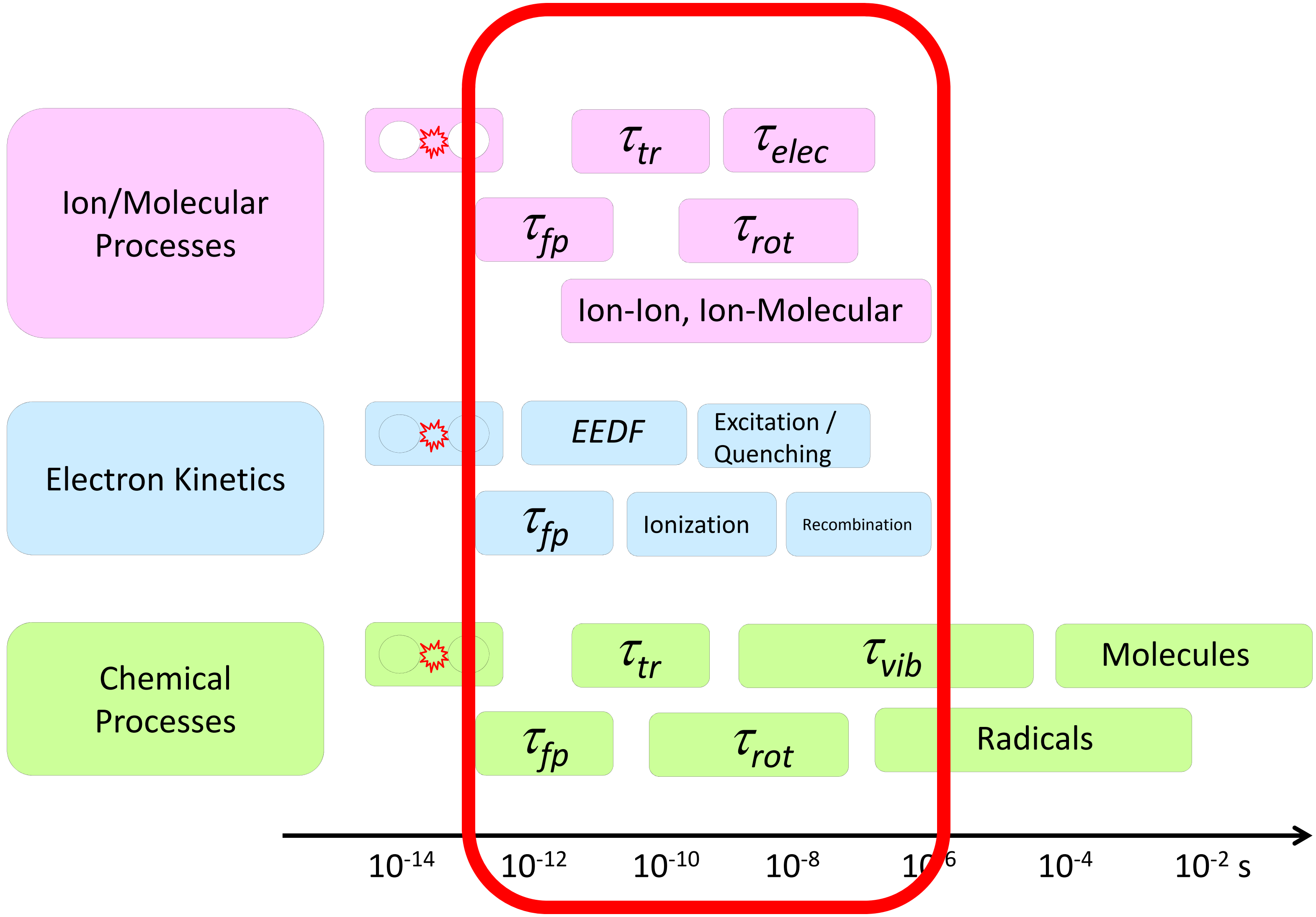
N.A.Popov. *Effect of a Pulsed High-Current Discharge on Hydrogen–Air Mixtures.* Plasma Physics Reports, 2008, Vol. 34, No. 5, pp. 376–391.

I.N. Kosarev, N.L. Aleksandrov, S.V. Kindysheva, S.M. Starikovskaia , A.Yu. Starikovskii. *Kinetics of ignition of saturated hydrocarbons by nonequilibrium plasma: C2H6- to C5H12-containing mixtures.* Combustion and Flame 156 (2009) 221–233

A.Starikovskiy, N.Aleksandrov. *Plasma-assisted ignition and combustion.* Progress in Energy and Combustion Science 39 (2013) 61-110

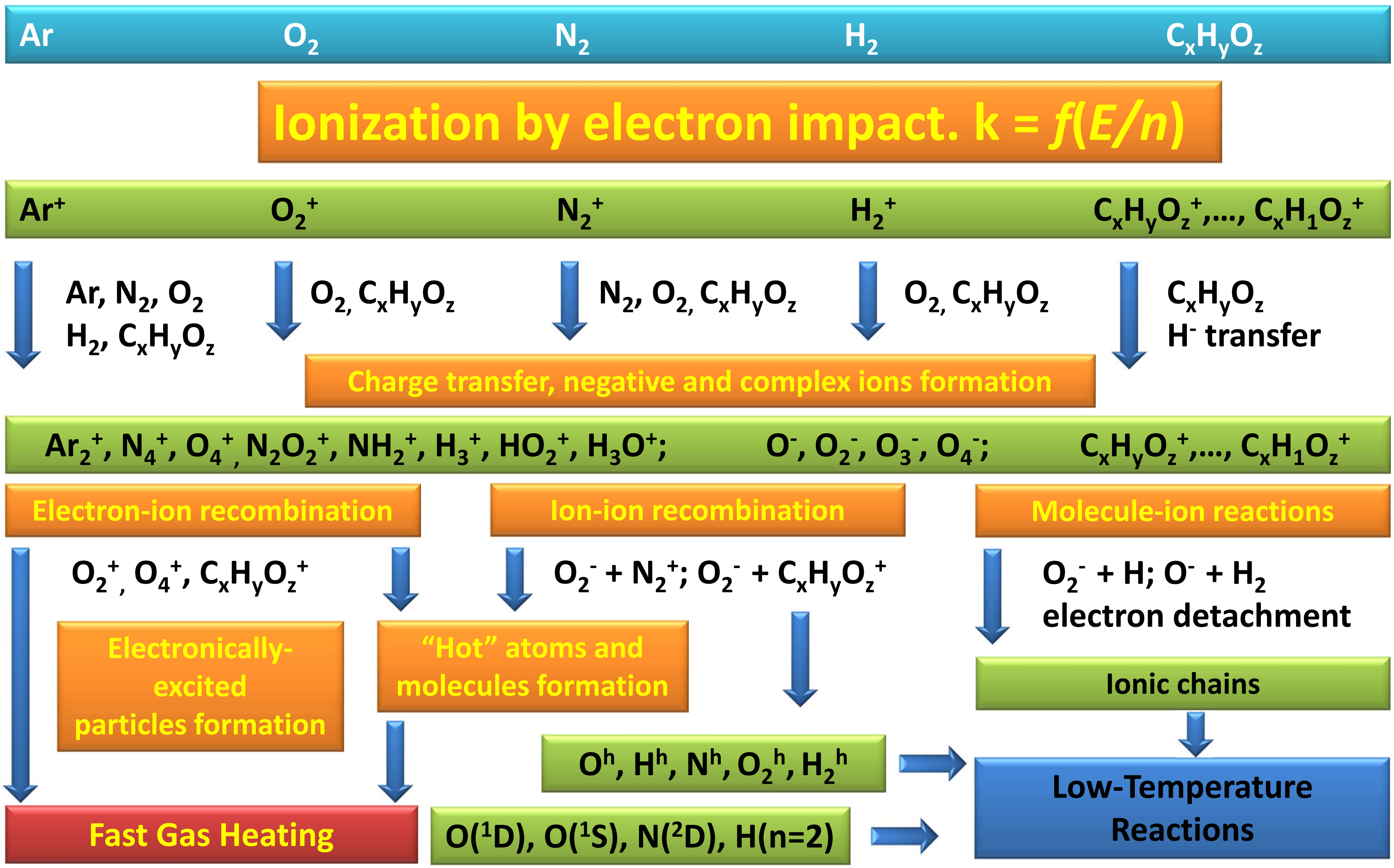
Predictive Modeling:

Key to Applications



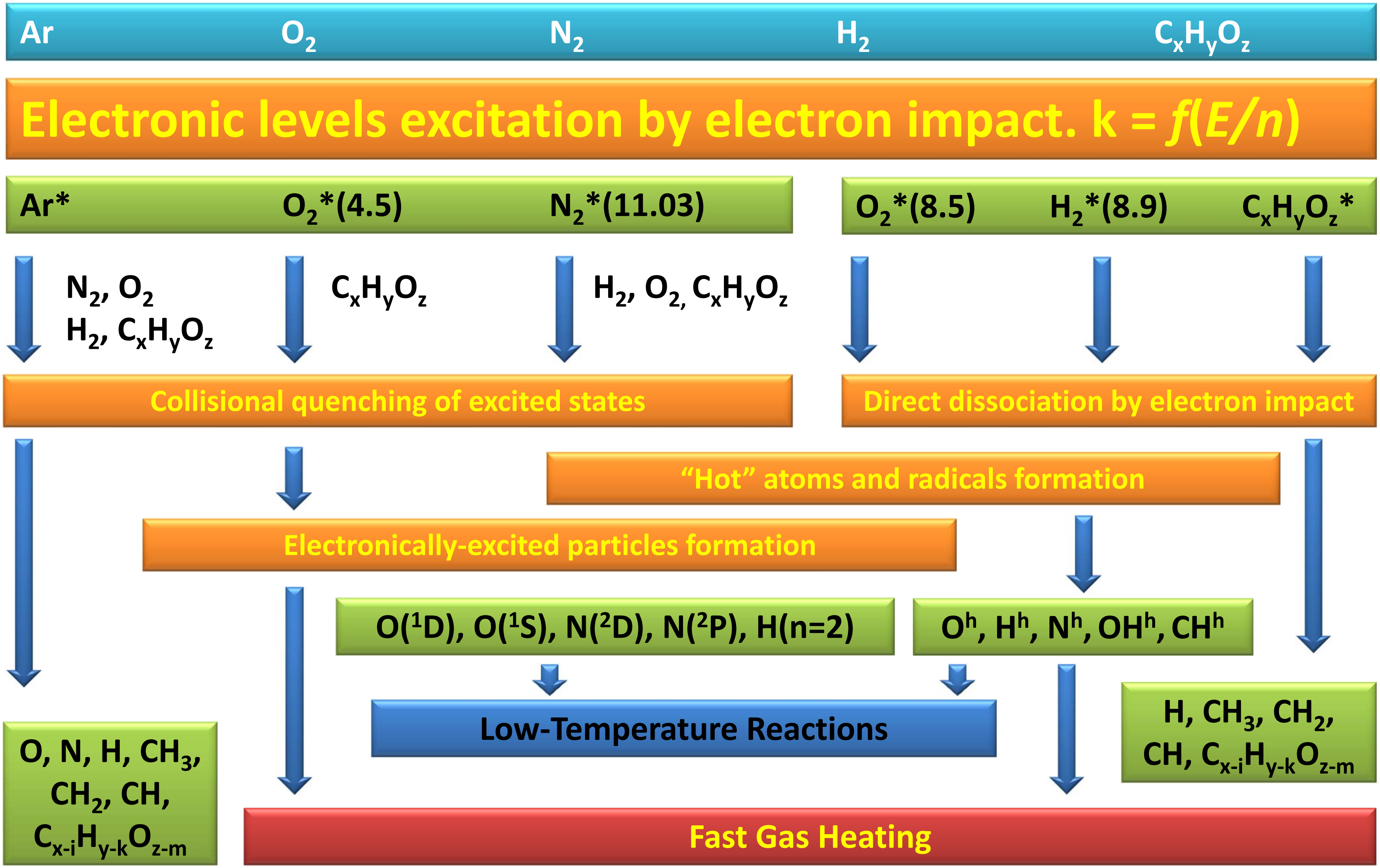
Princeton Plasma Combustion Kinetics

Major Pathways



Princeton Plasma Combustion Kinetics

Major Pathways



Princeton Plasma Combustion Kinetics

Major Pathways

Ar | O_2 | N_2 | H_2 | $C_xH_yO_z$

Vibrational levels excitation by electron impact. k = *f*(*E/n*)

N_2(vib)

VT relaxation

$N_2(v) + O$; $N_2(v) + H_2$

$N_2(v) + H_2O$; $N_2(v) + C_xH_y$

Slow Gas Heating

Energy transfer to reagents

$N_2(v) + HO_2 \rightarrow N_2 + HO_2(w)$

H_2(vib)

Reactions of vibrationaly excited molecules

$H_2(v) + O \rightarrow H + OH(w)$

$H_2(v) + OH \rightarrow H_2O + H$

Formation of vibrationaly-excited products

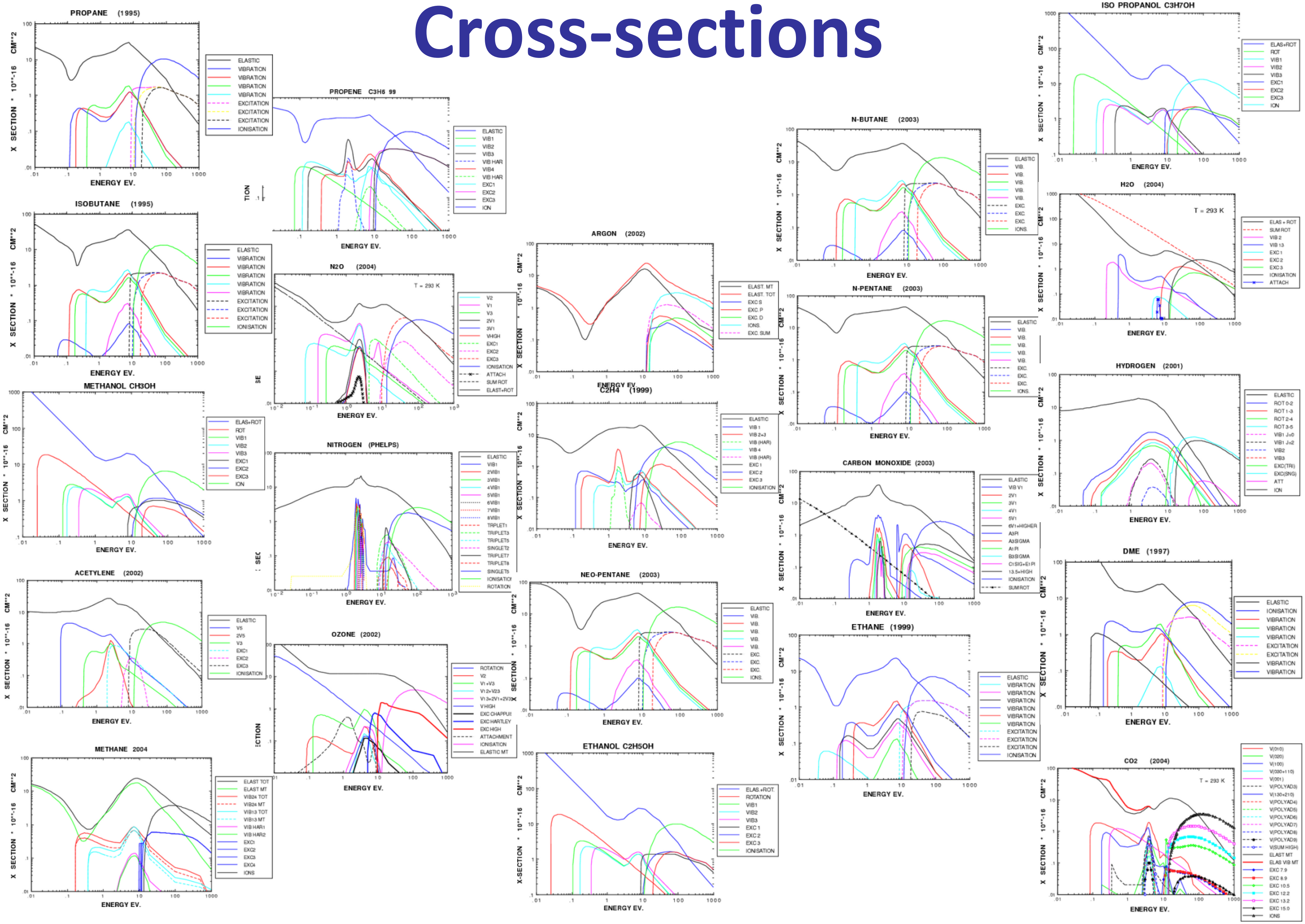
Energy transfer to buffer

$OH(w) + N_2 \rightarrow OH + N_2(v)$

Reactions of vibrationaly excited molecules

$HO_2(w) \rightarrow H + O_2$ $OH(w) + H_2 \rightarrow H_2O + H$

Cross-sections



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				

PAC Kinetic Mechanism

```
N2(+)+O2=N2+O2(+)

N2(+)+O2=>N2+O2(+)
N2(+)+O2=>O2(+)+N2

N2(+)+O=N+NO(+)

N2(+)+O=N2+O(+)

N2(+)+O3=>N2+O+O2(+)
N2(+)+N2(a3su)=>N+N3(+)
N2(+)+NO=N2+NO(+)

N2(+)+N2O=>N2+N2O(+)
N2(+)+N=N(+)+N2

N2(+)+H2=H2(+)+N2

N2(+)+H2O=H2O(+)+N2

N2(+)+CO =>CO(+)+N2
N2(+)+CO2=>CO2(+)+N2

N2(+)+N2+N2=N2+N4(+)

N2(+)+N2+M=>N4(+)+M

N2(+)+N+N2=>N2+N3(+)

N2(+)+H2=>HN2(+)+H

N2(+)+CH4=CH2(+)+N2+H2
N2(+)+CH4=CH3(+)+N2+H
N2(+)+CH4=>N2+CH3(+)+H

N2(+)+C2H5OH=>N2+ H5C2O(+)+H
N2(+)+C2H2=>N2+C2H(+)+H

C2H(+)+e=C2+H
C2H(+)+e=CH+C
C2H(+)+C2H2=C4H2(+)+H
C4H2(+)+C2H2=C6H3(+)+H
C4H2(+)+C2H2=C6H4(+)+PHOTON
C4H2(+)+e=C4H+H
C6H3(+)+e=C6H+H2
C6H3(+)+e=C6H2+H
C6H4(+)+e=C6H+H2+H
C6H4(+)+e=C6H2+H2

N2(+)+C2H4=>N2+C2H3(+) + H

C2H3(+)+e=C2H2+H

N2(+)+C2H6=>N2+C2H5(+)+H
N2(+)+C3H8=>N2+C3H7(+)+H
N2(+)+C4H10=>N2+C4H9(+)+H
N2(+)+C5H12=>N2+C5H11(+)+H
```

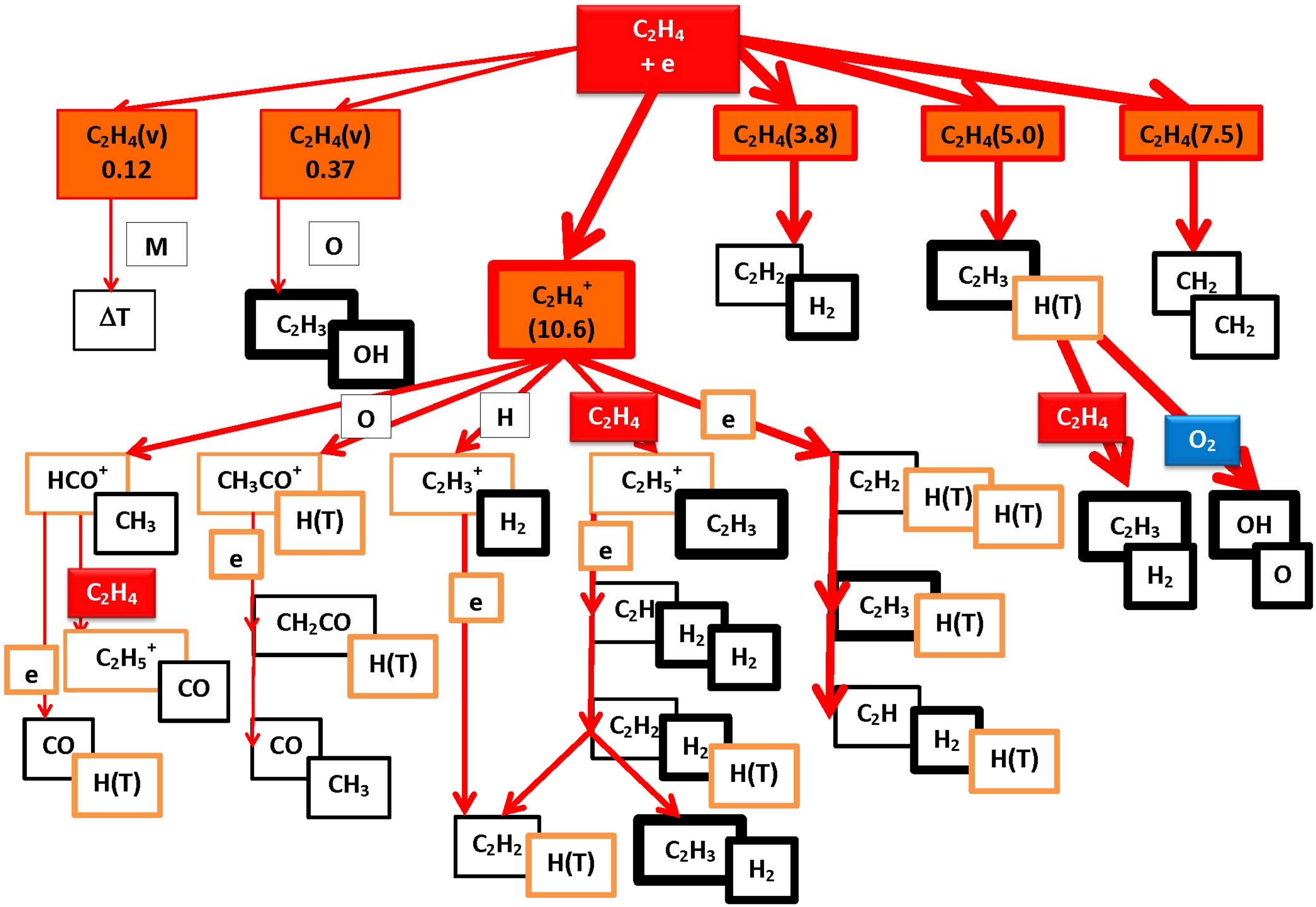
```
O(-)+N(+)=N+O

O(-)+N(+) +O2=>NO+O2
O(-)+N(+) +N2=>N2+NO

O(-)+O(+)=>O+O(5p)
O(-)+O(+)=>O(1d)+O(5s)
O(-)+O(+)=O+O

O(-)+O(+)+O2=>O2+O2
O(-)+O(+)+N2=>N2+O2

O(-)+N2(+)=>N2+O
O(-)+N2(+)=>N+N+O
O(-)+N2(+)+N2=>N2+N2O
O(-)+N2(+)+O2=>N2O+O2

O(-)+O2(+)=>O+O2
O(-)+O2(+)=>O+O+O
O(-)+O2(+)+O2=>O2+O3
O(-)+O2(+)+N2=>N2+O3

O(-)+N3(+)  =>N+N2+O
O(-)+N4(+)  =>N2+N2+O
O(-)+O4(+)=>O+O2+O2

O(-)+H2(+)=>H+OH
O(-)+CH4(+)=>H2+CH3
O(-)+C2H2(+)=>H2+C2H
O(-)+C2H5OH(+)=>H2+H5C2O
O(-)+C2H4(+)=>H2+C2H3
O(-)+C2H6(+)=>H2+C2H5
O(-)+C3H8(+)=>H2+C3H7
O(-)+C4H10(+)=>H2+C4H9
O(-)+C5H12(+)=>H2+C5H11

O(-)+NO(+)  =>NO+O
O(-)+NO(+)  =>N+O+O
O(-)+NO(+)+O2=>NO2+O2
O(-)+NO(+)+N2=>N2+NO2

O(-)+NO2(+) =>NO2+O
O(-)+NO2(+) =>NO+O+O
O(-)+NO3(+) =>NO+O+O2
O(-)+N2O(+) =>N+NO+O
O(-)+N2O(+) =>N2O+O
O(-)+N3O(+) =>N2+NO+O
O(-)+N2O2(+)=>NO+NO+O
O(-)+N2O2(+)=>N2+O+O2
```

```
H2(v)+N2=H2+N2
LT /-144.9 0.0/

H2(v)+O2=H2+O2
LT /-144.9 0.0/

H2(v)+CO2=H2+CO2
LT /-144.9 0.0/

H2(v)+H2O=H2+H2O
LT /-144.9 0.0/

H2(v)+H2=H2+H2
LT /-144.9 0.0/

H2(v)+OH=H2+OH
LT /-144.9 0.0/

H2(v)+H=H2+H
LT /0.0 0.0/

H2(v)+O=H2+O
LT /0.0 0.0/

CH4(v)+CH4=CH4+CH4
LT /-40.0 0.0/

CH4(v)+M=CH4+M
LT /-61.0 0.0/

C2H6(v)+M=C2H6+M
LT /0.0 0.0/

C2H2(v)+M=C2H2+M
LT /0.0 0.0/

C2H4(v)+M=C2H4+M
LT /0.0 0.0/

C2H5OH(v)+M=C2H5OH+M
LT /0.0 0.0/

C3H8(v)+M=C3H8+M
LT /0.0 0.0/

C4H10(v)+M=C4H10+M
LT /0.0 0.0/

C5H12(v)+M=C5H12+M
LT /0.0 0.0/
N2 + CO2(v) = CO2 + N2(v)
```

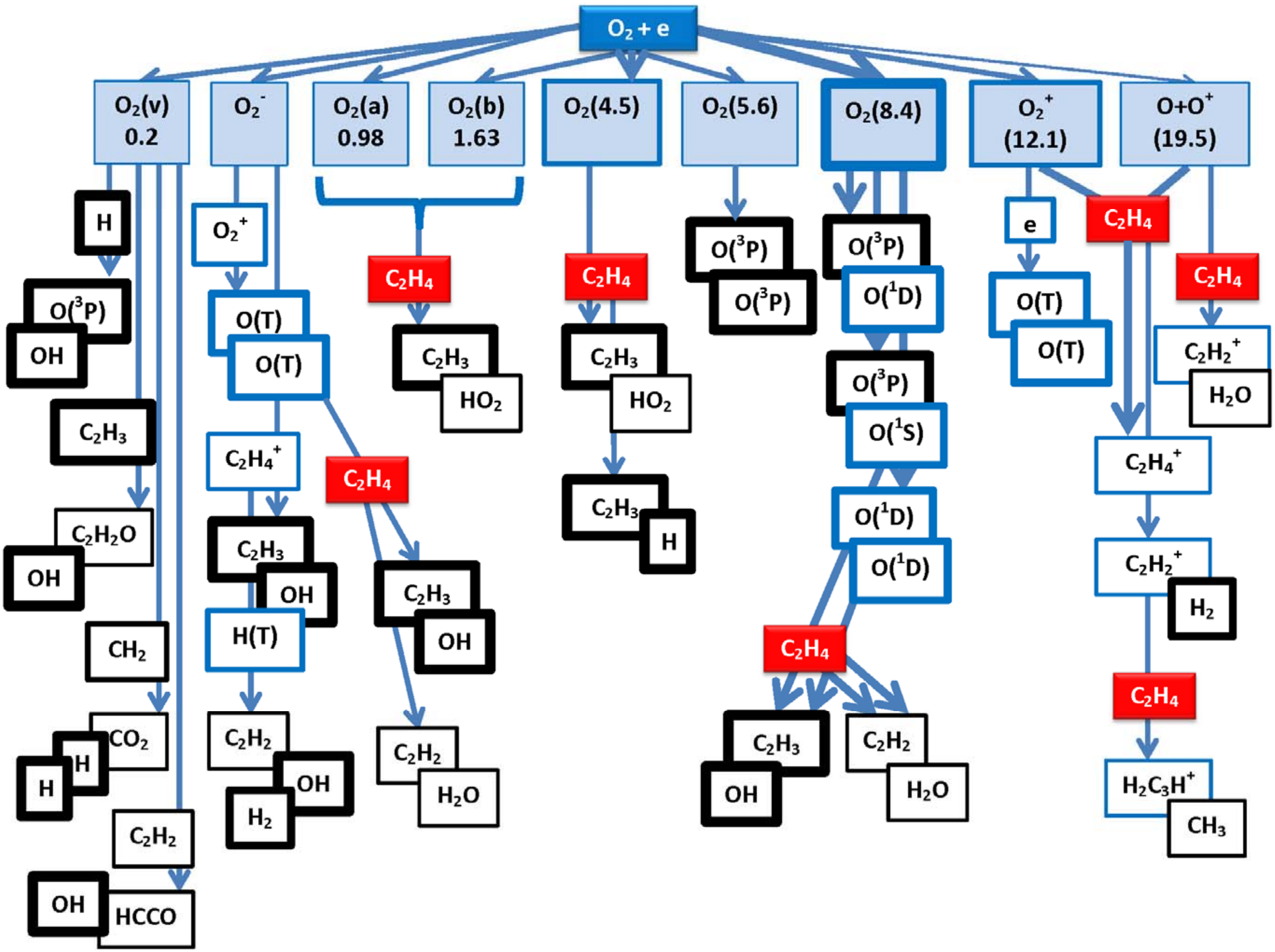
```
O2(v) + H = O + OH(v)
H2(v) + O = H + OH(v)
CH4(v) + O = CH3 + OH(v)
C2H2(v) + O = C2H + OH(v)
C2H4(v) + O = C2H3 + OH(v)
C2H6(v) + O = C2H5 + OH(v)
C2H5OH(v) + O = H2C2O + OH(v)
C3H8(v) + O = C3H7 + OH(v)
C4H10(v) + O = C4H9 + OH(v)
C5H12(v) + O = C5H11 + OH(v)

H2+OH(V)=H+H2O
CH4+OH(V)=CH3+H2O
C2H4+OH(V)=C2H3+H2O
C2H2+OH(V)=CH3+CO
C2H6+OH(V)=C2H5+H2O
C3H8+OH(V)=NC3H7+H2O
C4H10+OH(V)=PC4H9+H2O
NC5H12+OH(V)=C5H11-1+H2O

H(T) + H2 = H + H2
H(T) + M = H + M
O(T) + H2 = O + H2
O(T) + M = O + M

O2 + H(T) = O + OH(v)
H2 + O(T) = H + OH(v)
CH4 + O(T) = CH3 + OH(v)
C2H2 + O(T) = C2H + OH(v)
C2H4 + O(T) = C2H3 + OH(v)
C2H6 + O(T) = C2H5 + OH(v)
C2H5OH + O(T) = H2C2O + OH(v)
C3H8 + O(T) = C3H7 + OH(v)
C4H10 + O(T) = C4H9 + OH(v)
C5H12 + O(T) = C5H11 + OH(v)

HO2(v) = O2 + H
H2O2(v) = OH + OH

!H2O2+O  =  OH+HO2
!H2O2+OH =  H2O+HO2
!HO2+O   =  OH+O2
!HO2+OH  =  H2O+O2
```

```
N2(c3pu)=>N2(b3pg)
N2(c3pu)=>N2(b3pg)+hn

N2(c3pu)+N=>N+N2(b3pg)
N2(c3pu)+N=>N(2p)+N2

N2(c3pu)+N2=>N2+N2
N2(c3pu)+N2=>N2(a'1)+N2
N2(c3pu)+N2=N2+N2(a'1su)

N2(c3pu)+N2=N2+N2(a1su)

N2(c3pu)+N2=N2+N2(b3pg)

N2(c3pu)+O2=>N2+2O(T)
N2(c3pu)+O2=>N2+2O(T)
N2(c3pu)+O2=>N2(a3su)+O2
N2(c3pu)+O2=>N2+O(T)+O(1d)
N2(c3pu)+O2=>N2+O2

N2(c3pu)+NO=>N2+NO

N2(c3pu)+H2=>N2+2H(T)

N2(c3pu)+CH4=>N2+CH3+H(T)
N2(c3pu)+CH4=>N2+CH2+2H(T)
N2(c3pu)+CH4=>N2+CH2+H2
N2(c3pu)+CH4=>N2+CH+H(T)+H2

N2(c3pu)+C2H2=>N2+C2H+H(T)
N2(c3pu)+C2H2=>N2+CH+CH

N2(c3pu)+C2H4=>N2+C2H3+H(T)
N2(c3pu)+C2H4=>N2+C2H2+2H(T)
N2(c3pu)+C2H4=>N2+CH2+CH2

N2(c3pu)+C2H6=>N2+C2H5+H(T)
N2(c3pu)+C2H6=>N2+C2H4+2H(T)
N2(c3pu)+C2H6=>N2+C2H4+H2
N2(c3pu)+C2H6=>N2+CH3+CH3

N2(c3pu)+C2H5OH=>N2+C2H4OH+H(T)
N2(c3pu)+C2H5OH=>N2+C2H3OH+2H(T)
N2(c3pu)+C2H5OH=>N2+C2H5+HO
N2(c3pu)+C2H5OH=>N2+CH3+CH2OH

N2(c3pu)+C3H8=>N2+C3H7+H(T)
N2(c3pu)+C3H8=>N2+C3H6+2H(T)
N2(c3pu)+C3H8=>N2+C3H6+H2
N2(c3pu)+C3H8=>N2+CH3+C2H5

N2(c3pu)+C4H10=>N2+C4H9+H(T)
N2(c3pu)+C4H10=>N2+C4H8+2H(T)
N2(c3pu)+C4H10=>N2+C4H8+H2
N2(c3pu)+C4H10=>N2+CH3+C3H7
N2(c3pu)+C4H10=>N2+C2H5+C2H5

N2(c3pu)+C5H12=>N2+C5H11+H(T)
N2(c3pu)+C5H12=>N2+C5H10+2H(T)
N2(c3pu)+C5H12=>N2+C5H10+H2
N2(c3pu)+C5H12=>N2+CH3+C4H9
N2(c3pu)+C5H12=>N2+C2H5+C3H7
```

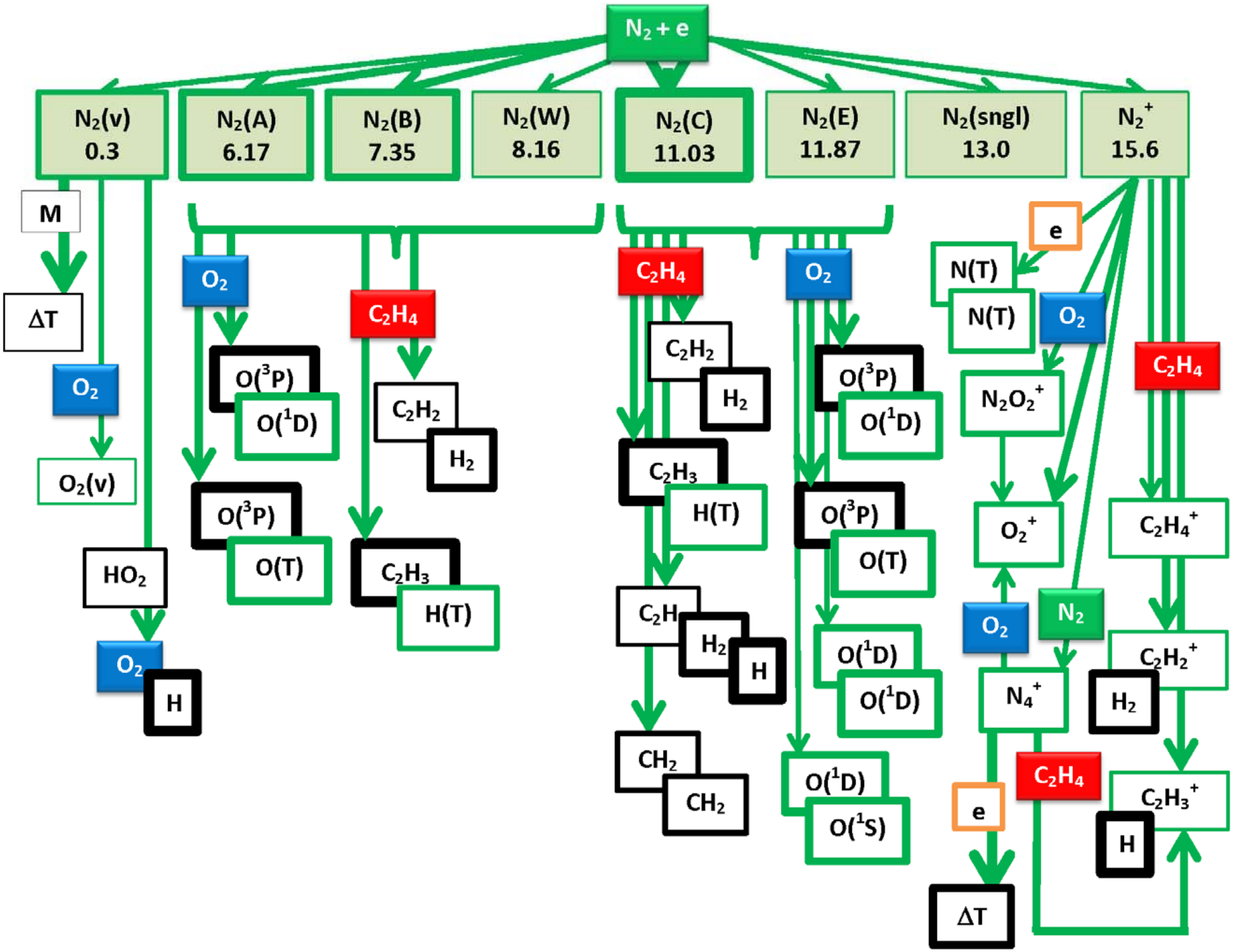
PAC Pathways: C_2H_4-air



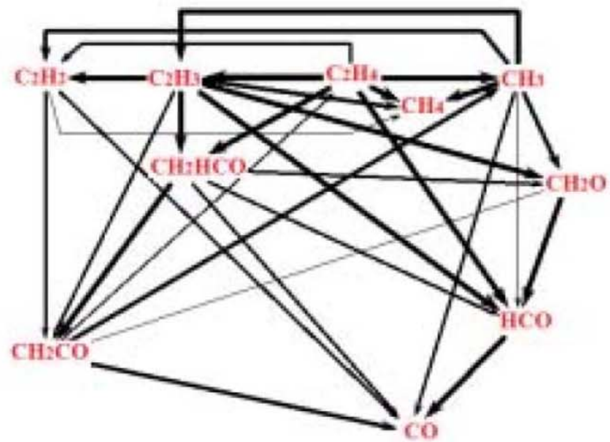
PAC Pathways: C_2H_4-air



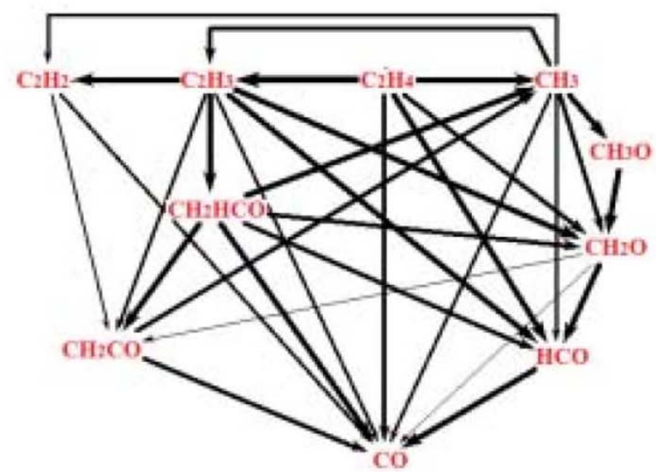
PAC Pathways: C_2H_4-air



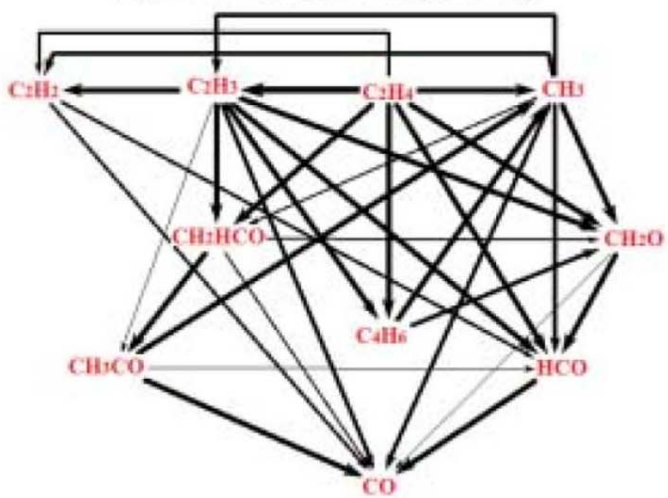
Pathway analysis in ignition process at the time of T=1360K for Ø = 1, Ar=92%, P=2.1atm and initial T=1350K. Konnov, 2014



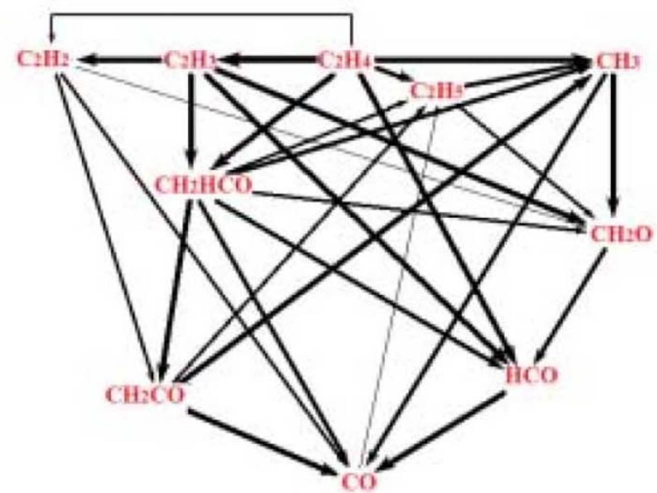
(LLNL nButane mechanism)



(USC mechanism)

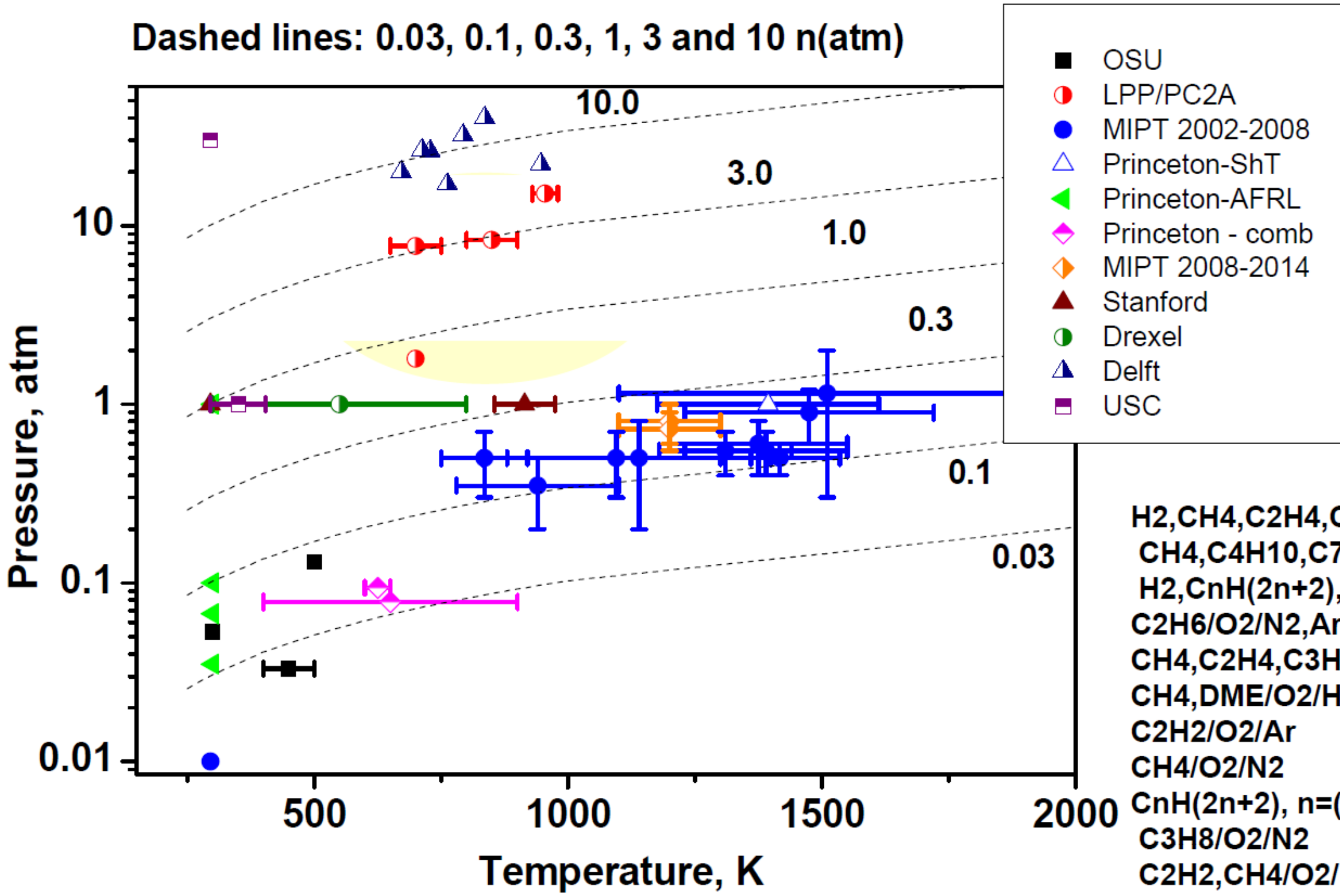


(Konnov mechanism)



(UCSD mechanism)

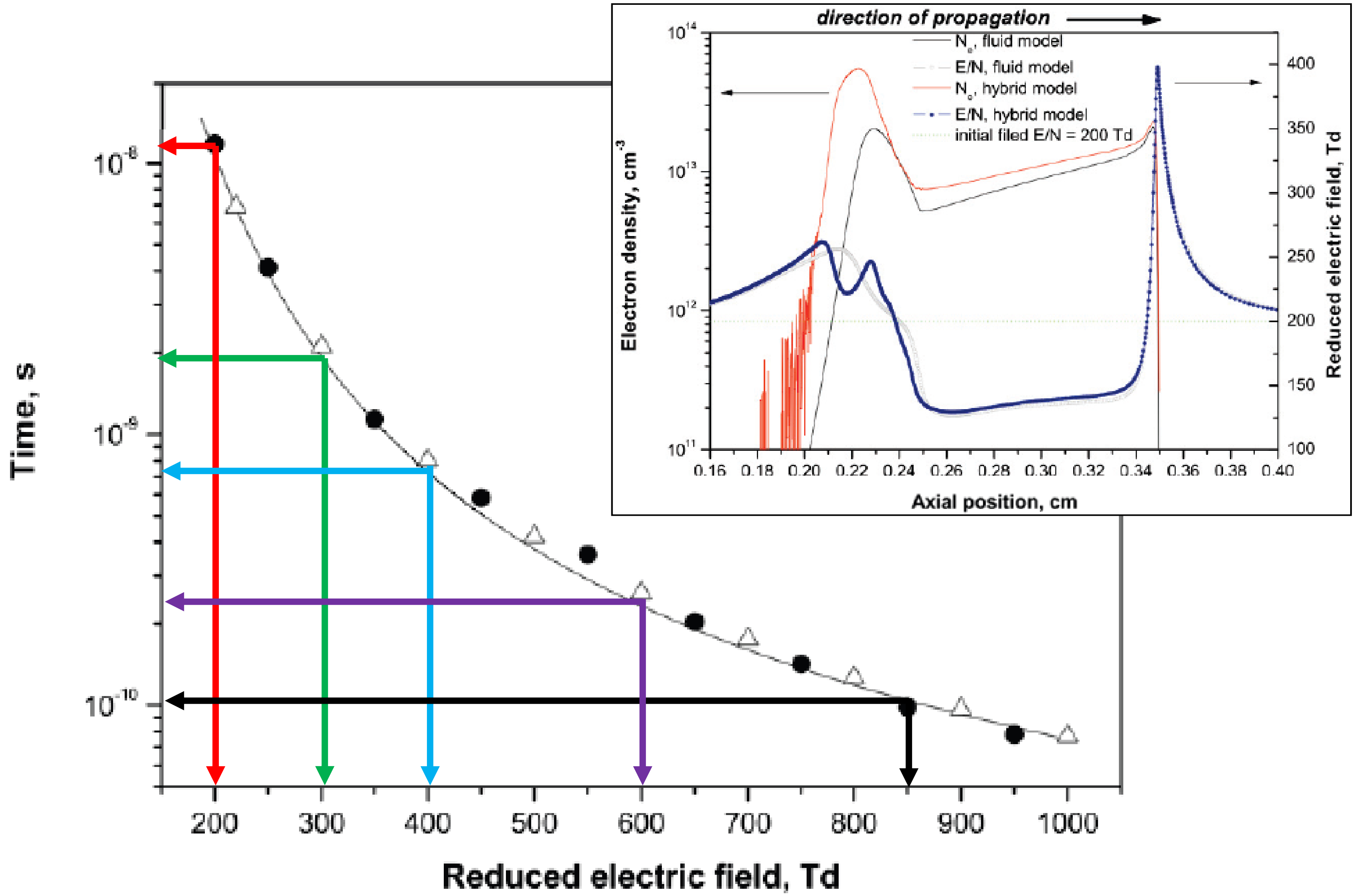
Where PAC Experimental Data is Available



H2,CH4,C2H4,C3H8/O2/N2,Ar
CH4,C4H10,C7H16/O2/N2,Ar
H2,CnH(2n+2), n=(1-10)/O2,N2O/N2,Ar,He
C2H6/O2/N2,Ar
CH4,C2H4,C3H8/O2/N2,Ar
CH4,DME/O2/He,Ar
C2H2/O2/Ar
CH4/O2/N2
CnH(2n+2), n=(1-5)/O2/N2
C3H8/O2/N2
C2H2,CH4/O2/N2

S M Starikovskaia, J. Phys. D.: Appl. Phys, 47 (2014) 353001(34pp)

Avalanche to Streamer Transition in Uniform Electric Field (air, 1 bar, 300 K, 1 cm, various E/n)

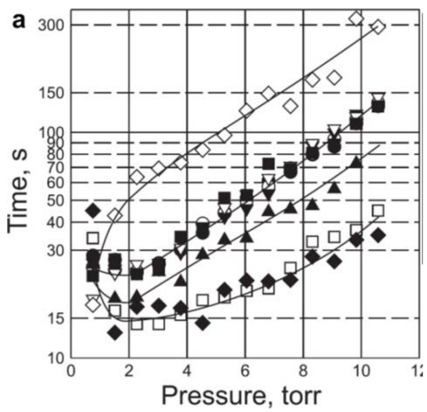


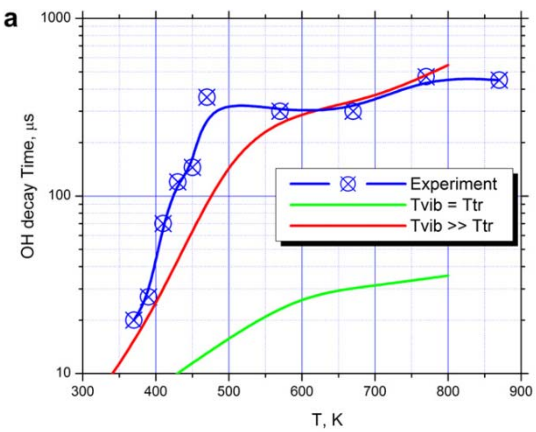
Princeton Plasma Combustion Kinetics

Mechanism Validation

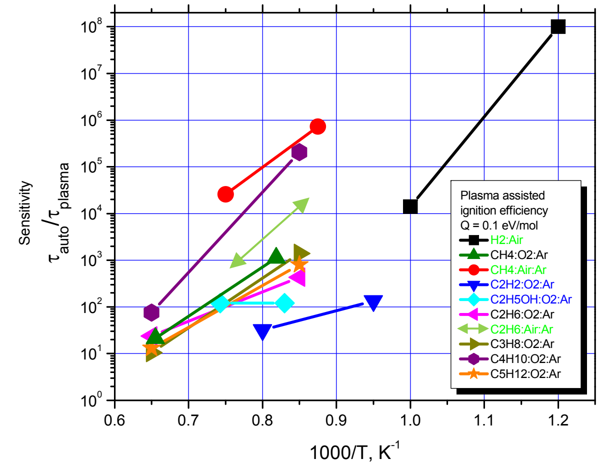
T = 300 K	T = 300 - 800 K	T = 800 – 1700 K

Slow Oxidation of H_2, C1-C10 P = 1-10 Torr



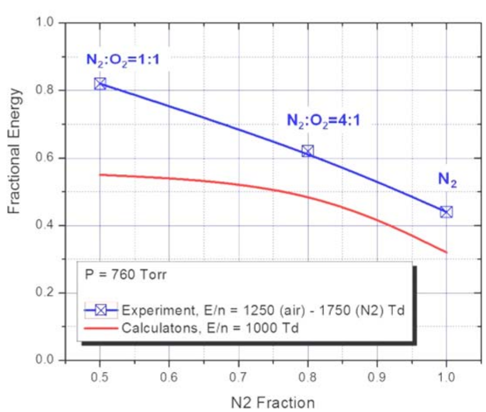


Ignition Delay Time Reduction. H_2, C1-C5, C_2H_2, C_2H_5OH – O_2-Ar Mixtures. P = 0.3-0.5 atm

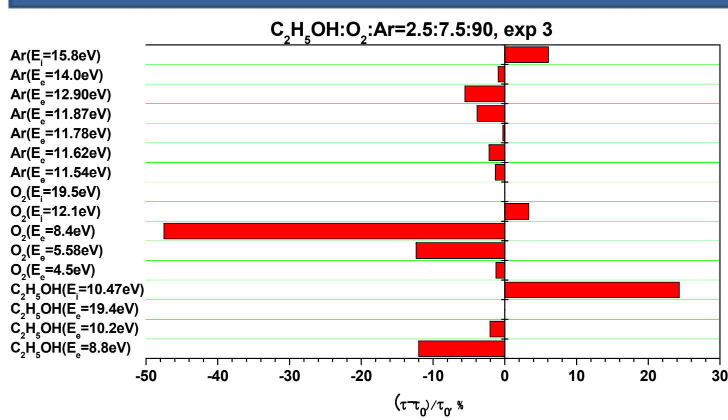


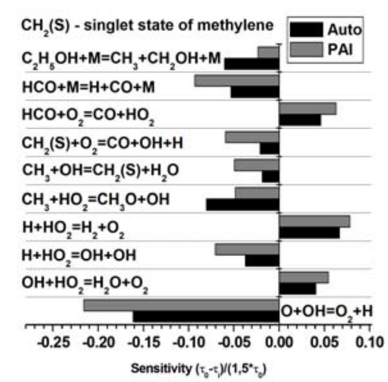
Oxidation Chains Development in Lean H_2, CO, C1-C4 - Air Mixtures. P = 1 atm

Fast Gas Heating Mechanism. N_2-O_2 mixtures P = 0.2 – 1 atm

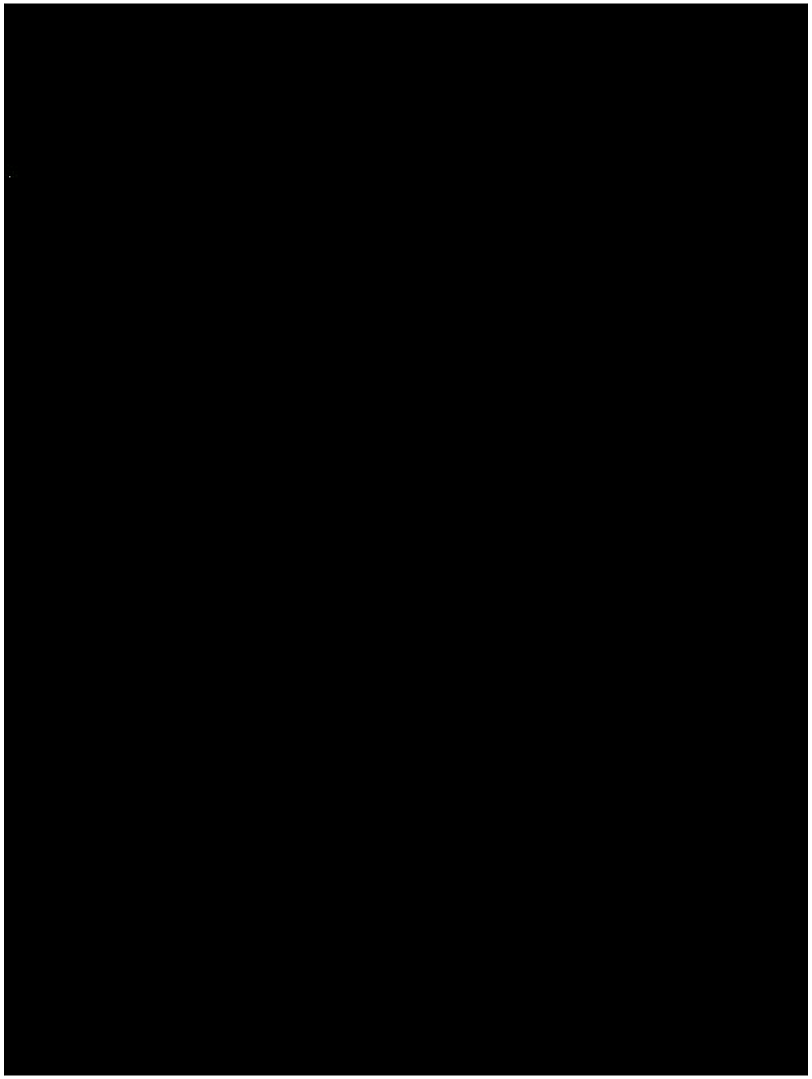


Sensitivity Analysis for Discharge and Combustion Stages





SDBD Discharge and Fast Heating



Gate = 0.5 ns

Time shift between frames is 1 ns

The movie duration is 41 ns

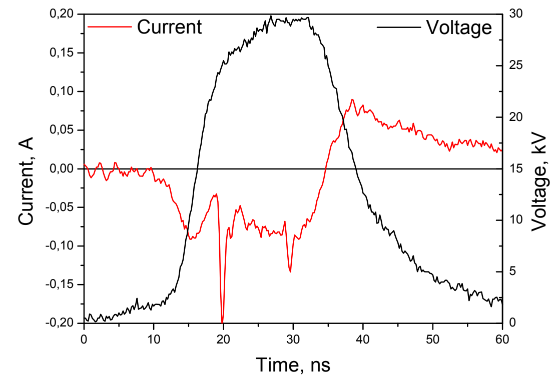
Impulse Parameters

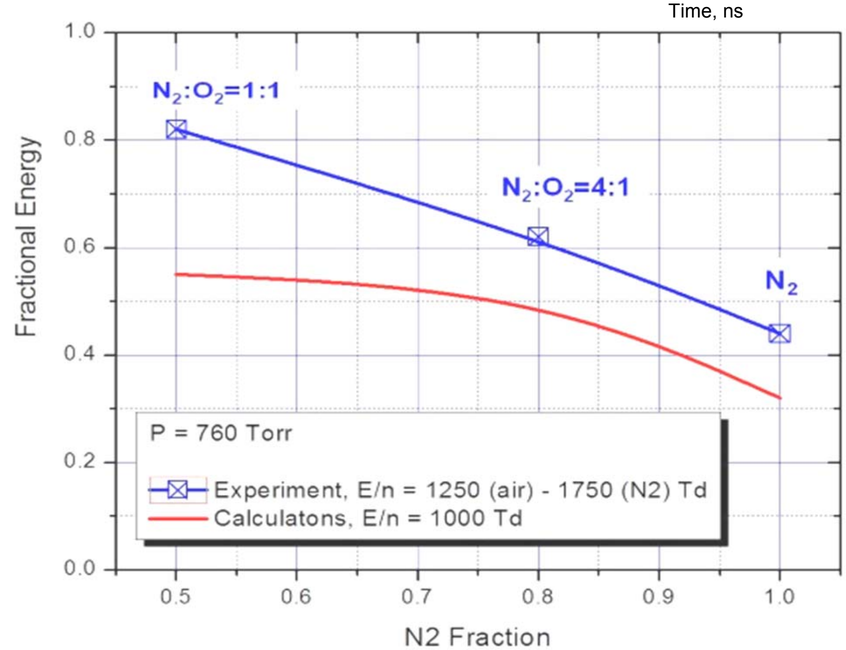
V = 14 kV

$t_{1/2}$ *= 20 ns*

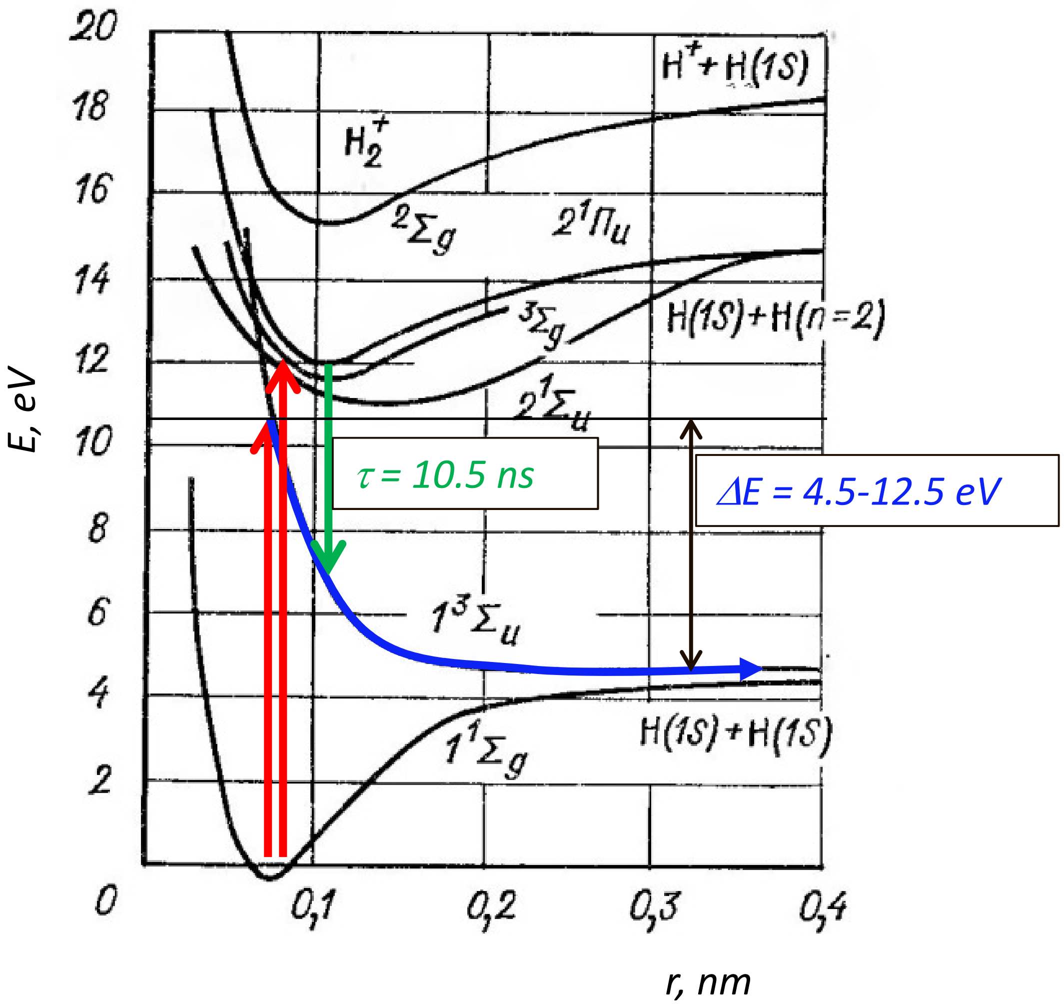
Frequency = 1 kHz

Velocity = 0.4 mm/ns





Potential Energy Curves of Molecular Hydrogen

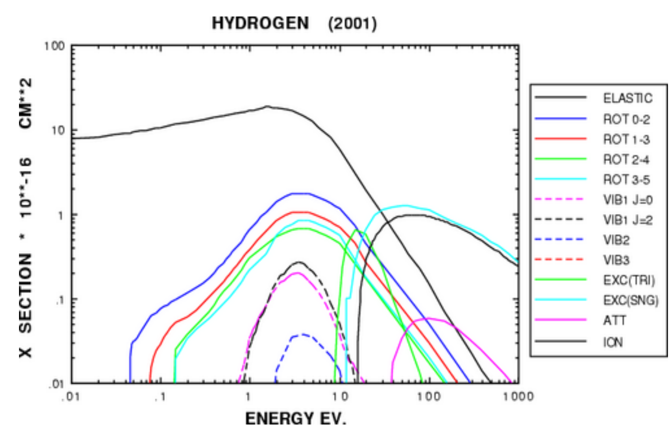


$H_2(b^3\Sigma_u)$, 8.9 eV
σ_{max} = 0.33 A^2 (17 eV)

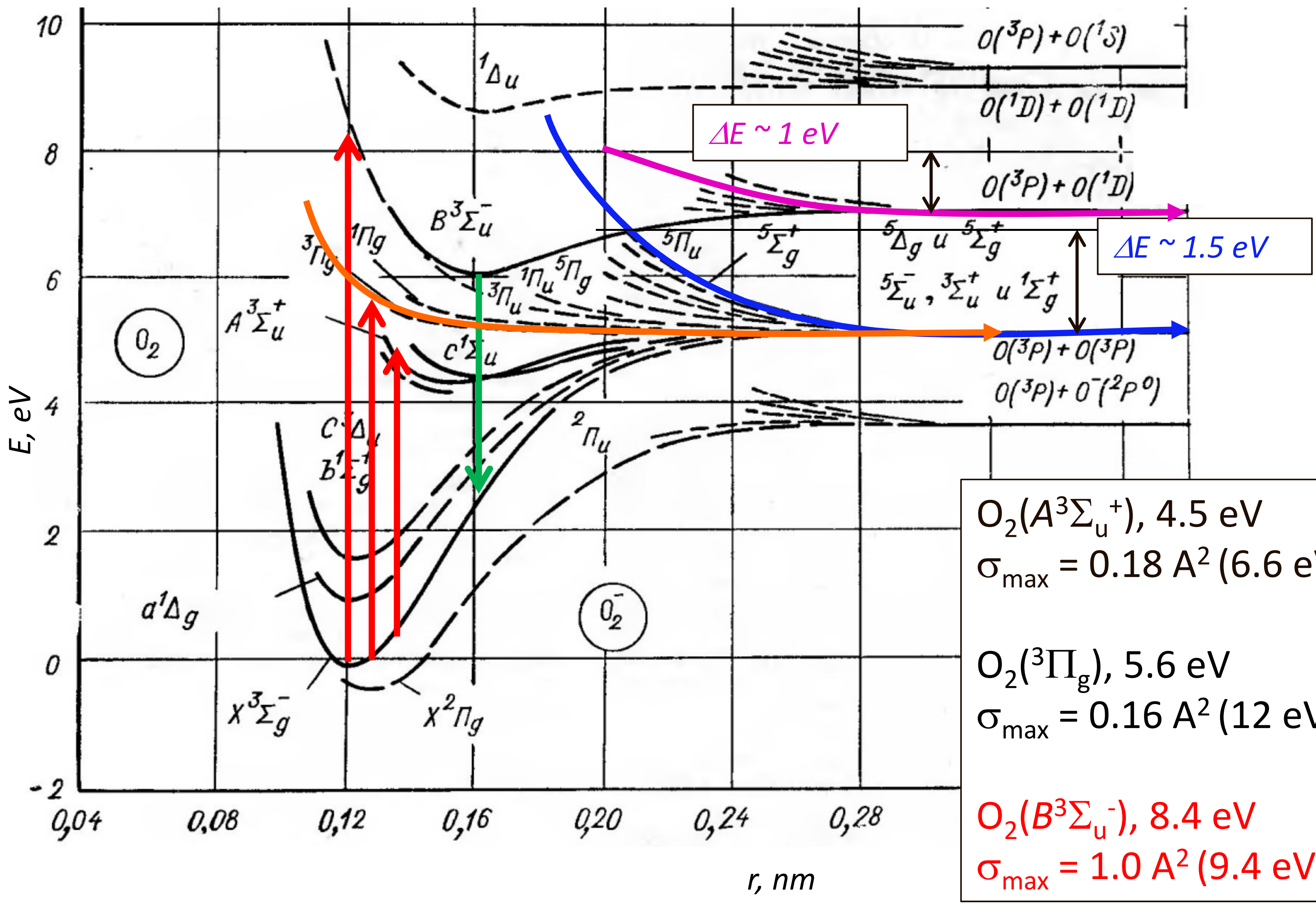
$H_2(a^3\Sigma_g)$, 11.8 eV
σ_{max} = 0.12 A^2 (15 eV)

$H_2(B^1\Sigma_u)$, 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

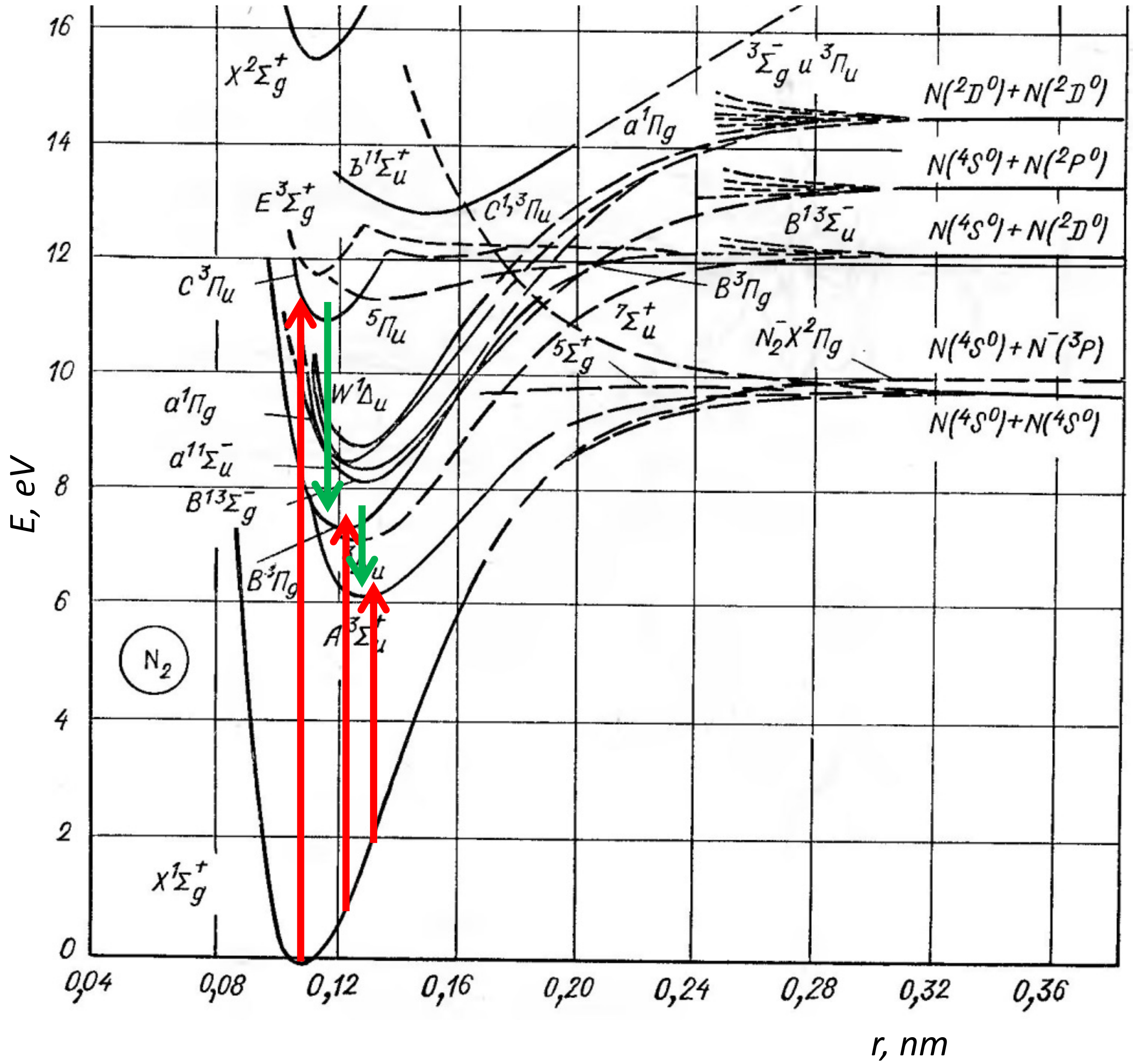


$O_2(A^3\Sigma_u^+)$, 4.5 eV
σ_{max} = 0.18 A^2 (6.6 eV)

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

$O_2(B^3\Sigma_u^-)$, 8.4 eV
σ_{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)

Major Channels of Hot Atoms Production

$N_2 + e = N_2(C^3\Pi_u) + e$; $k = f(E/n)$

$N_2(C^3\Pi_u) + H_2 = N_2 + 2H(^1S) + 6.55\ eV$; $k = 3.2\times10^{-10}\ cm^3/s$

$N_2(C^3\Pi_u) + O_2 = N_2 + 2O(^3P,^1D) + 3.9\ eV$; $k = 2.7\times10^{-10}\ cm^3/s$

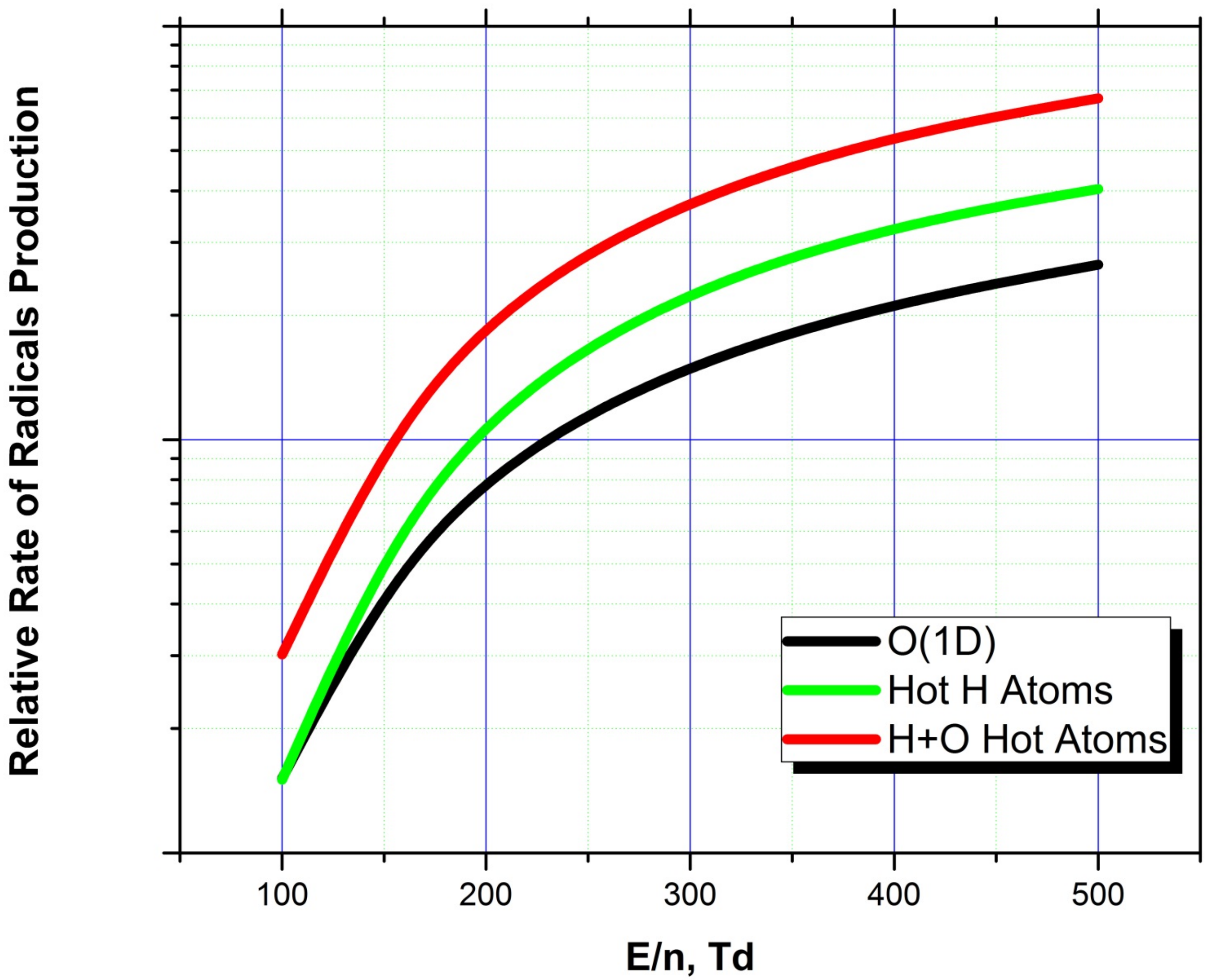
$O_2 + e = e + 2O(^3P,^1D) + 1.3\ eV$; $k = f(E/n)$

$H_2 + e = e + 2H(^1S) + 4.4\ eV$; $k = f(E/n)$

Chain Initiation/Branching Reactions

$H + O_2 = O + OH$	$k = 1.6x10^{-10}$ x $\exp(-7470/T)$ cm^3/s	
	$k(300) = 2.5x10^{-21}$ cm^3/s	
	$k(hot) = 1.6x10^{-10}$ cm^3/s	
$H + O_2 + M = HO_2 + M$	$k(300, 1\ atm) = 1.6x10^{-12}$ cm^3/s	$T_{crit} \sim T_{autoignition}$
$O + H_2 = H + OH$	$k = 8.5x10^{-20}$ x $T^{2.67}$ x $\exp(-3160/T)$ cm^3/s	
	$k(300) = 9.3x10^{-18}$ cm^3/s	
	$k(hot) = 1.5x10^{-10}$ cm^3/s	
	$k(^1D) = 1.1x10^{-10}$ cm^3/s	
$O + O_2 + M = O_3 + M$	$k(300, 1\ atm) = 2.2x10^{-14}$ cm^3/s	$T_{crit} \sim 650K$
$H(hot) + (N_2,H_2) = H + (N_2,H_2)$	$k \sim 2m/M\ k_{gk} \sim 1.6x10^{-10}$ cm^3/s	
$O(hot) + (N_2,O_2) = O + (N_2,O_2)$	$k \sim 2m/M\ k_{gk} \sim 1.3x10^{-10}$ cm^3/s	
$H(hot) + O_2 = H + O + O$		
$H(hot) + H_2 = H + H + H$		
$O(^1D) + (M) = O + (M)$	$k = 2.6x10^{-11}$ cm^3/s $(M = O_2)$	
	$k = 1.3x10^{-11}$ cm^3/s $(M = N_2)$	
	$k = 5.2x10^{-11}$ cm^3/s $(M = H_2)$	

Radicals Production Increase in Cold H_2-Air Mixture Due to Hot Atoms Formation

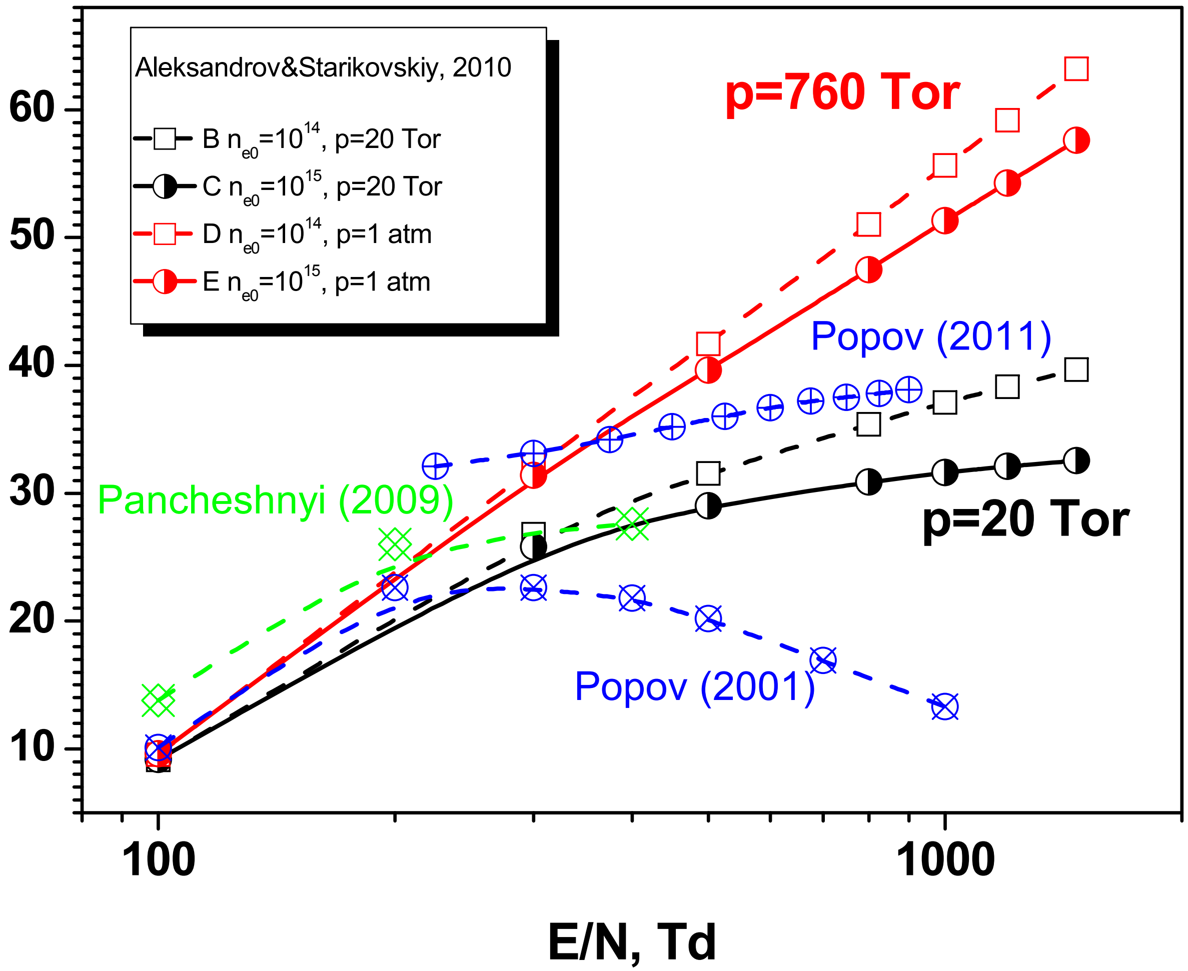


Mechanism of Fast Heating in Discharge Plasmas (high E/N)

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

$O_2^- + O_2^+ + M \rightarrow 2O_2 + M + \Delta E$

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

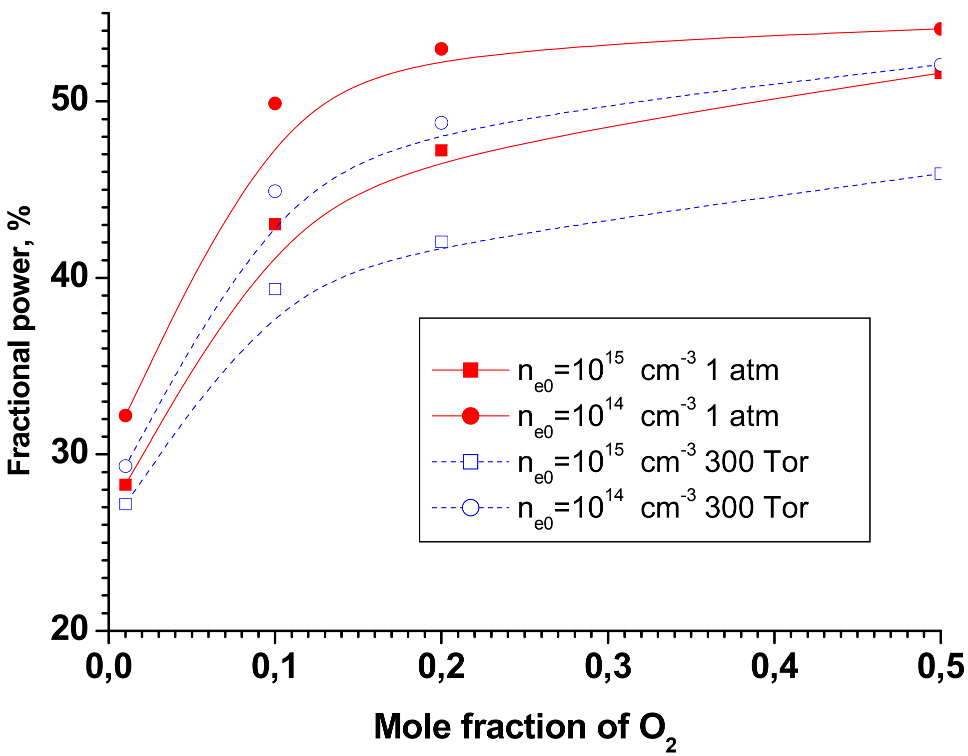


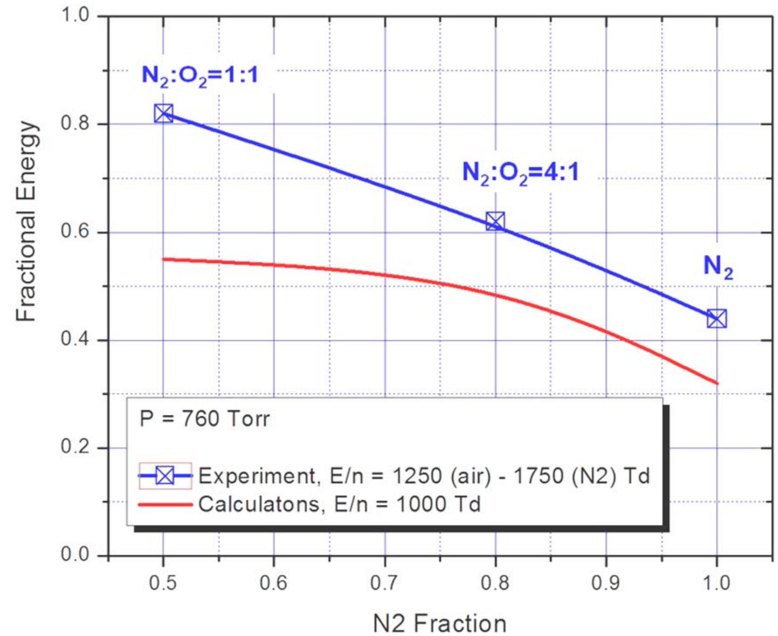
High (> 200 Td) E/N:

electron-ion and ion-ion recombination kinetics

Fractional Electron Power Transferred Into Heat in N_2:O_2 Mixtures

$E/N = 10^3$ Td





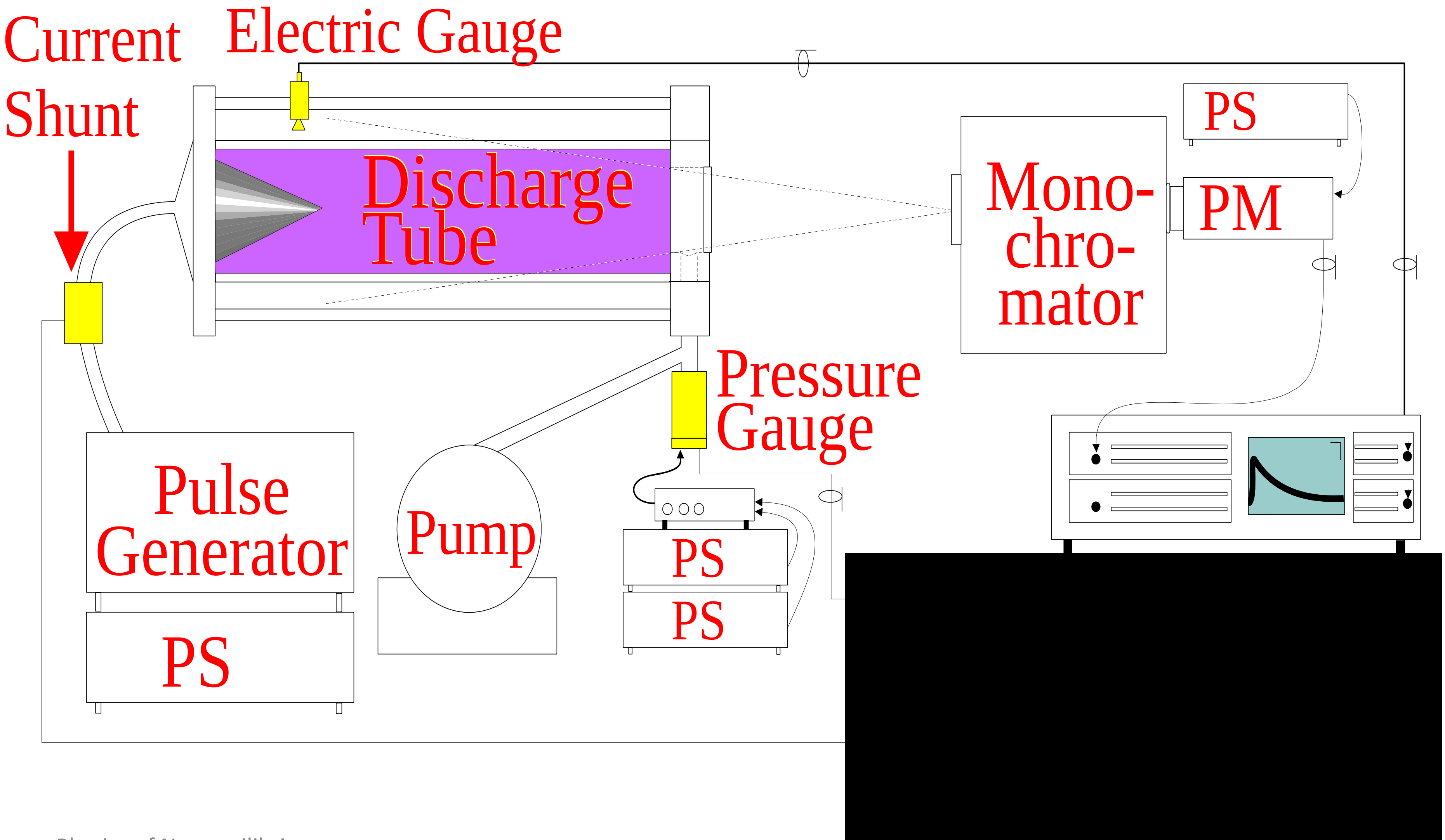
Oxygen is required for efficient fast heating!

$AB^+ + O_2^-$ (+ M) $\rightarrow$ products + ΔE

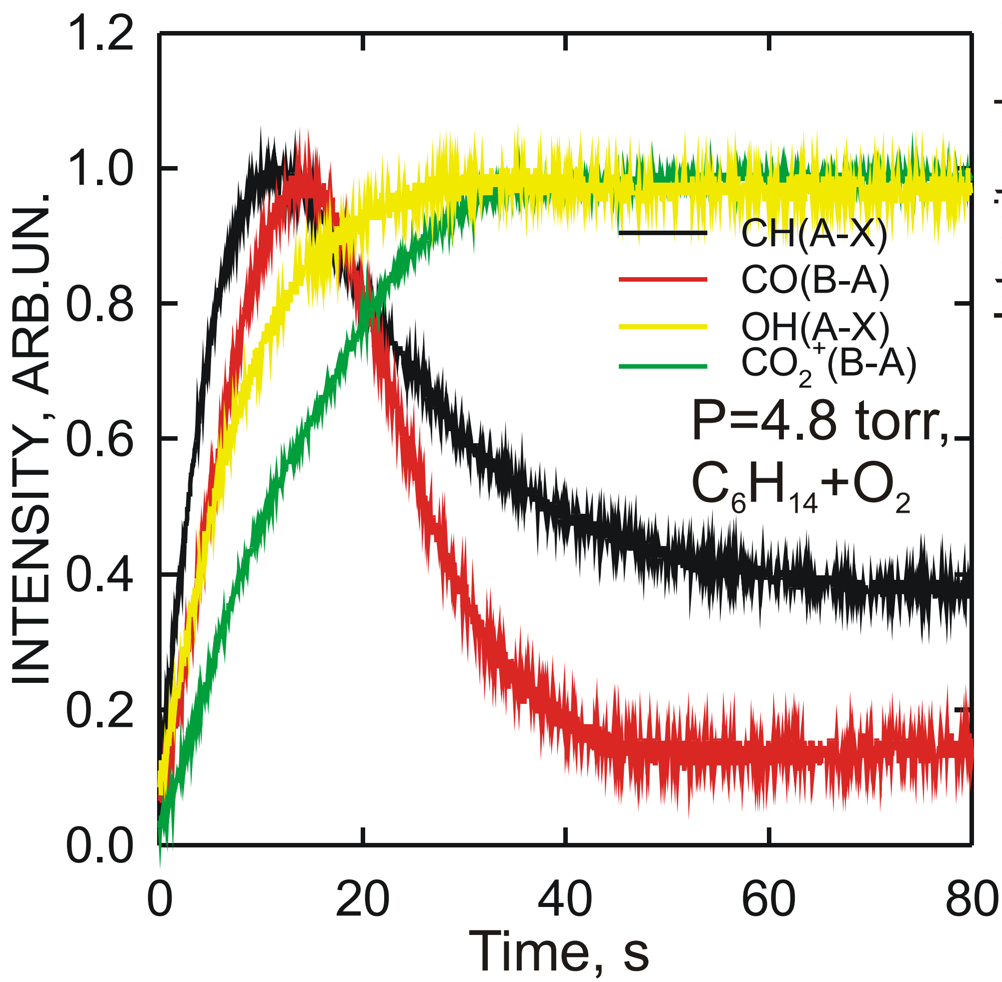
N_2(A,B,C,a) + $O_2 \rightarrow$ e + 2O + ΔE

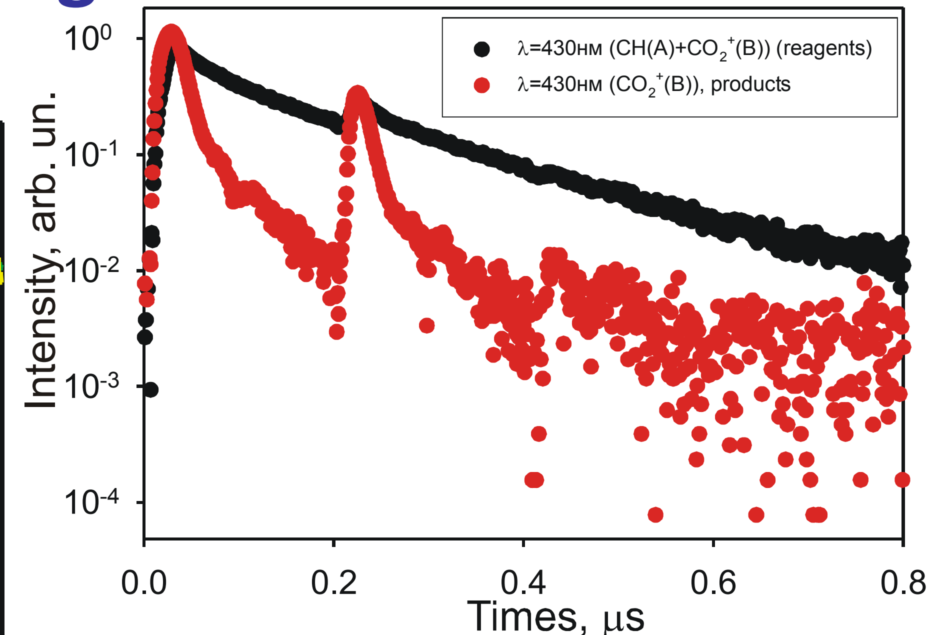
…

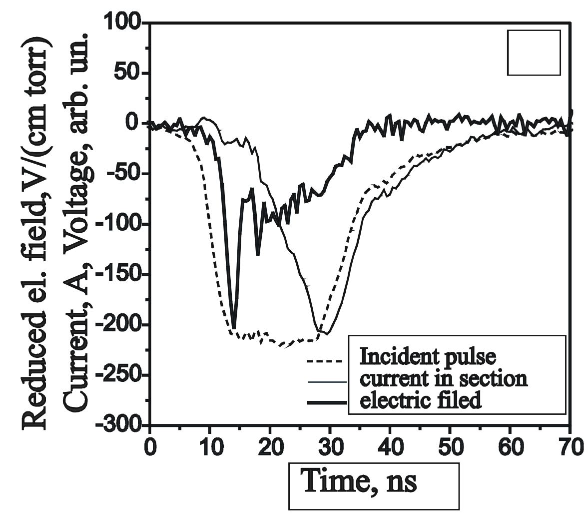
Experimental Setup



Hexane Oxidation by Pulsed Nanosecond Discharge

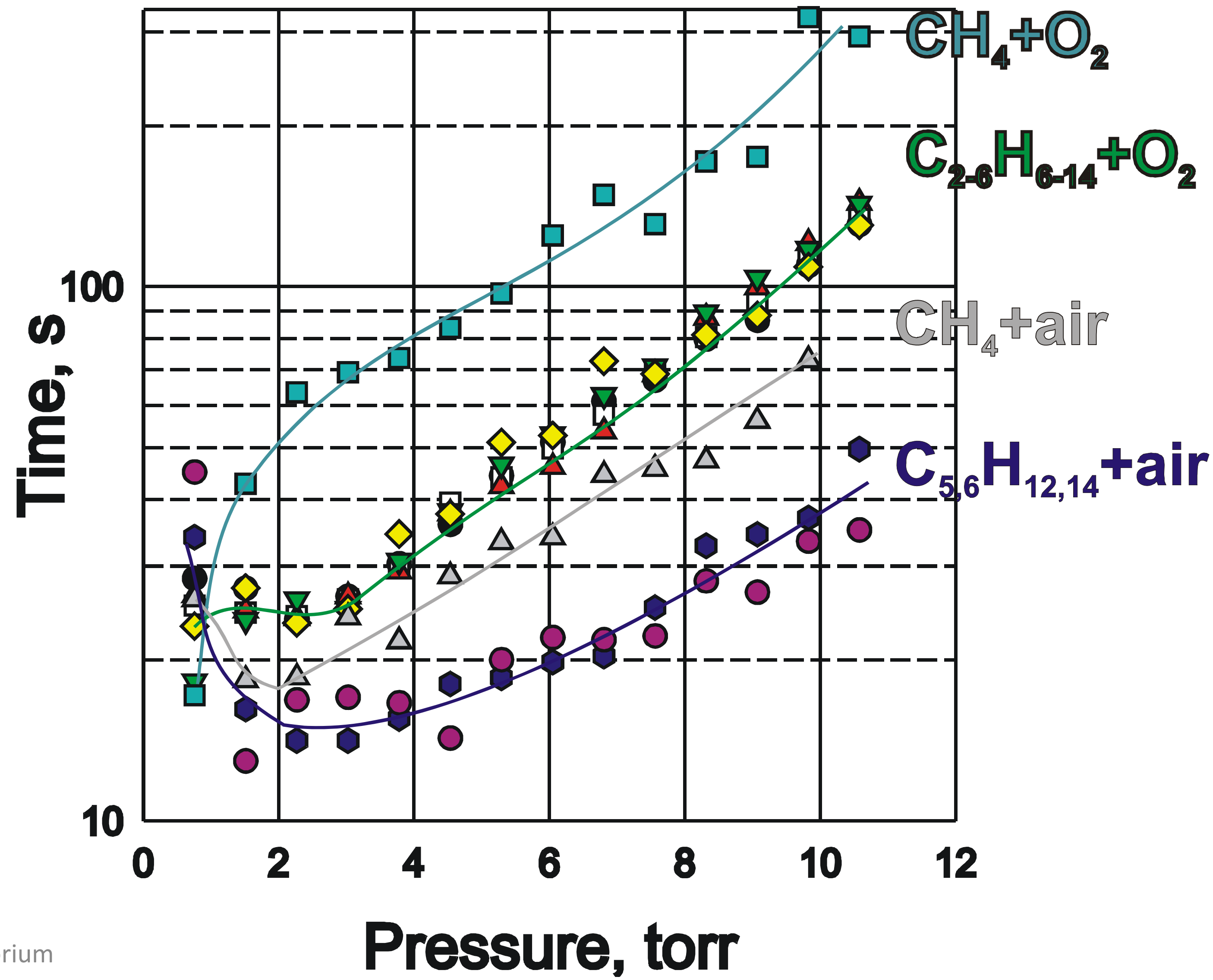




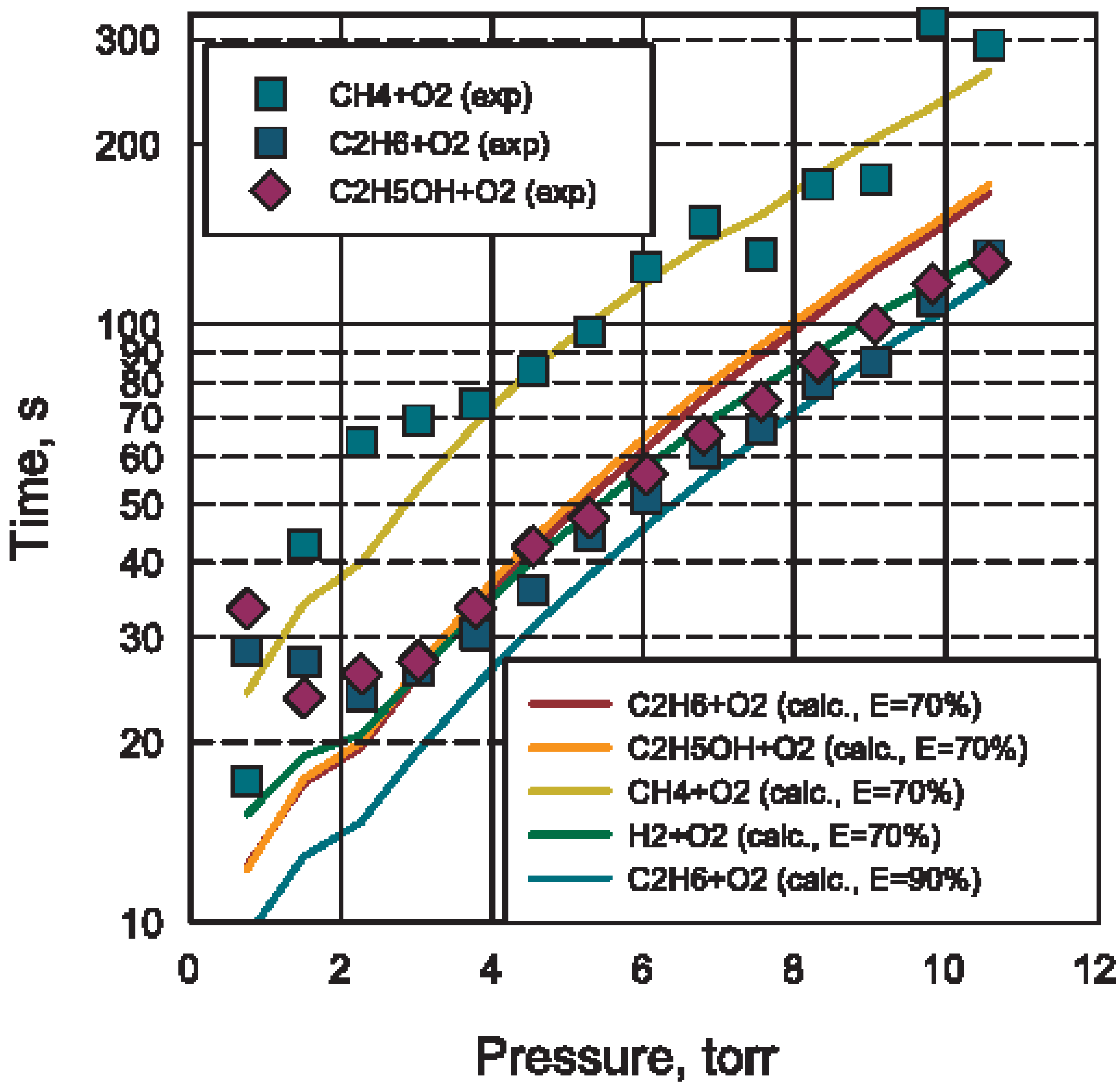


Physics of Nonequilibrium
Systems Laboratory

Hydrocarbon Oxidation Efficiency for C_1-C_6 / O_2 / Air Mixtures

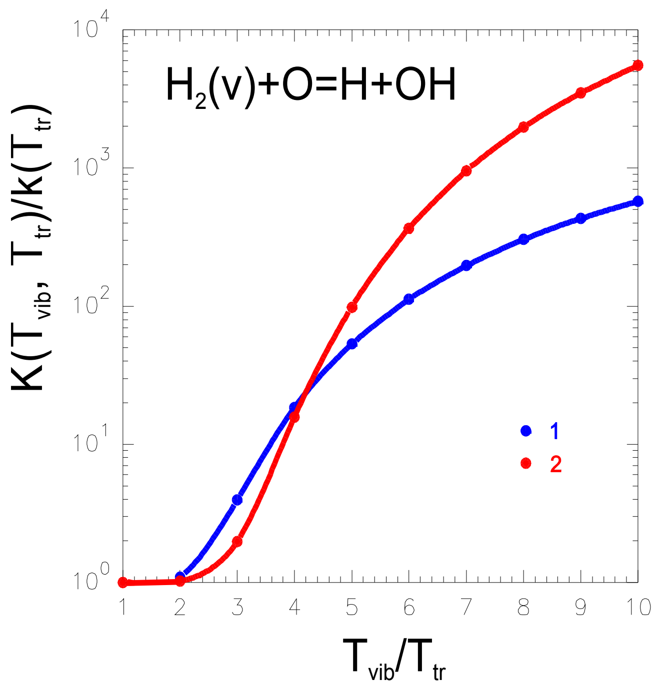


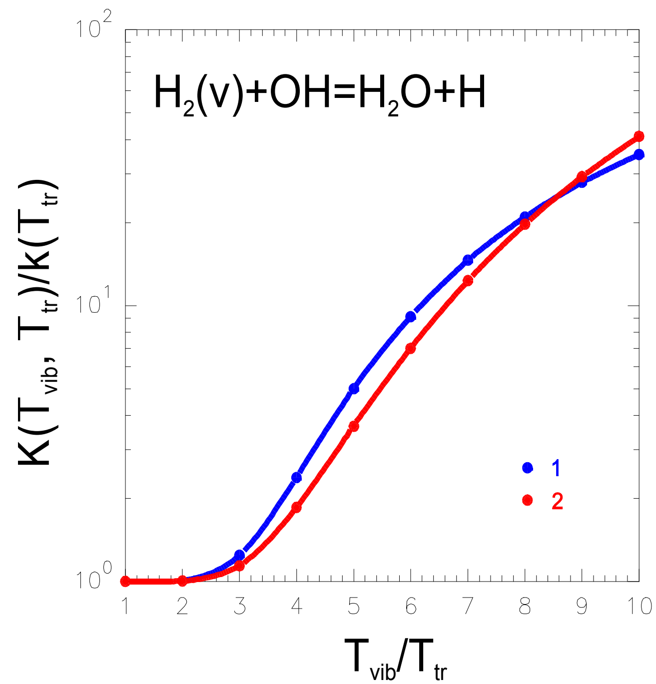
Calculated and Measured Times of Oxidation



Chemical Reactions with Excited Reagents

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





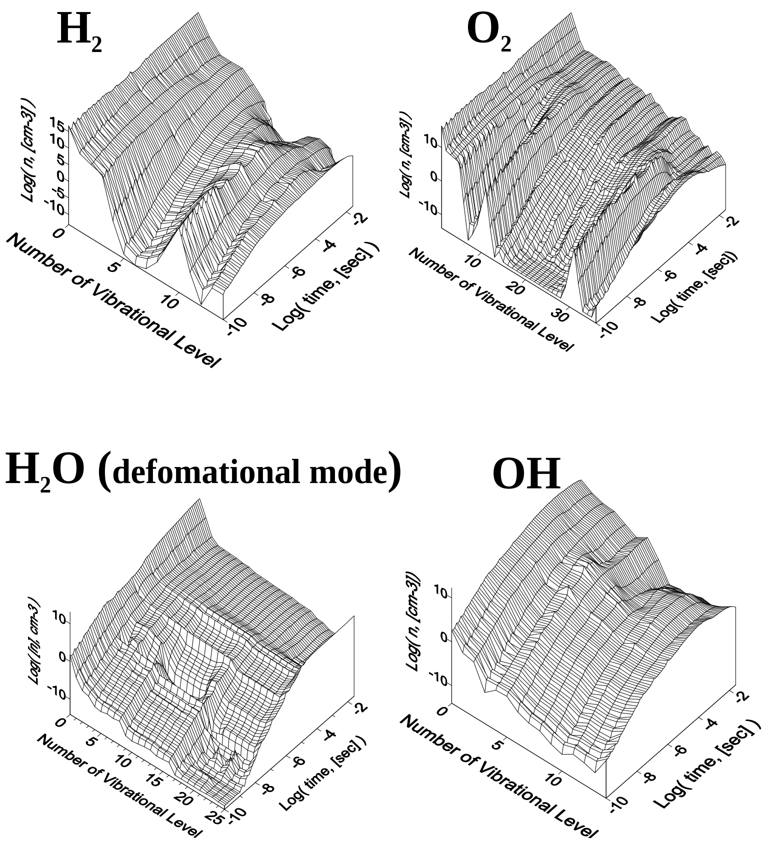
$$H_2(v=1) + O = OH(w=1) + H \qquad (R1)$$

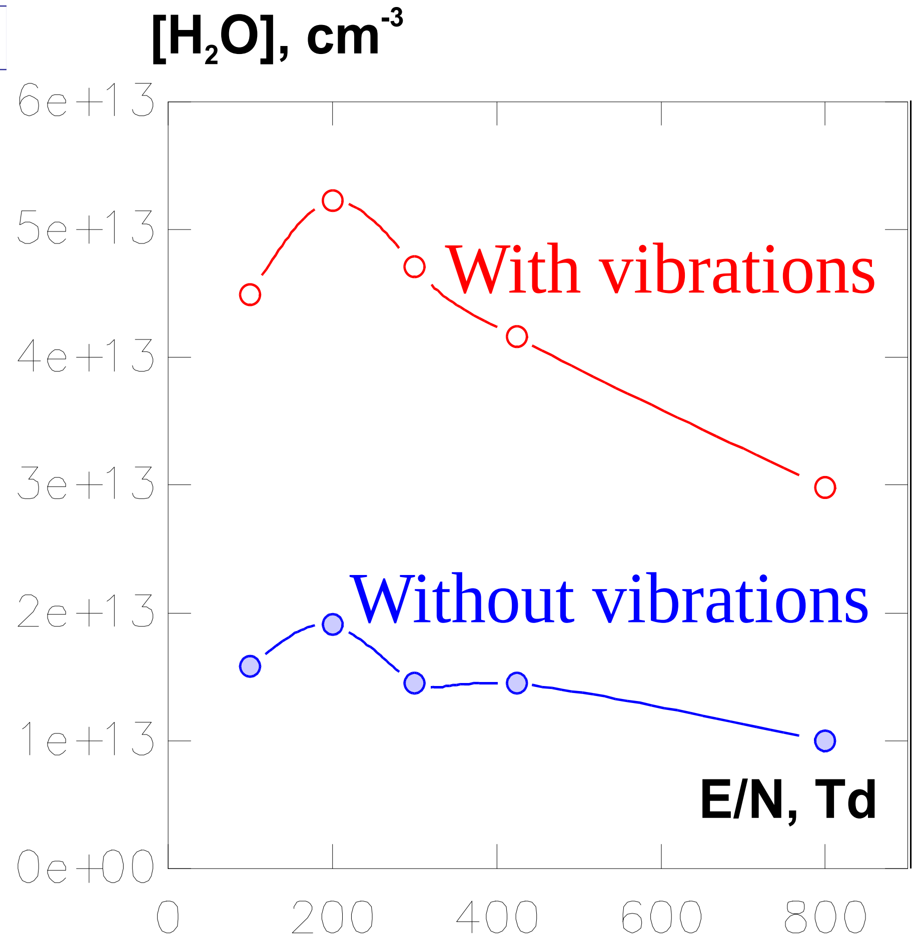
$$H_2(v=0) + O = OH(w=0) + H \qquad (R2)$$

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

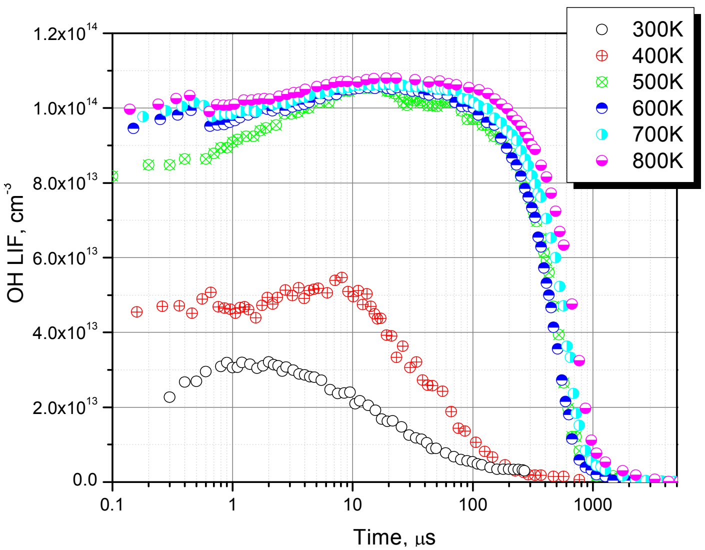
Kinetics. Influence of Vibrations

Distribution Of Vibrational-Excited Components



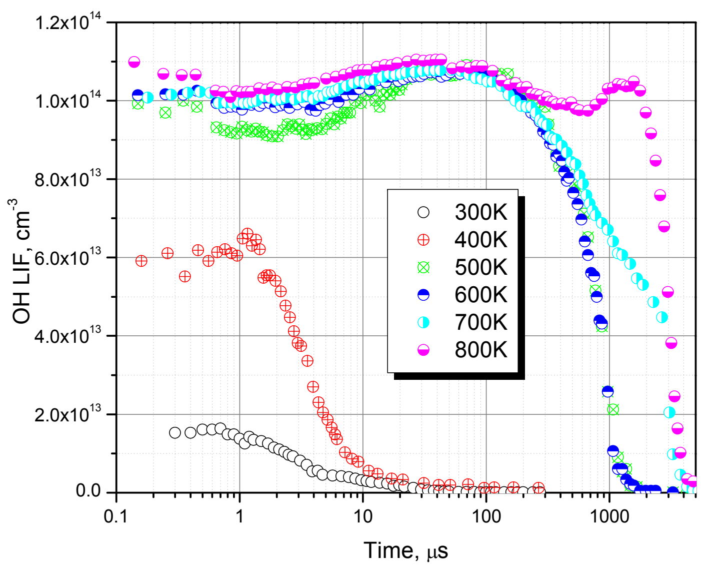


Influence of Vibrational Excitation on Low-Temperature Kinetics

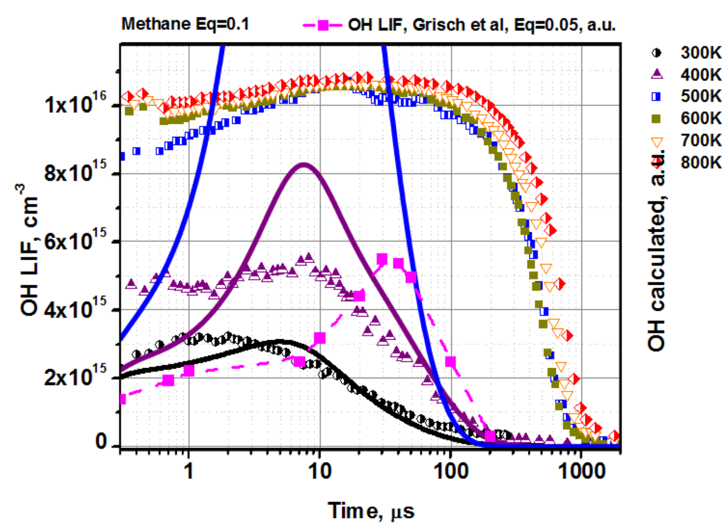


CH4-air

$$N_2 + e = N_2(C^3) + e$$
$$N_2(C^3) + O_2 = N_2 + O + O$$
$$O_2 + e = O + O + e$$
$$N_2 + e = N_2(v) + e$$
$$N_2(v) + HO_2 = N_2 + HO_2(v)$$
$$HO_2(v) = O_2 + H$$



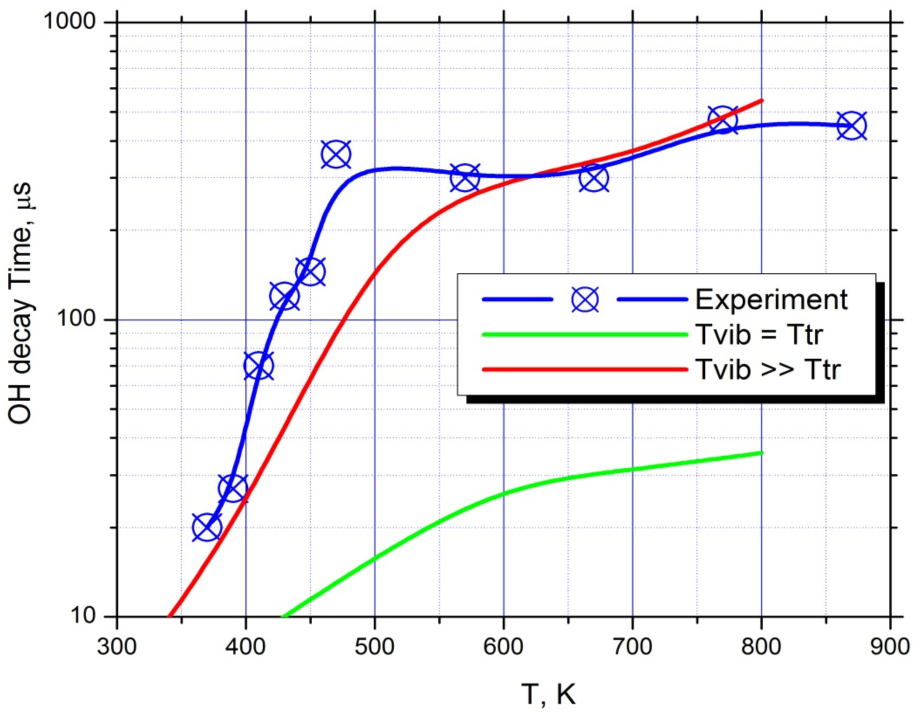
C4H10-air

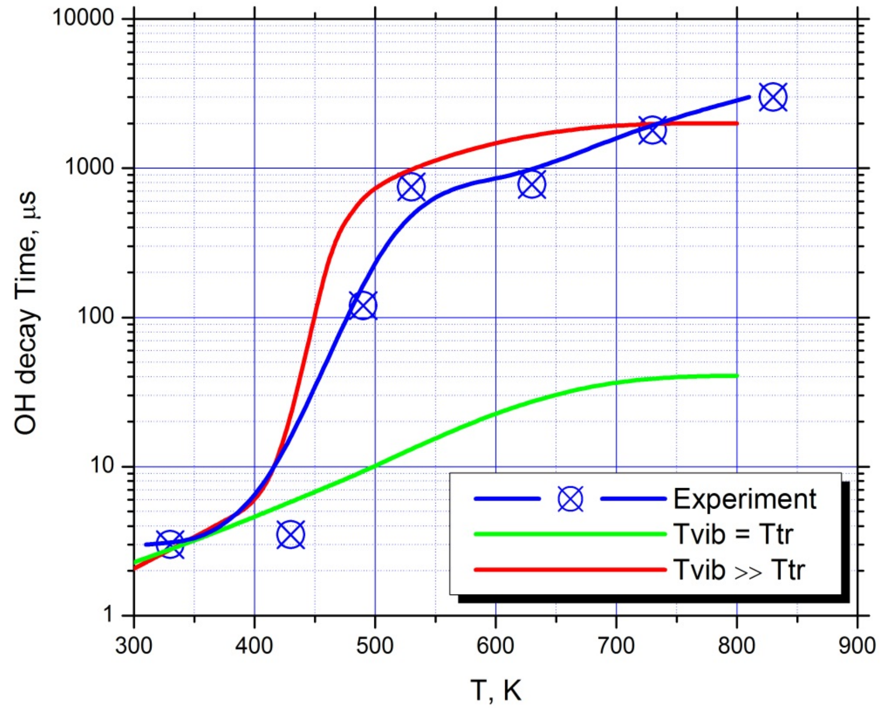


Experiments: L Wu, J Lane, N P Cernansky, D L Miller, A A Fridman, A Yu Starikovskiy, *Proc. of Comb. Inst.*, 2010

Modelling: D Levko, A I Schedrin, V V Naumov, S Starikovskaia, 2010

Influence of Vibrational Excitation on Low-Temperature Kinetics: H_2O_2 Decomposition

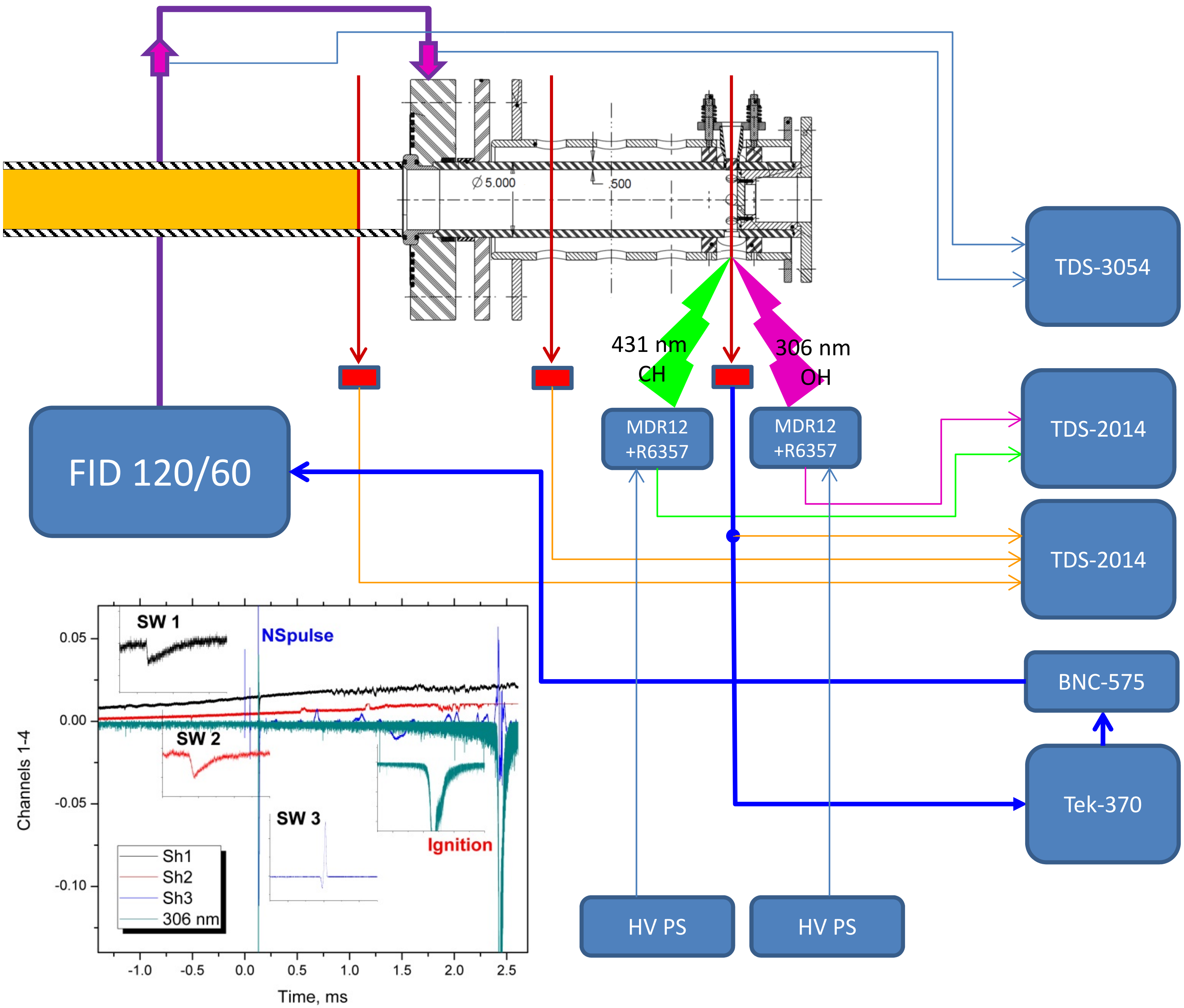


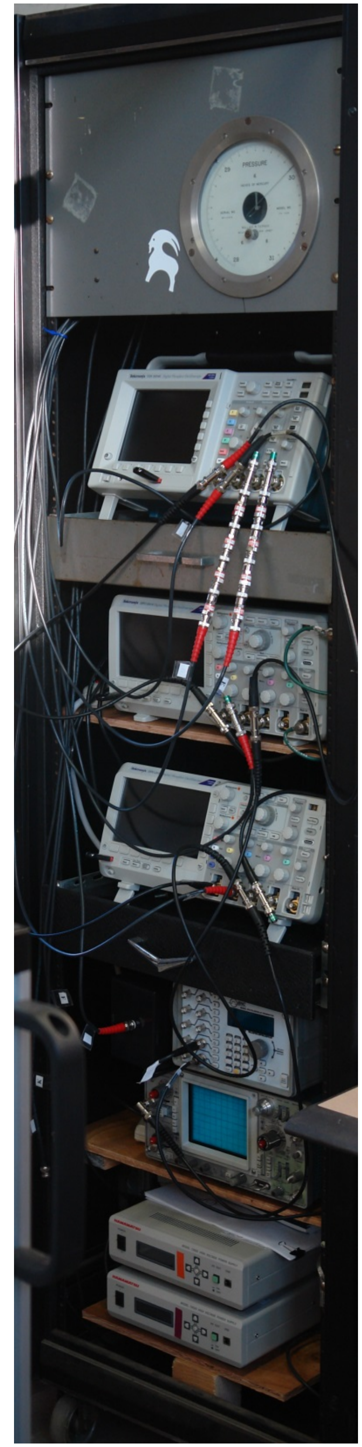


Measured and calculated OH decay time. P = 1 atm.

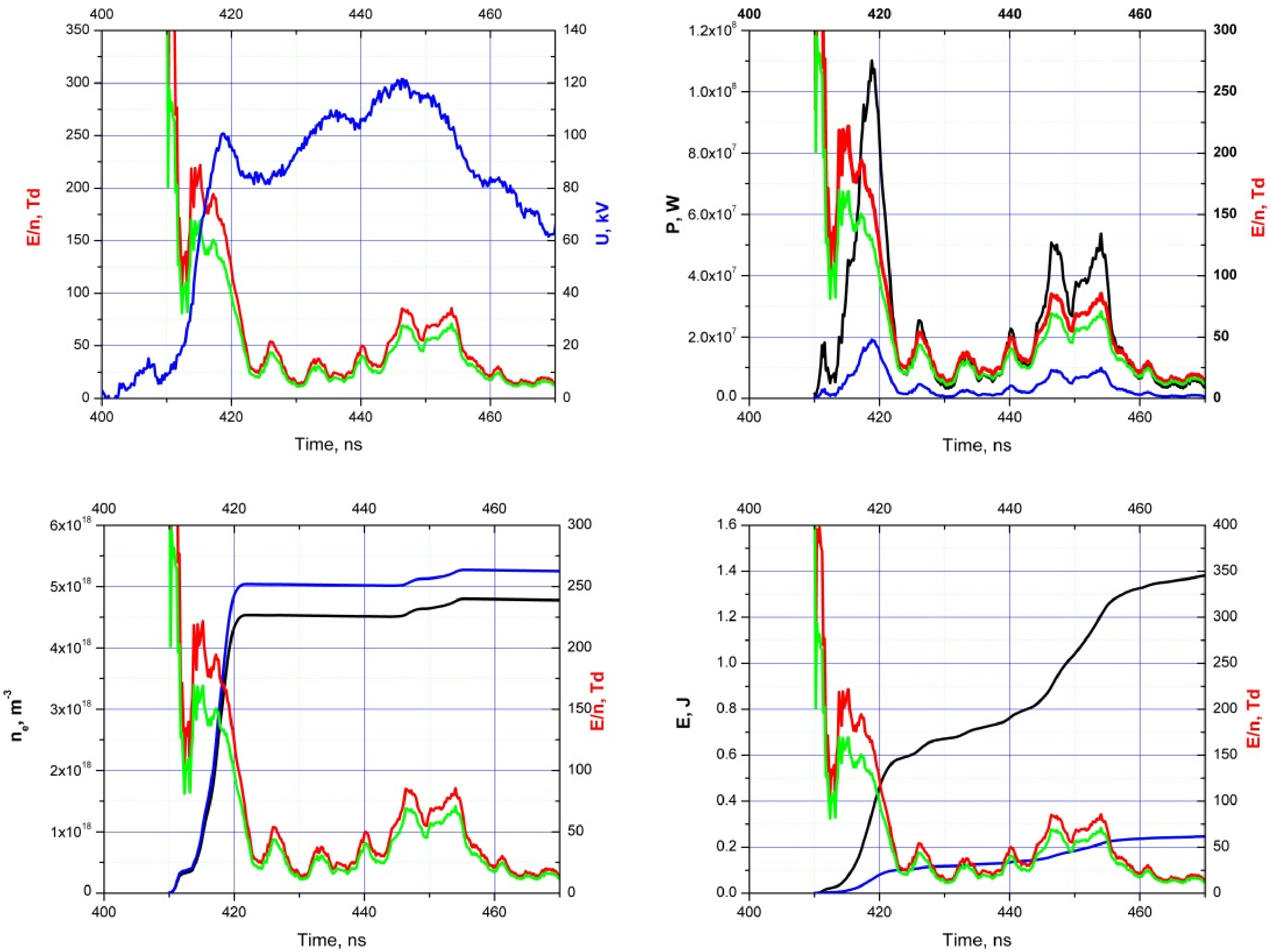
a) 3%H_2 + air; b) 0.3%C_4H_{10} + air.

Plasma Shock Tube



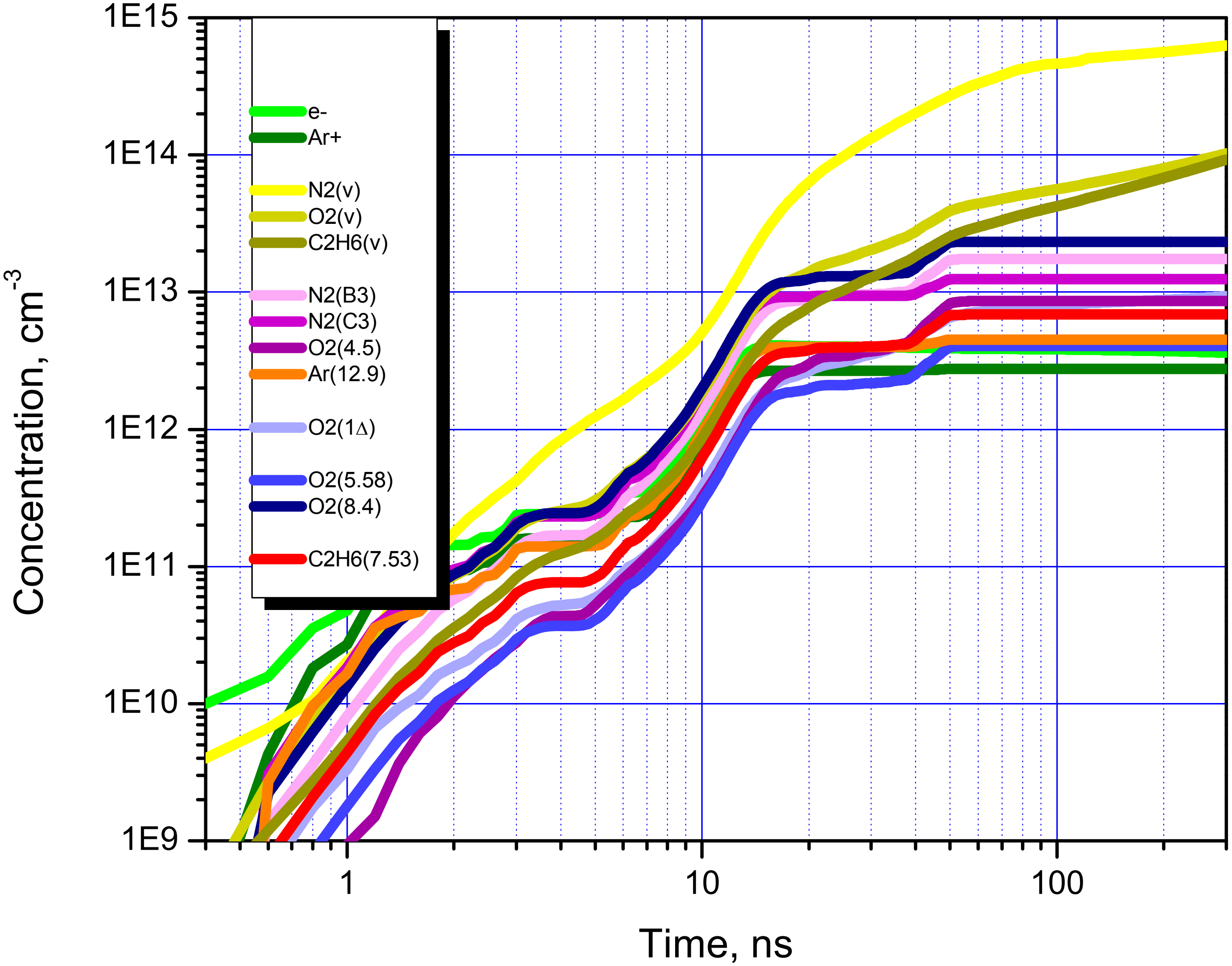


Discharge Dynamics

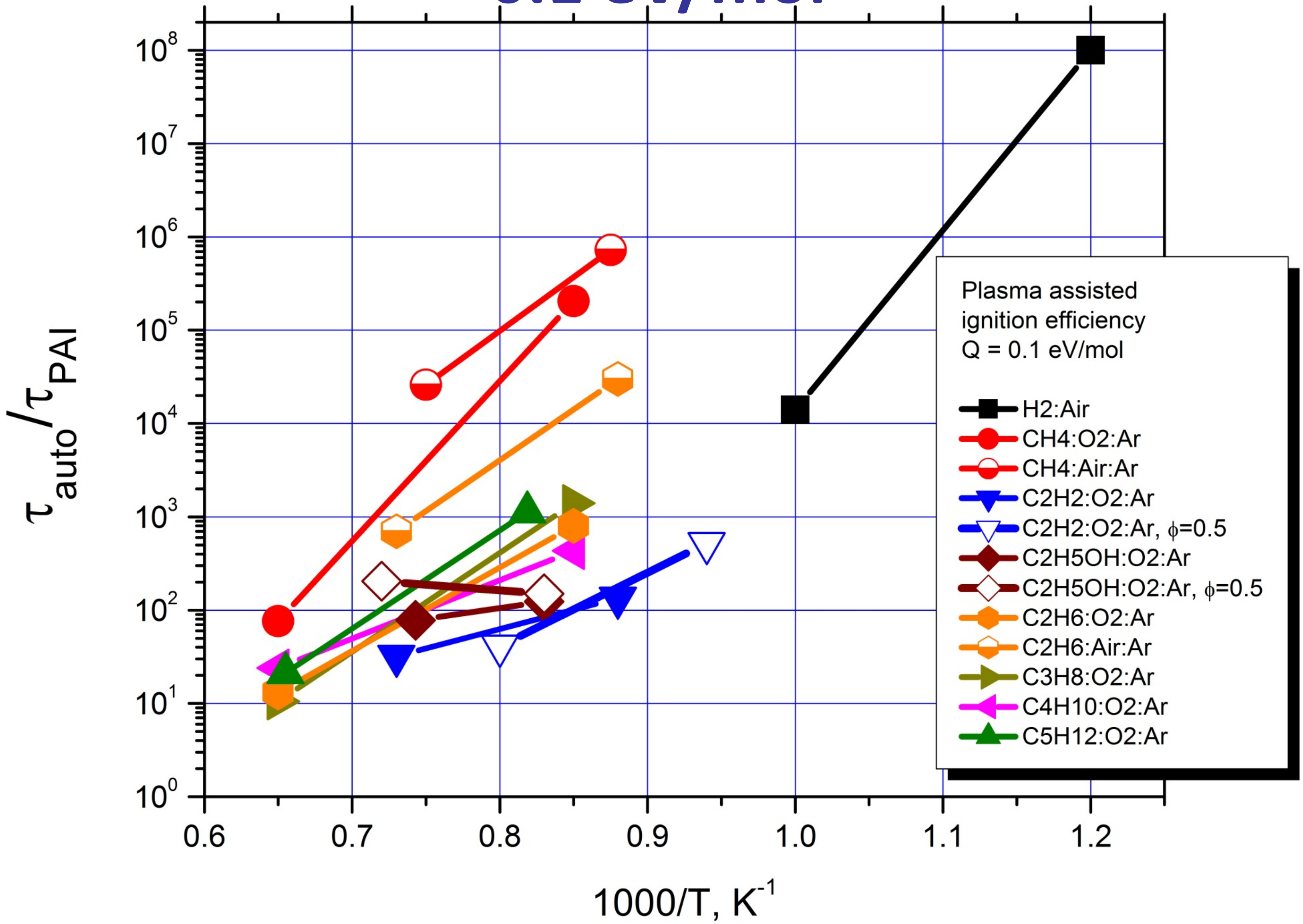


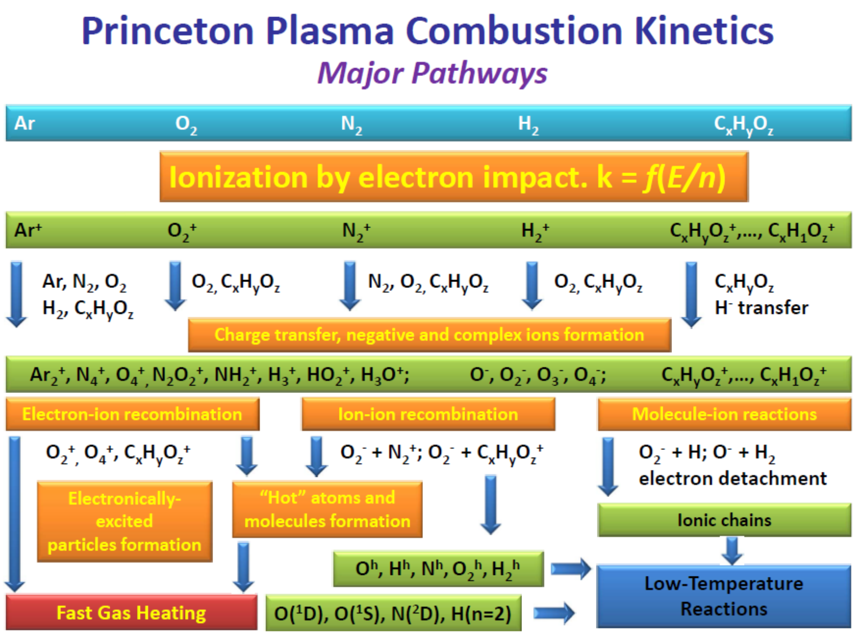
Active Particle Production – Discharge Phase

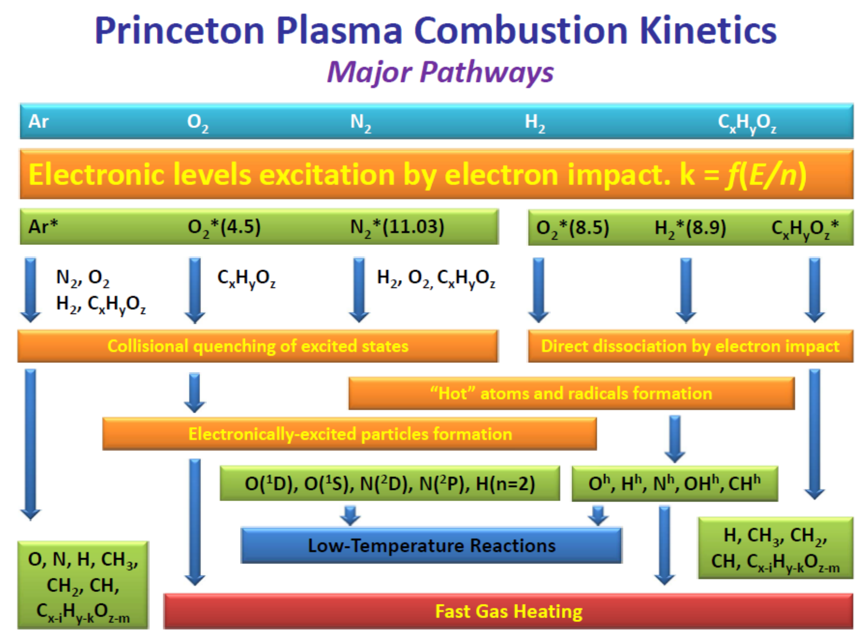
U_s = 943.6 m/s; P_0 = 17 Torr; P_5 = 1.04 atm; T_5 = 1525 K

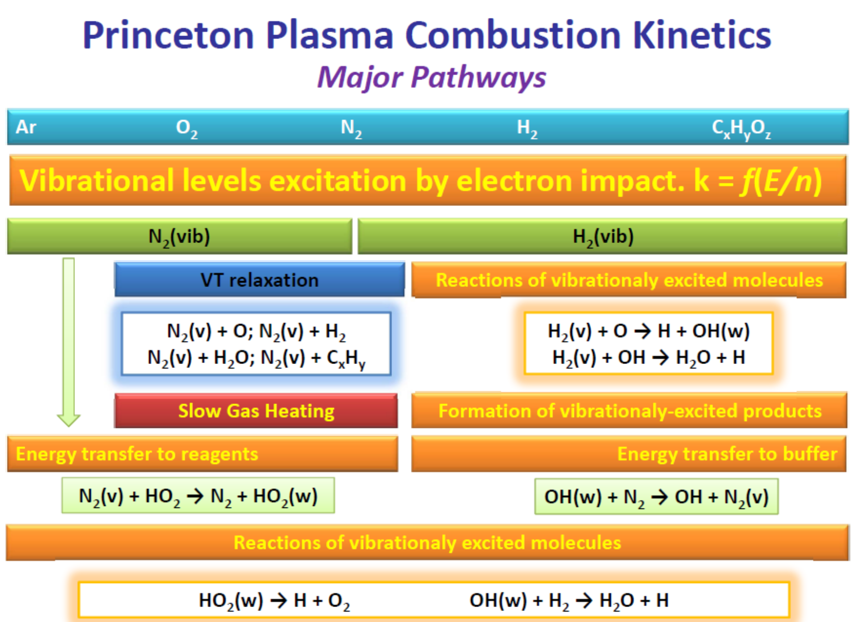


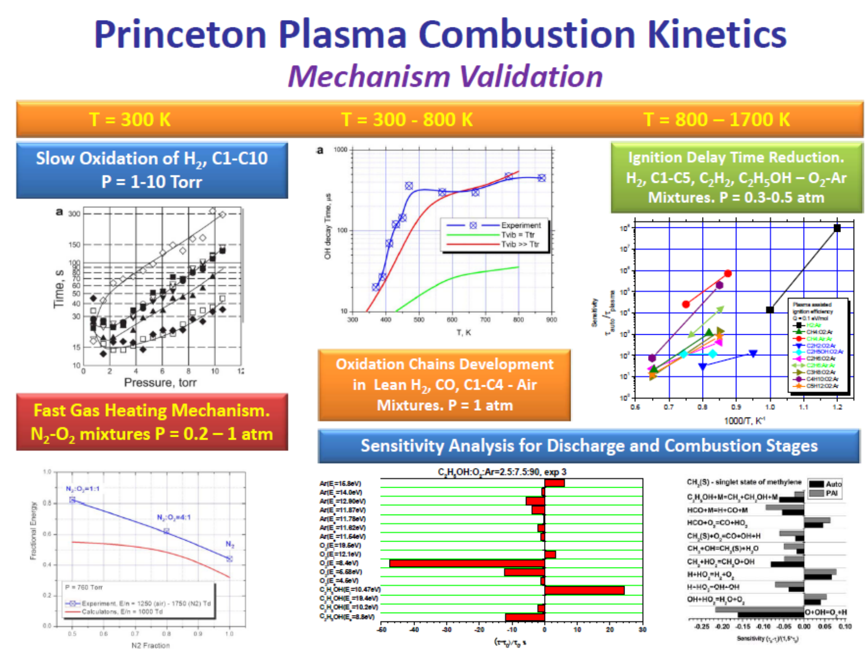
Plasma Ignition Sensitivity
0.1 eV/mol



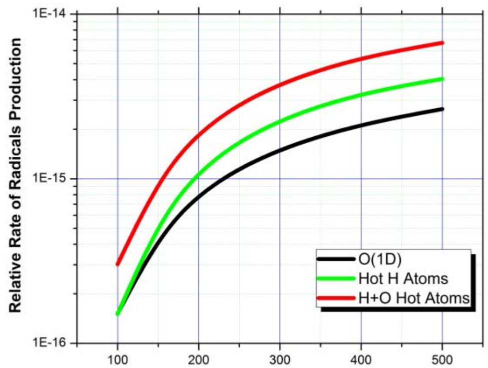

Princeton Plasma Combustion Kinetics
Major Pathways
Ar O_2 N_2 H_2 $C_xH_yO_z$
Ionization by electron impact. k = f(E/n)
Ar^+ O_2^+ N_2^+ H_2^+ $C_xH_yO_z^+$,..., $C_xH_1O_z^+$
Ar, N_2, O_2 H_2, $C_xH_yO_z$
O_2, $C_xH_yO_z$
N_2, O_2, $C_xH_yO_z$
O_2, $C_xH_yO_z$
$C_xH_yO_z$ H^- transfer
Charge transfer, negative and complex ions formation
Ar_2^+, N_4^+, O_4^+, $N_2O_2^+$, NH_2^+, H_3^+, HO_2^+, H_3O^+; O^-, O_2^-, O_3^-, O_4^-; $C_xH_yO_z^+$,..., $C_xH_1O_z^+$
Electron-ion recombination
Ion-ion recombination
Molecule-ion reactions
O_2^+, O_4^+, $C_xH_yO_z^+$
O_2^- + N_2^+; O_2^- + $C_xH_yO_z^+$
O_2^- + H; O^- + H_2 electron detachment
Electronically-excited particles formation
"Hot" atoms and molecules formation
Ionic chains
O^h, H^h, N^h, O_2^h, H_2^h
Low-Temperature Reactions
Fast Gas Heating
$O(^1D)$, $O(^1S)$, $N(^2D)$, H(n=2)

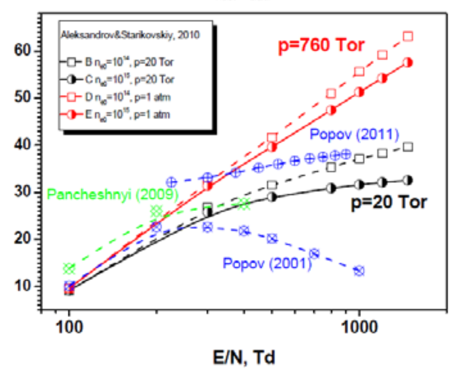

Princeton Plasma Combustion Kinetics
Major Pathways
Ar O_2 N_2 H_2 $C_xH_yO_z$
Electronic levels excitation by electron impact. k = f(E/n)
Ar* O_2*(4.5) N_2*(11.03) O_2*(8.5) H_2*(8.9) $C_xH_yO_z$*
N_2, O_2 H_2, $C_xH_yO_z$
$C_xH_yO_z$
H_2, O_2, $C_xH_yO_z$
Collisional quenching of excited states
Direct dissociation by electron impact
"Hot" atoms and radicals formation
Electronically-excited particles formation
$O(^1D)$, $O(^1S)$, $N(^2D)$, $N(^2P)$, H(n=2)
O^h, H^h, N^h, OH^h, CH^h
Low-Temperature Reactions
H, CH_3, CH_2, CH, $C_{x-i}H_{y-k}O_{z-m}$
O, N, H, CH_3, CH_2, CH, $C_{x-i}H_{y-k}O_{z-m}$
Fast Gas Heating

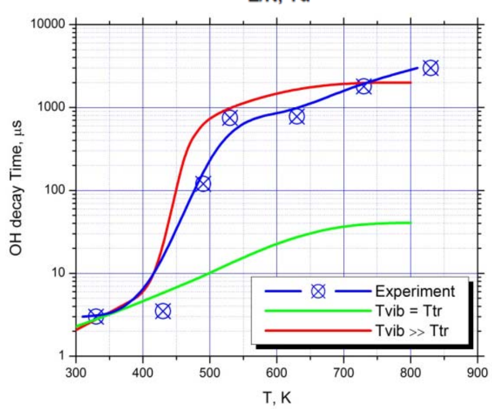

Princeton Plasma Combustion Kinetics
Major Pathways
Ar O_2 N_2 H_2 $C_xH_yO_z$
Vibrational levels excitation by electron impact. k = f(E/n)
N_2(vib)
H_2(vib)
VT relaxation
Reactions of vibrationaly excited molecules
N_2(v) + O; N_2(v) + H_2
N_2(v) + H_2O; N_2(v) + C_xH_y
H_2(v) + O → H + OH(w)
H_2(v) + OH → H_2O + H
Slow Gas Heating
Formation of vibrationaly-excited products
Energy transfer to reagents
Energy transfer to buffer
N_2(v) + HO_2 → N_2 + HO_2(w)
OH(w) + N_2 → OH + N_2(v)
Reactions of vibrationaly excited molecules
HO_2(w) → H + O_2
OH(w) + H_2 → H_2O + H


Princeton Plasma Combustion Kinetics
Mechanism Validation
T = 300 K
T = 300 - 800 K
T = 800 – 1700 K
Slow Oxidation of H_2, C1-C10
P = 1-10 Torr
Ignition Delay Time Reduction. H_2, C1-C5, C_2H_2, C_2H_5OH – O_2-Ar Mixtures. P = 0.3-0.5 atm
Time, s
Pressure, torr
Experiment
Tvib = Ttr
Tvib >> Ttr
T, K
1000/T, K⁻¹
Oxidation Chains Development in Lean H_2, CO, C1-C4 - Air Mixtures. P = 1 atm
Fast Gas Heating Mechanism. N_2-O_2 mixtures P = 0.2 – 1 atm
Sensitivity Analysis for Discharge and Combustion Stages
Fractional Energy
N2 Fraction
$C_2H_5OH:O_2:Ar$=2.5:7.5:90, exp 3

Other Major Results





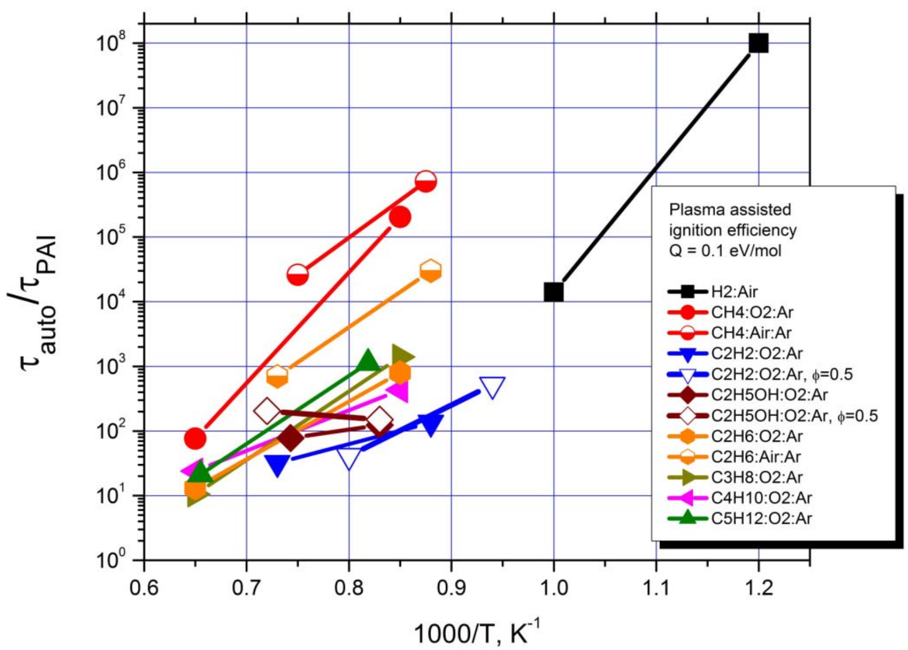


3 NEW MECHANISMS:

- **Radicals Production Increase Due to Translationally Hot Atoms Formation**
- **Mechanism of Fast Heating in Plasmas at high E/n**
- **Vibrational Decomposition of Peroxides (HO2, H2O2, etc)**

EXPERIMENTAL DATABASE:

- **Plasma Ignition Delay Time database for H2, C1-C5, acetylene, ethylene, ethanol**



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AFOSR

Technical Monitor

Dr Chiping Li

PRINCETON
University