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# Innovations in combustion technologies for propulsion

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## Motivation

- Combustion of variable fuels (gaseous, solid, and liquid) is in the heart of the modern propulsion systems including aero and rocket engines and energetic machines
- Enhancement of combustion makes it possible to reduce the fuel consumption and pollutant emission and to improve the flight characteristics of the aircrafts and rockets
- For past decades great attention was paid to exploring the possibility of combustion intensification by chemical and physical techniques

## Background of the methodology

- **The ignition and combustion of the majority of the mixtures (hydrogen/air, hydrocarbon/air and others) occur by chain-branching reactions**
- **The common principal stages of chain process**
  - Chain initiation
    $A \rightarrow r + D$:
    $H_2 + O_2 = H + HO_2$
  - Chain propagation
    $r + A = C + lr$ ($l$=1,2,…)
    $H + O_2 = OH + O$ ($l$=2)
    $O + H_2 = OH + H$
  - Chain termination
    $r + r = r_2$
    $H + O_2 + M = HO_2 + M$
    $2OH + M = H_2O_2 + M$

## Background of the methodology

**In order to intensify the ignition and combustion it is needed to accelerate**
- reaction of chain initiation
- reaction of chain propagation

**or decelerate** the reaction of chain termination

**One can distinguish a few classes of methods for combustion enhancement**

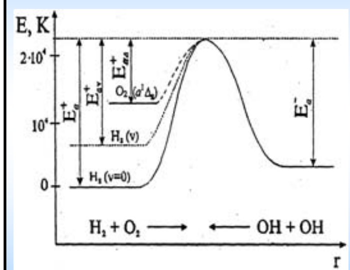
- **Gas dynamic methods**
  - preheating the mixture
  - shock induced combustion
- **Chemical method**
  - admixture of the species which can produce highly reactive radicals in the course of their decomposition (promoters): $H_2O_2 \rightarrow 2OH$
- **Physical methods**
  - dissociation of reacting molecules by means of ionized radiation, electron beam, laser photons, electrical discharge ($10\text{-}10^3$ eV/molecule )
  - excitation of vibrational and electronic states of reactive atoms and molecules by means of electron impact, resonance laser radiation (0.1-2 eV/molecule )

## Background of Methodology

- Among the physical methods of exerting on ignition and combustion only two approaches can be considered as the most pronounced and the least energy consuming ones
- **Exposure of target molecules to resonance laser radiation**
  1. $O_2(X^3\Sigma_g^-) + h\nu(\lambda=762\ nm) = O_2(b^1\Sigma_g^+)$
  2. $O_3(000) + h\nu(\lambda=9.6\ \mu m) = O_3(001)$
  3. $O_2(X^3\Sigma_g^-) + h\nu(\lambda=193.3\ nm) = O(^3P) + O(^1D)$
- **Activation of reacting molecules by electron impact in a specially arranged electrical discharge**
  1. $O_2(X^3\Sigma_g^-) + e(E \geq 5\ eV/molecule) = O(^3P) + O(^3P)$
  2. $O_2(X^3\Sigma_g^-) + e(E \approx 0.98\ eV/molecule) = O_2(a^1\Delta_g)$
  3. $H_2(V=0) + e(E \approx 0.5\ eV/molecule) = H_2(V=1)$
  4. $N_2(V=0) + e(E \approx 0.2\ eV/molecule) = N_2(V=1)$

## Accelerating of chemical reactions

The experimental data revealed that chemical reactions with vibrationally and electronically excited molecules occur much faster than those with non-excited ones




1. **Vibrational excitation**

*Light G.C. J. Chem. Phys. 1978. V.68. p.2831.*

$O(^3P) + H_2(V) \Rightarrow OH(V) + H$

The rate of reaction with $H_2(V)$ is by a factor of $10^3$ higher than that with non-excited hydrogen

2. **Electronic excitation**

$O_2(a^1\Delta_g) + H = OH + O$

*Cupitt L.T. Et al., Int. J. Chem. Kinet., 1982, 14, 487.*

At T=300 K the rate constant of the reaction with $O2(a^1\Delta g)$ is thousand fold greater than that with normal oxygen $O_2(X^3\Sigma_g^-)$

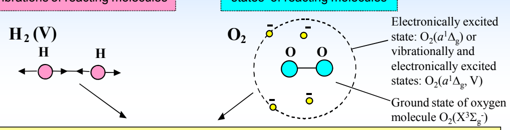
Vibrational and electronic energy of molecules is much more effective than translational and rotational energy in overcoming the barriers of endoergic reactions

## Control of combustion processes by selective excitation of internal degrees of freedom of reacting molecules

We should enhance the rate of active radical formation or the rate of chain propagation reactions

Excitation of molecular vibrations of reacting molecules

Excitation of electronic states of reacting molecules




An increase of rate constant for chemical reactions with excited molecules by a factor of $10^2$–$10^3$

$$k = \int_{E_b}^{\infty} \sigma(\varepsilon)\sqrt{\varepsilon} f(\varepsilon) d\varepsilon$$

- **Promotion of combustion processes**
- **Reduction of ignition threshold**
- **Decrease in combustion zone length in supersonic flow**
- **Enhancement of efficiency of chemical energy release during combustion**
- **Controlling of the rate of pollutant formation during combustion**
- **Initiation of combustion and detonation at low input energy**
- **Stabilization of combustion processes**

## Methods of combustion control

- **Heating of a reactive mixture by arc discharge and plasma torches or by resonance laser radiation**

*(Kato, R., and I. Kimura. 1996. Numerical simulation of flame-stabilization and combustion promotion by plasma jet... Takita, K. 20... airflow. C...*

- **The fo... dissoci...**

*(Lucas, D., L... ozone. Co... Chintala, N. ... thermal ig... Paper 20 04-0835. )*

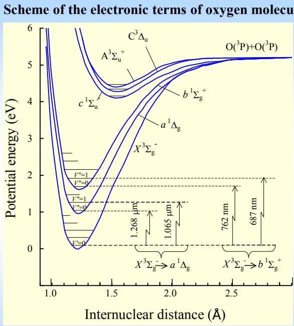
The latter method is the most promising one from the standpoint of low temperature combustion initiation and the energy consumption.
It needs:
**0.19 eV** to excite $O_2$ molecule to the lower vibrational state,
**0.98 eV** to excite the $O_2$ molecule to the electronic state, $a^1\Delta_g$,
**5.1 eV** to dissociate the $O_2$ molecule

- **The enhancement of chain reactions by production of vibrationally or electronically excited molecules**

*(Starik, A. M., and N. G. Dautov. 1996. The effect of vibrational excitation of molecules on the dynamics of detonation combustion of $H_2$+air mixture behind shock waves. High Temperature 34(5): 726-39. Starik, A. M., and N. S. Titova. 2001. Initiation of combustion and detonation in $H_2+O_2$ mixtures by excitation of electronic states of oxygen molecules. In: High-Speed Deflagration and Detonation: Fundamentals and Control. Eds. G. Roy, S. Frolov, D. Netzer, and A. Borisov. Moscow: Elex-KM Publishers. 63-78 )*

## Excitation of $O_2$ Molecules to the $a^1\Delta_g$ and $b^1\Sigma_g^+$ States by Resonant Laser Radiation

**Scheme of the electronic terms of oxygen molecule**




**Excitation:**

$$O_2(X^3\Sigma_g^-,V') + h\nu_{I_1} \rightarrow O_2(a^1\Delta_g,V')$$
$$O_2(X^3\Sigma_g^-,V') + h\nu_{I_2} \rightarrow O_2(b^1\Sigma_g^+,V')$$

$\lambda_I$ =1.268 µm, $\lambda_I$ =762 nm

For $V'$=0, $V''$=1, and ${}^QP(9)$ branch:

$\lambda_I$ =1.065 µm, $\lambda_I$ =687 nm

Radiation life time:

$a^1\Delta_g$: $\tau_{s\Delta}=3.87\cdot10^3$ s

$b^1\Sigma_g^+$: $\tau_{s\Sigma}=1.18\cdot10^1$ s

$(X^3\Sigma_g^-, V')\rightarrow(a^1\Delta_g, V'')$, $(X^3\Sigma_g^-, V')\rightarrow(b^1\Sigma_g^+, V'')$ transitions are allowed in the magnetic-dipole approximation

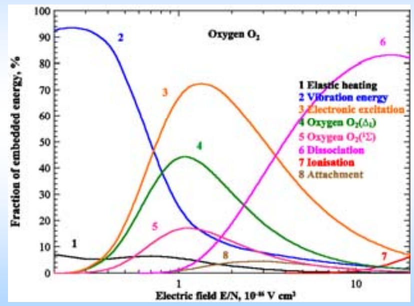
**Deexcitation:** $O_2(b^1\Sigma_g^+) + M = O_2(a^1\Delta_g, V) + M$; $O_2(a^1\Delta_g, V) + M = O_2(X^3\Sigma_g^-, V) + M$ — E-V processes

$2O_2(a^1\Delta_g, V) = O_2(b^1\Sigma_g^+, V) + O_2(X^3\Sigma_g^-, V)$ — EV → EV processes

**For $T_0$=300-700 K, $P_0=10^3$–$10^4$ Pa, $I_0$=1–10 kW/cm², the time of induced transition at $\lambda_I$ =1.268 µm $\tau_I=3\cdot10^{-2}$–$3\cdot10^{-4}$ s and E-T relaxation time $\tau_R$ =1-0.1 s and at $\lambda_I$ =762 nm $\tau_I=10^{-3}$–$10^{-5}$ s, $\tau_R$ =0.2-0.01 s, $\tau_I \ll \tau_R$**

## Modeling of $O_2$ electrical discharge

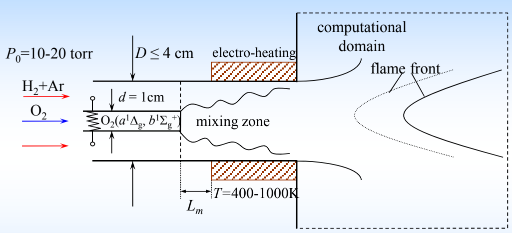
**The fraction of the discharge power utilized for each electron energy loss process as a function of the reduced electric field, E/N**




At E/N ≈ $1.1\cdot10^{-16}$ V/cm²

Over 40% of energy goes to excitation of $O_2(a^1\Delta_g)$ state and 15% goes to excitation of $O_2(b^1\Sigma_g^+)$ state

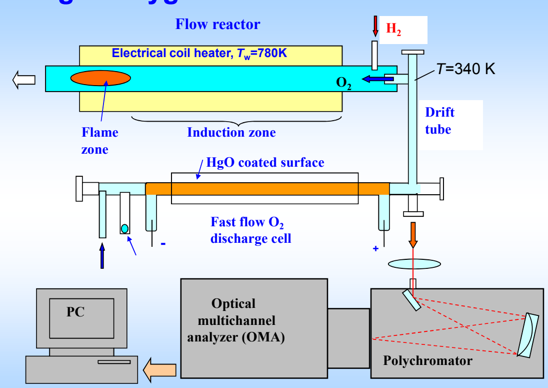
## Plasma-chemical assisted combustion in subsonic flow by self-sustained discharge




The schematic of the test facilities to investigate influence of singlet delta and singlet sigma oxygen molecules on the enhancement of ignition/combustion of $H_2/O_2$ and $CH_4/O_2$ mixture in low pressure subsonic flow (self-sustained discharge).

**Measurements: concentrations of $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma^+_g)$ (spontaneous emissions at $\lambda_I$=1.268 µm and 762 nm, respectively), OH(v) - LIF; temperature - CARS.**

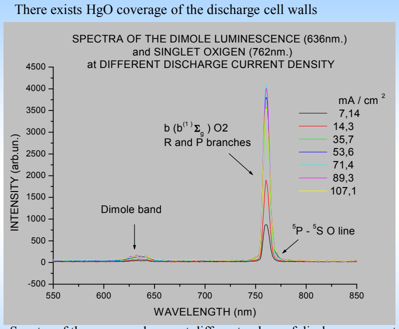
## Singlet oxygen-assisted combustion




**Schematic of the experimental set up**

## Spontaneous emissions of oxygen plasma

There exists HgO coverage of the discharge cell walls




Spectra of the oxygen plasma at different values of discharge current density

$P_0$=10 torr

$E/N=6\cdot10^{-16}$ V·cm²

Given value of $E/N$ is larger than optimal one to produce maximal amount of singlet oxygen $E/N=1.1\cdot10^{-16}$ V·cm²

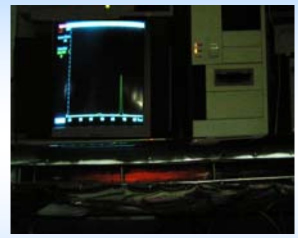
The intensity of $O(^5P)\rightarrow O(^5S)$ line (λ=778 nm) is negligible

Coverage of surface of the discharge cell by HgO leads to the strong quenching of atomic oxygen. The radiation intensity at λ=762 nm ($O_2(b^1\Sigma_g^+)$) is much stronger than that at λ=778 nm and 636 nm ($2O_2(a^1\Delta_g)$)

## Singlet oxygen-assisted combustion

**No discharge: $I$=0 mA**

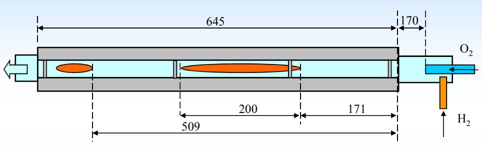
**There exists discharge: $I$=5 mA, Es=59J/mmol**



**The photo of the flame in $H_2/O_2$ fuel rich mixture ($H_2/O_2$=5/2) at $V_F$=17 m/s in reactor the temperature of reactor wall is as small as 780 K for two cases: (1) free diffusion flame; (2) the singlet oxygen-assisted flame**

## Singlet oxygen-assisted combustion

**The geometrical characteristics of the induction length shortening**
**(V.V. Smirnov, O.M. Stelmakh,V.I. Fabelinsky, D.N. Kozlov, A.M. Starik, N.S. Titova.. J. Phys. D: Applied Phys. 41, 2008, 192001)**




Parameters in flow reactor:
$V_F$=17 m/s,
$T_W$=780 K ,
$P_0$=10 torr.

At $I$=10 mA
$E_s$=107 J/mmol,
$T_{ax}$=700 K at
x=$L_{in}$=171mm

**The generation of singlet oxygen even in a small amount (~1-4%) by low pressure self-sustained glow DC discharge makes it possible to enhance the combustion in $H_2/O_2$ mixture and to reduce the induction zone length by a factor of 3 even at non-optimal conditions.**

## Kinetic Model

Electronically Excited Species: $O_2(a^1\Delta_g, V)$, $O_2(b^1\Sigma_g^+, V)$, $O(^1D)$

Electronically Unexcited Species:

✦for $H_2$/air mixture: $H_2$, $O_2$, H, O, OH, $H_2O$, $HO_2$, $H_2O_2$, $O_3$, N, $N_2$, NO, $NO_2$, $N_2O$

✦for $CH_4$/air mixture: $H_2$, $O_2$, H, O, OH, $H_2O$, $HO_2$, $H_2O_2$, $O_3$, C, CO, $CO_2$, $CH_m$ (m=1-4), $C_2H_p$(p=1-6), HCO, $CH_2O$, $CH_3O$, $CH_2OH$, $CH_3OH$, $CH_3O_2$, $CH_3O_2H$, N, $N_2$, NO, $NO_2$, $N_2O$

Vibrationally Excited Modes:

✦ di-atomic molecules: $O_2(X^3\Sigma_g^-, V)$, $O_2(a^1\Delta_g, V)$, $O_2(b^1\Sigma_g^+, V)$, $H_2(V)$, $OH(V)$, $CO(V)$ $N_2(V)$

✦ Tri-atomic molecules: $HO_2(V_1V_2V_3)$, $O_3(V_1V_2V_3)$, $NO_2(V_1V_2V_3)$, $N_2O(V_1V_2V_3)$, $CO_2(V_1V_2V_3)$

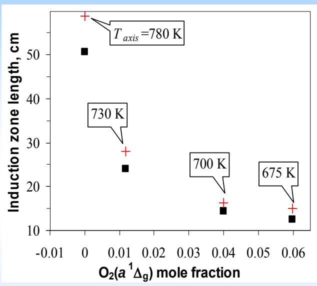
✦ Multi-atomic molecules $H_2O_2(V_1V_2V_3 V_4V_5)$, $CH_4(V_i)$, $CH_3(V_i)$, $C_2H_2(V_i)$

Processes:
- intramode vibrational-vibrational exchange $A(V{=}1)+B(V{=}0)=A(V{=}0)+B(V{=}1)$
- vibrational-tranlational relaxation $A(V{=}1)+M=A(V{=}0)+M$
- electronic-vibrational exchange $A(e'')+M=A(e',V{=}1)+M$

Model:
- electronically excited molecules: state to state kinetics
- vibrationally excited molecules: mode approximation (model of vibrational temperatures)

$$k_q^e(T,T_V)=k_q(T,e)\chi_q(T,T_V)$$

## Singlet oxygen-assisted combustion




The measured and predicted values of induction zone length in a flow reactor versus $O_2(a^1\Delta_g)$ mole fraction in the oxygen flow at the exit of drift tube: **black squares** are the experimental data and **red crosses** are the predictions.

**Parameters in flow reactor:**
$V_F$=17 m/s, $T_W$=780 K, $P_0$=10 torr.

**The values of input energy $E_s$=0; 59; 107; 246 J/mmol are related to $T_{axis}$=780; 730; 700; 675 K at $x=L_{in}$.**

**Both the experiments and modeling exhibit a strong influence of the presence of singlet oxygen molecules in the oxygen plasma on the induction zone length and even on the ignition temperature. The predictions are consistent well with experimental data and demonstrate great potentialities of the approach based on the excitation of $O_2$ molecules to enhance the combustion**

## Combustion arranging in a supersonic flow

In recent years, much attention has been concentrated on studying the processes of ignition and combustion stabilization in a supersonic flow. This is due to the prospect of designing new engines for high-speed vehicles.

- **The key question in this problem is how to shorten the induction and energy release zones in organizing combustion.**
- **To solve this problem several approaches have being considered:**

• Purely gas-dynamic approach based on the creation of flow zones with a higher temperature and reduced gas velocity behind bluff bodies (stabilizers). **Disadvantages:** considerable losses, low efficiency, and possible collapse of combustion when the flow parameters vary.

• Generation of an oblique shock. **Disadvantages:** in order to ignite the mixture at appropriate distances from the front (~1 m) the shock intensity must be fairly high. **At small angles of inclination of the front to the free-stream velocity vector (β < 35°) and substantial gas velocities (Mach number $M_0$ =5–7) even a hydrogen-air mixture can not be ignited at a distance smaller than 10 m.**

## CIAM EXPERIENCE

**High velocity air-breathing engines**


## IGNITION AND FLAME STABILIZATION PROBLEMS IN HIGH VELOCITY FLOW

- **High static temperature, small residence time (ignition and stabilization by shocks)**
- **Low static temperature, high total temperature (ignition and stabilization in self-sustained gasdynamic structure after combustor starting/ cavities or steps, pilot flames)**
- **Low total temperature (igniters and cavities or steps / base regions of pylons / high enthalpy jets)**

**Alternative methods (excitation of internal degrees of freedom of molecules of reagents)**

# Shock induced combustion in a supersonic flow at high Mach numbers, low levels of pressure and temperature

- **Flow conditions: M = 5 - 6, pressure $10^3$ - $10^5$ Pa, $T$ = 300 - 600 K**
- **Excitation of internal degrees of molecules of the reacting species as the method of solution of the ignition and combustion problems**

## Thermally non-equilibrium effects in combustion

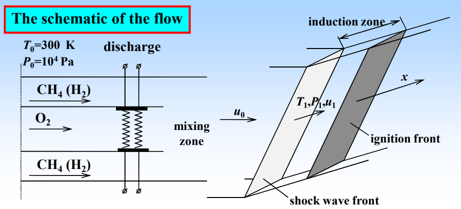
- Shock-induced combustion
- Plasma-assisted combustion: abundance of electronically and vibrationally excited species: $H_2(v)$, $N_2(v)$, $O_2(X^3\Sigma^-_g,v)$, $O_2(a^1\Delta_g,v)$, $CO(v)$
- Laser-induced combustion: $O_2(X^3\Sigma^-_g,v=0)+h\nu(678\ nm)=O_2(b^1\Sigma^+_g,v=1)$; $O_3(000)+h\nu(9.6\ \mu m)=O_3(001)$; $O_3+h\nu(243\ nm)=O_2(a^1\Delta_g,v)+O(^3P)$

➢ Thermally equilibrium chemical kinetic model $T=T_{rot}=T_{v_i}$

➢ Thermally non-equilibrium model: $T=T_{rot}\neq T_{v_i}$

## Plasma-chemical initiation of detonation in a supersonic flow

**The schematic of the flow**




**The system of equations describing the flow behind shock wave front**

$$\frac{d(\rho u)}{dx}=0 \qquad u\frac{du}{dx}+\frac{1}{\rho}\frac{dP}{dx}=0 \qquad \frac{dH}{dx}+u\frac{du}{dx}=0 \qquad u\frac{dN_i}{dx}=G_i$$

$$G_i=\sum_{q=1}^{M}S_{iq} \qquad S_{iq}=(\alpha^-_{iq}-\alpha^+_{iq})\left[R^+_q-R^-_q\right] \qquad R^{+(-)}_q=k_{+(-)q}\prod_{j=1}^{n^{+(-)}_q}N_j^{\alpha^{+(-)}_{jq}}$$

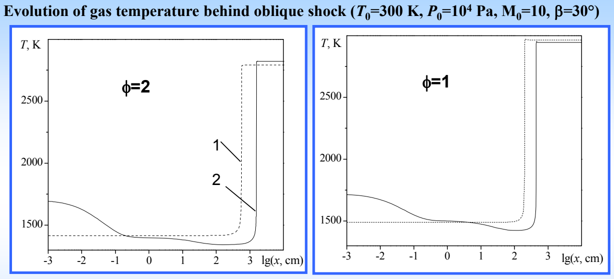
**Kinetic schemes**

**$H_2/O_2$ mixture** - 78 reactions, 11 species:
$H_2$, $O_2$, H, O, OH, $H_2O$, $HO_2$, $H_2O_2$, $O_3$ and electronically excited oxygen molecules $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$

**$CH_4/O_2$ mixture** - 307 reactions, 31 species:
$H_2$, $O_2$, H, O, OH, $H_2O$, $HO_2$, $H_2O_2$, $O_3$, $O_2(a^1D_g)$, $O_2(b^1S_g^+)$,
C, $CO_n$ (n=1,2), $CH_m$ (m=1-4), $C_2H_p$ (p=1-6), HCO, $CH_2O$, $CH_3O$, $CH_3O_2$, $CH_2OH$, $CH_3OH$, $CH_3O_2H$

## Ignition behind oblique shock wave in $CH_4$/air mixture

**Evolution of gas temperature behind oblique shock ($T_0$=300 K, $P_0$=$10^4$ Pa, $M_0$=10, β=30°)**




| ϕ=2 | ϕ=1 |
|---|---|
| **(1) thermally equilibrium chemistry: $L_{in}$=5.65 m; (2) thermally non-equilibrium chemistry: $L_{in}$=15.7 m** | **(1) thermally equilibrium chemistry: $L_{in}$=2 m; (2) thermally non-equilibrium chemistry: $L_{in}$=4.4 m** |

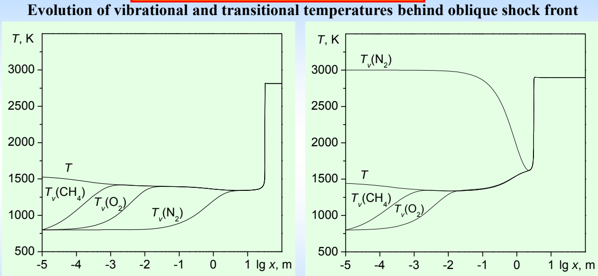
The neglect of non-equilibrium excitation of molecular vibrations of reagents results in a significant underestimation of predicted induction zone length (by a factor of three)

## Ignition behind oblique shock wave

**Stoichiometric $CH_4$/air mixture, $P_0=10^4$ Pa, $T_0=800$ K, $M_0=5$, $\beta=30°$**

**Thermally non-equilibrium chemistry**

**Evolution of vibrational and transitional temperatures behind oblique shock front**



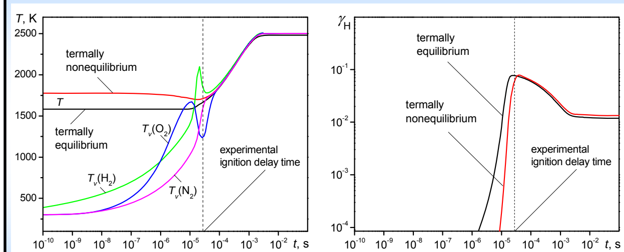

$T_v^0(N_2) = T_v^0(O_2) = T_v^0(CH_4)=T_0$ $\quad$ $T_v^0(N_2) = 3000$ K, $T_v^0(O_2) = T_v^0(CH_4)=T_0$

Preliminary excitation of molecular vibrations of $N_2$ leads to a significant decrease in the induction zone length (by a factor of 10-12) due to exclusion of the thermally non-equilibrium delayed excitation of $N_2$ vibrations behind the oblique shock front

## Thermally non-equilibrium effects behind shock wave

Evolution of vibrational, $T$(M), and tranlational temperatures behind the incident shock ($M_0$=5.77) in $H_2/O_2$ ($\phi$=0.13) mixture predicted by thermally equilibrium and thermally nonequilibrium models

Variation of H mole fraction behind the incident shock ($M_0$=5.77) in $H_2/O_2$ ($\phi$=0.13) predicted using thermally equilibrium and thermally nonequilibrium models




Thermally equilibrium model: $\tau_{ign}$=15 μs $\quad$ Experiment (Belles,1965): $\tau_{ign}$=21 μs

There is no consistency between data predicted using the thermally equilibrium kinetic model and measurements. This model underestimates the ignition delay time. Thermally non-equilibrium model predicts more reliable results ($\tau_{ign}$=23 μs).

## Discharge model

The self-consistent 1D model is based

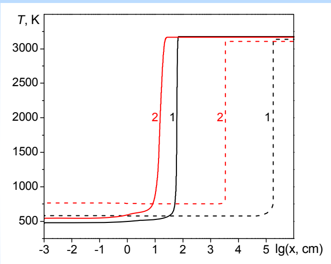
- Kinetic Boltzmann equation for EEDF in standard quasi-stationary approximation
- Kinetic rate balance equations for charged and neutral species: $e$, $O^+$, $O^-$, $O_2^+$, $O_2^-$, $O_3^-$, $O_4^+$, $O_2(X^3\Sigma_g^-)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, $O_2(A^3\Sigma_u^+, C^3\Delta_u, c^1\Sigma_u^-)$, $O_2(B^3\Sigma_u^-)$, $O(^3P)$, $O(^1D)$, $O_3(^1A_1)$ including vibrationally excited $O_2(X^3\Sigma_g^-)$ molecules
- 1D gas dynamic equations

## Activation of molecular oxygen in electrical discharge

Predicted concentration of the main species and temperature at the discharge outlet for different $E_s$ values at $E/N=1.1\cdot10^{-16}$ V·cm², $T_0$=300 K, $P_0=5\cdot10^3$ Pa , $M_0$=5

| Species | $E_s$, J/cm³ | | |
|---|---|---|---|
| | $1.2\cdot10^{-2}$ | $3\cdot10^{-2}$ | $6\cdot10^{-2}$ |
| $O_2(X^3\Sigma_g^-)$ | 0.9953 | 0.9589 | 0.917 |
| O | $4.02\cdot10^{-4}$ | $1.2\cdot10^{-3}$ | $3.09\cdot10^{-3}$ |
| $O_3$ | $3.382\cdot10^{-5}$ | $3.521\cdot10^{-5}$ | $3.18\cdot10^{-5}$ |
| $O_2(a^1\Delta_g)$ | $2.946\cdot10^{-3}$ | $3.221\cdot10^{-2}$ | $6.43\cdot10^{-2}$ |
| $O_2(b^1\Sigma_g^+)$ | $1.316\cdot10^{-3}$ | $7.663\cdot10^{-3}$ | $1.55\cdot10^{-2}$ |
| $T_v$ ($O_2(X^3)$), K | 686 | 985 | 1596 |
| Temperature, K | 322 | 354 | 400 |

## Plasma-chemical initiation of detonation in a supersonic flow of $H_2/O_2$ mixtures




Heating the gas – dashed lines. Activation of $O_2$ molecules in electrical discharge – solid lines

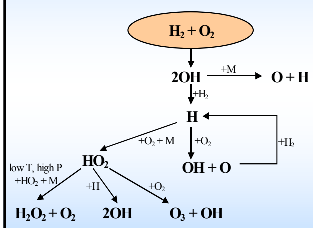
**Activation is much more efficient to initiate the ignition than the conventional heating the gas**

Variation of the gas temperature behind the oblique (β=15°) shock front in stoichiometric $H_2/O_2$ ($P_0$=0.1 bar, $M_0$=6) at different values of the specific energy deposited to the oxygen in electrical discharge: $E_s=3\cdot10^{-2}$ (1) and $6\cdot10^{-2}$ J/cm$^3$ (2).

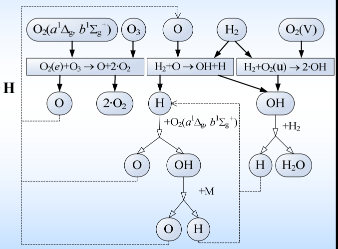
**A.M. Starik, B.I. Lukhovitskii, V.V. Naumov, N.S. Titova. Technical Physics, 2007, V.52, No.10, P.1281-1290.**

## Kinetic Mechanisms of Combustion Initiation in $H_2+O_2$ Mixture

1. Without excitation of $O_2$ molecules




2. With excitation of $a^1\Delta_g$, $b^1\Sigma_g^+$ electronic states of $O_2$ molecules

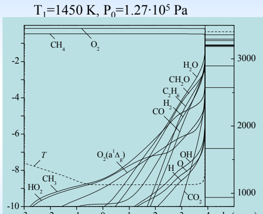



## Plasma-chemical combustion initiation in a supersonic flow behind oblique shock wave

Premixed flow of $CH_4$-$O_2$ stoichiometric mixture

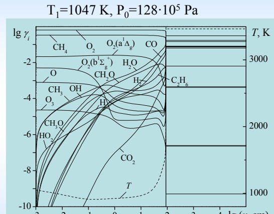
Heating the mixture: T=571 K

Parameters behind the shock front
$T_1$=1450 K, $P_0$=1.27·10$^5$ Pa



Initiation by non-equilibrium oxygen plasma: $T_0$=400 K

Parameters behind the shock front
$T_1$=1047 K, $P_0$=128·10$^5$ Pa



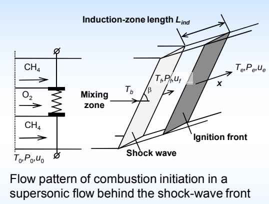
Evolution of the species mole fractions along the flow behind the shock front at $P_0=10^4$ Pa, $M_0$=8, β=25°, $E_s=3\cdot10^{-2}$ J/cm$^3$.

Excitations of oxygen molecules to the $a^1\Delta_g$ and $b^1\Sigma^+_g$ electronic states is much more efficient in shortening the induction zone length than the heating the gas.

## Combustion enhancement in $CH_4$-$O_2$ mixture

- Singlet oxygen-assisted combustion in a supersonic flow

**A.M. Starik, B.I. Lukhovitskii, N.S. Titova. Combustion, Explosion, and Shock Waves, 2008, V. 44, No. 3, P. 249-261**.




Flow pattern of combustion initiation in a supersonic flow behind the shock-wave front

***$L_{ind}$*=54 cm**
***$E_m$*=190 J/g=3·10$^{-2}$ J/cm$^3$**

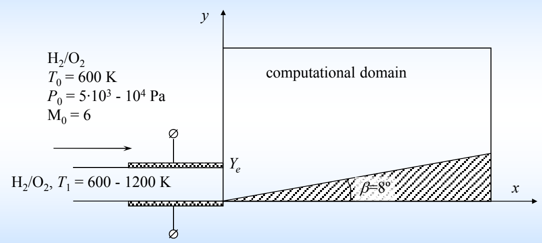
Gas-Dynamic Parameters of the Initial Mixture and Combustion Exhausts; Energy Input to the Gas and Chemical Energy Converted to Heat

| Method of combustion initiation | $T_b$, K | $T_e$, K | $P_e$, kPa | $M_e$ | $\Delta H_{ch}$, J/g | $E_m$, J/g |
|---|---|---|---|---|---|---|
| Excitation of $O_2$ molecules | 354 | 3466 | 691 | 1.65 | **3273** | **190** |
| Heating of the mixture | 750 | 3382 | 286 | 2.76 | **2214** | 582 |

**The excitation of $O_2$ molecules to the singlet electronic states makes it possible to increase the fraction of chemical energy that may be converted to thermal energy during combustion as compared to initiation of combustion by heating the mixture. The gain in terms of $\Delta H_{ch}$ may be as large 50%**

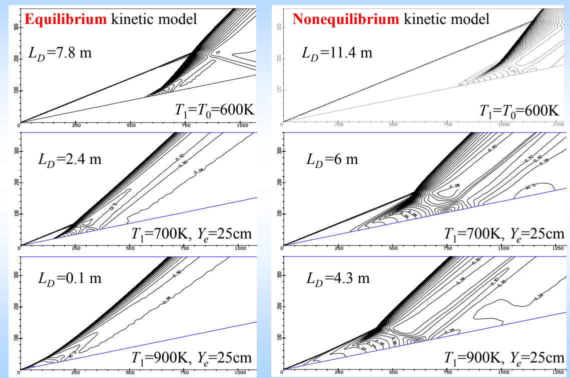
## The effect of non-equilibrium excitation of molecular vibrations behind shock front

**Schematic of the flow and computational domain**



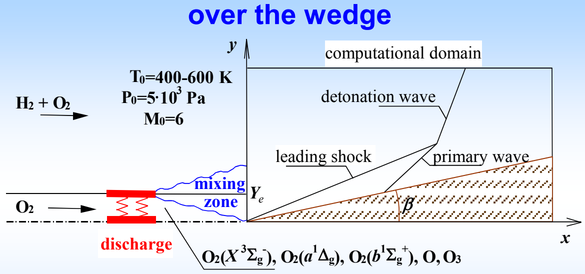

**L.V. Bezgin, V.I. Kopchenov, A.M. Starik, N.S. Titova. Combustion, Explosion, and Shock Waves, 2006, V. 42, No. 1, P.68-75**

## The effect of non-equilibrium excitation of molecular vibrations behind shock front




Pressure fields in the flow of $H_2/O_2$ = 2/1 mixture ($P_0 = 5\cdot10^3$ Pa, $T_0$ = 600 K, $M_0$ = 6)

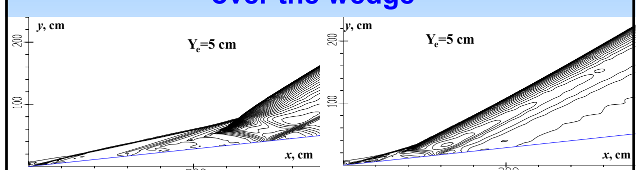
## Plasma-assisted initiation of detonation over the wedge




**The principal scheme of the flow for simulation of plasma-chemical initiation of detonation in supersonic flow over the wedge**

**Bezgin L.V., Kopchenov V.I., Starik A.M., Titova N.S.. In Pulse Detonation Propulsion. Eds. G.D. Roy, S.M. Frolov, J. Shepherd. Moscow. Torus. Press Ltd. 2006. P.147-164.**

## Plasma-assisted detonation initiation over the wedge




Without activation: $E_s$=0, $L_d$=2.6 m:

With activation: $E_s$=0.03 J/cm³, $L_d$=1 m

Flow parameters : $P_{out}=P_{in}=5\cdot10^3$ Pa, $M_{out}=M_{in}$=6, $T_{out}$=500 K, $T_{in}$=354 K

Predicted pressure fields for a $H_2$-$O_2$ supersonic flow over the wedge for following cases: (a) the inner $O_2$ flow does not contain excited oxygen molecules ($T_{in}$ = 354 K); (b) the inner flow is activated by electrical discharge ($E_s = 3\cdot10^{-2}$ J/cm³).

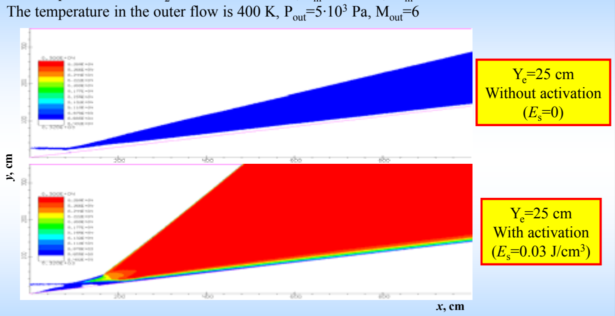
At $E_s$=0.03 J/cm³ and $T_{out}$=500 K the activation of molecular oxygen in the region with d=5 cm leads to shortening the induction and detonation zone lengths

## Plasma-assisted detonation initiation over the wedge

**Nonpremixed flow with and without activation of oxygen in electrical discharge**

The temperature in the $O_2$ inner flow is 354 K, $P_{in}=5\cdot10^3$ Pa, $M_{in}=6$

The temperature in the outer flow is 400 K, $P_{out}=5\cdot10^3$ Pa, $M_{out}=6$

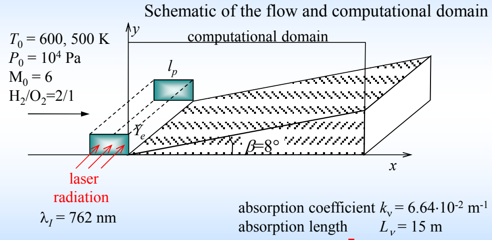



**Predicted temperature field for the flow of the $H_2/O_2$ mixture under activation of molecular oxygen**

## Detonation wave initiation by laser-induced excitation of oxygen molecules

**L.V. Bezgin, V.I. Kopchenov, A.M. Starik, N.S. Titova. Technical Physics, 2007, Vol. 52, N 1, P. 39-46.**

Schematic of the flow and computational domain



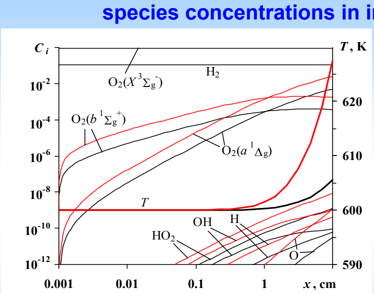

absorption coefficient $k_v = 6.64\cdot10^{-2}$ m$^{-1}$

absorption length $L_v = 15$ m

$O_2(X^3\Sigma_g^-) + h\nu \Rightarrow O_2(b^1\Sigma_g^+)$

- Supersonic flow can be irradiated by multiple scanning across the flow by a rather narrow beam of low intensity

## Initiation of a detonation wave above a wedge: species concentrations in irradiation zone




Concentration of excited $O_2$ molecules in the irradiation zone depends on the radiation energy absorbed by single $O_2$ molecule

$$E_s = I_0 \int_0^{l_p} \frac{k_v}{u N_1} dx$$

Variation of the species mass fraction and gas temperature with distance in irradiation zone.

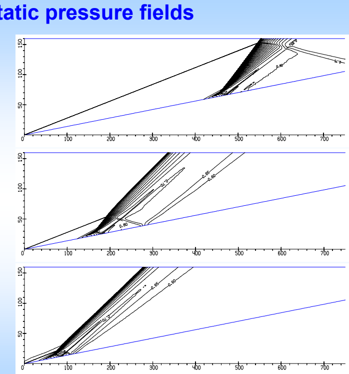
Flow parameters: $H_2/O_2$=2/1 mixture, $M_0$ = 6, $P_0$ = $10^4$ Pa, $T_0$ = 600 K.

Laser radiation: $\lambda_l$ = 762 nm.

$E_s$ = 0.01 eV/($O_2$ molecule) (black lines)

$E_s$ = 0.05 eV/($O_2$ molecule) (red lines).

## Initiation of a detonation wave above a wedge: static pressure fields



**$E_s$ = 0**
**$L_{ind}$ = 4.24 m**
**$L_d$ = 5.45 m**

**$E_s$ = 0.01 eV/(molecule $O_2$)**
**$L_{ind}$ = 1.31 m**
$L_d$ = 1.91 m

**$E_s$ = 0.05 eV/(molecule $O_2$)**
**$L_{ind}$ = 0.45 m**
**$L_d$ = 0.76 m**

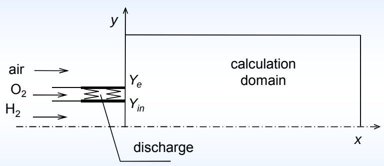
Flow parameters: $H_2/O_2$=2/1 mixture, $M_0$ = 6, $P_0$ = $10^4$ Pa, **$T_0$ = 600 K**

Laser radiation: $\lambda_l$ = 762 nm, **$Y_e$ = 2 cm**

## Flow scheme: diffusion mode of combustion

As compared to the homogeneous flow, the mixing influences the ignition delay length and in the case of pre-excitation of reactive molecules can decrease the concentration of excited molecules due to their quenching at the longer length.

**A.M. Starik, N.S. Titova, L.V. Bezgin, V.I. Kopchenov. J. of Phys. D: Applied Phys., 2008, V.41, 125210**




(1) inner $H_2$ flow - $0<Y<Y_{in}$=25 cm, $M_{in}$=2.5, $P_{in}$=0.1 bar, $T_{in}$=450 K

(2) intermediate flow of $O_2$ discharge products – $Y_{in}<Y<Y_e$, $d=Y_e-Y_{in}$
discharge inlet parameters $M_{O2}$=2, $P_{O2}$=0.1 bar, $T_{O2}$=300 K

(3) outer air flow - $Y_e<Y$, $M_{air}$=3.5, $P_{air}$=0.1 bar, $T_{air}$=750, 900 K

## Discharge parameters

In order to provide the maximal yield of singlet oxygen molecules the reduced electric field should be equal $1.1\cdot10^{-16}$ V·cm². At $E/N=1.1\cdot10^{-16}$ V·cm² and rather high pressure, $P_{O2}$=0.1 bar, the discharge should be non-self-sustained.

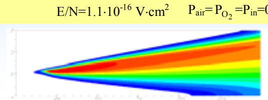
| Component | $E_s$, J/cm³ | | | |
|---|---|---|---|---|
| | 0 | $1.3\cdot10^{-2}$ | $2\cdot10^{-2}$ | $2.6\cdot10^{-2}$ |
| $O_2(X^3\Sigma_g^-)$ | 1 | 0.9817 | 0.9732 | 0.9636 |
| $O(^3P)$ | 0 | $5.04\cdot10^{-4}$ | $7.45\cdot10^{-4}$ | $9.82\cdot10^{-4}$ |
| $O(^1D)$ | 0 | $9.1\cdot10^{-10}$ | $1.41\cdot10^{-9}$ | $1.92\cdot10^{-9}$ |
| $O_3$ | 0 | $2.44\cdot10^{-5}$ | $2.21\cdot10^{-5}$ | $2.01\cdot10^{-5}$ |
| $O_2(a^1\Delta_g)$ | 0 | $1.43\cdot10^{-2}$ | $2.14\cdot10^{-2}$ | $2.85\cdot10^{-2}$ |
| $O_2(b^1\Sigma_g^+)$ | 0 | $3.31\cdot10^{-3}$ | $4.95\cdot10^{-3}$ | $6.59\cdot10^{-3}$ |
| Temperature, K | 300 | 325 | 339 | 352 |
| Pressure, bar | 0.1 | 0.111 | 0.117 | 0.123 |

- **An increase in the value of the input specific energy results in a noticeable growth in the concentration of excited oxygen molecules.**
- **The concentrations of O atoms and $O_3$ molecules in the oxygen plasma at such discharge parameters are considerably smaller than those for $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ molecules.**

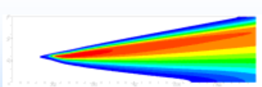
## Plasma-assisted combustion in a supersonic flow

| Air | Oxygen | Hydrogen |
|---|---|---|
| $M_{air}$=3.5 | $M_{O_2}$=2 | $M_{in}$=2.5 |
| $T_{air}$=900 K | $T_{O_2}$=300 K | $T_{in}$=450 K |
| | $E/N=1.1\cdot10^{-16}$ V·cm² | $P_{air}=P_{O_2}=P_{in}$=0.1 bar |

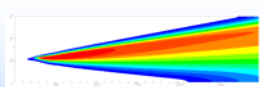
$E_s$=0, $d_e$=5 mm



$E_s=2\cdot10^{-2}$ J/cm³, $d_e$=5 mm



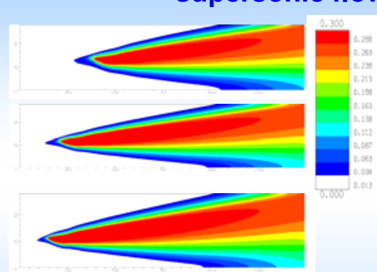
$E_s=1.3\cdot10^{-2}$ J/cm³, $d_e$=5 mm



$E_s=2.6\cdot10^{-2}$ J/cm³, $d_e$=5 mm

$H_2O$ mass fraction field for diffusion $H_2/O_2$/air combustion in a supersonic flow upon activation of $O_2$ molecules in electrical discharge

## Plasma-assisted combustion in a supersonic flow



$E_s = 1.3\cdot10^{-2}$ J/cm³

$E_s = 2\cdot10^{-2}$ J/cm³

$E_s = 2.6\cdot10^{-2}$ J/cm³

Predicted water vapor mass fraction fields for $T_0$=750 K at $d$=1 cm.

- **Increasing the flow rate of oxygen plasma ($d$=1 cm) makes it possible to ignite the mixture at the distance of 81 cm from the discharge outlet for $E_s$=0.026 J/cm³.**

## Plasma-assisted combustion in a supersonic flow

Ignition delay length (in cm) versus the transversal dimension of excitation region *d* for air temperature of 750 K and different values of $E_s$.

| Type of influence | *d*, cm | $E_s$, J/cm³ | | | |
|---|---|---|---|---|---|
| | | 0 | 0.013 | 0.02 | 0.026 |
| | 0 | 9855.6 | | | |
| discharge | 0.5 | 9594.9 | 1374.0 | 703.3 | 332.5 |
| | 1 | 9195.4 | 256.3 | 117.3 | **81.6** |
| heating | 0.5 | 9594.9 | 9490.0 | 9399.2 | 9331.0 |
| | 1 | 9195.4 | 9081.1 | 9075.1 | **9029.5** |
| discharge without O atoms | 0.5 | 9594.9 | 2145.3 | 1221.8 | 734.4 |
| | 1 | 9195.4 | 475.5 | 225.3 | 141.2 |

## Plasma-assisted combustion in a supersonic flow

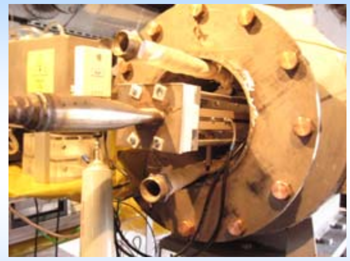


Photo of experimental set up with the discharge chamber and the system to supply $O_2$/Ar mixture

## Plasma-assisted combustion in a supersonic flow

Photo of the section for measurement the spontaneous emissions and for occurrence of special diagnostics

## Increase of fame speed

One of the most important fundamental characteristics in combustion science is the <u>velocity of laminar flame propagation</u>.

- **An increase of burning rate is an extremely important problem in creating the prospective combustors**
- **The possibility of the flame speed increase by means of electrical discharge was first demonstrated for lean low pressure $H_2$-$O_2$ mixture by Basevich and Kogarko (*Kinetika i Kataliz. 1966*).An attempt to explain this phenomenon was undertaken by Basevich and Belyaev (*Chem. Phys. Report. 1989*).**
- **The comprehensive analysis of the effect of the presence of the singlet oxygen molecules in $H_2$-$O_2$ mixture has been done recently by our group (Starik et al. *J. Phys. D: Appl. Phys.2008; Combustion, Explosion and Shock Waves,2008*)**

# Velocity of flame propagation

## $H_2/O_2$ mixture

The predicted laminar flame velocities for hydrogen–oxygen mixtures with 10.5% and 8.5 % $H_2$ at $P_0$=0.068 bar, $T_0$=329 K.

| | $U_n$, cm/s | $U_n^{dis}$, cm/s | $U_n^{dis}/U_n$ | |
|---|---|---|---|---|
| $H_2$ volume fraction | without discharge $T_0$=329 K | with discharge $T_0$=329 K | calculation | experiment |
| 10.5% | 17.07 | 36.51 | 2.14 | 1.66 |
| 8.5% | 6.07 | 16.91 | 2.78 | 1.92 |

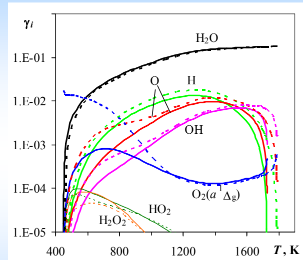
Burning rate increases by a factor of ~**2.1** at 10.5% $H_2$ concentration
by a factor of ~**2.8** at 8.5% $H_2$ concentration.

Such a tendency (the flame velocity grows stronger at smaller $H_2$ concentration in the mixture) was observed in experiments.

Some discrepancy between experimental data and calculations in the values of flame speed may be explained by the fact that the experimental parameters of glow discharge is not known exactly and composition of discharge plasma may be calculated only approximately.

# Kinetic processes in flame front region

## $H_2$/air mixture




Variation of species mole fractions versus temperature in the flame front for fuel lean $H_2$-air mixture ($\phi$=0.5) at $[O_2(a^1\Delta_g)]$= 0 (solid curves), $[O_2(a^1\Delta_g)]$= 0.1 $[O_2]$ (dashed curves)

The diffusion of H atoms from the high temperature flame region to low temperature zone

↓

The presence of a large amount of $O_2(a^1\Delta_g)$ molecules in the low temperature zone of the flame increases the rate of chain-branching
$H+O_2(a^1\Delta_g)=OH+O$

↓

O atom concentration is tenfold higher

↓

The rate of the second chain-branching reaction $H_2+O=OH+H$ increases.

# Velocity of flame propagation

- In modern combustion technologies the hydrocarbon fuels are widely used. Unfortunately, until now, there were no any researches on the analysis of kinetic mechanisms of the flame speed increase due to the abundance of singlet molecules both in $H_2$-air and in hydrocarbon-air mixtures.
- It is very important to highlight the principle mechanisms of the influence of activation of oxygen molecules in electrical discharge on the speed of laminar flame propagation in hydrogen-air and methane-air mixtures.

# Comparison of flame propagation

## in $H_2$/air and $CH_4$/air mixture

| | $CH_4$-air | | $H_2$-air | |
|---|---|---|---|---|
| | 0% $O_2(a^1\Delta_g)$ | 10% $O_2(a^1\Delta_g)$ | 0% $O_2(a^1\Delta_g)$ | 10% $O_2(a^1\Delta_g)$ |
| | $\phi$=0.45 | | $\phi$=0.45 | |
| $T_e$, K | 1496 | 1542 | 1606 | 1686 |
| $U_n$, cm/s | 10.1 | 17.0 | 112 | 179.7 |
| $\Delta U_n/U_{n0}$ | | 0.68 | | 0.60 |
| | $\phi$=1 | | $\phi$=1 | |
| $T_e$, K | 2276 | 2305 | 2429 | 2452 |
| $U_n$, cm/s | 72.3 | 85.6 | 388 | 465 |
| $\Delta U_n/U_{n0}$ | | 0.18 | | 0.20 |
| | $\phi$=1.9 | | $\phi$=1.9 | |
| $T_e$, K | 1772 | 1827 | 2239 | 2266 |
| $U_n$, cm/s | 11.1 | 14.2 | 484 | 553.3 |
| $\Delta U_n/U_{n0}$ | | 0.28 | | 0.14 |

**An increase in flame speed may be as large as 70% for fuel lean mixture.**

# Kinetic processes in flame front region

## $CH_4$/air mixture

The diffusion of $CH_3$, $CH_2O$ radicals from the high temperature flame region to low temperature zone

⇩

The presence of $O_2(a^1\Delta_g)$ molecules in the low temperature zone of the flame increases the rates of reactions :

$CH_3+O_2(a^1\Delta_g)=CH_3O+O$

$CH_2O+O_2(a^1\Delta_g)=HCO+HO_2$

⇩

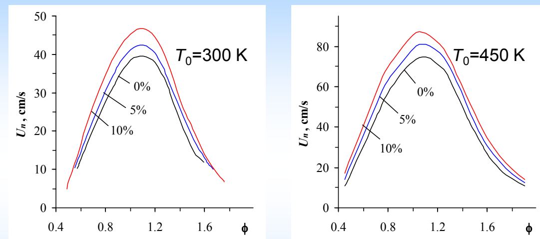
Concentration of O atoms is much higher in low temperature region than that without O2($a^1\Delta_g$) molecules in the low temperature zone

⇩

Due to larger O atom concentration in the low temperature zone the rate of reaction $CH_4+O=CH_3+OH$ increases.

# Velocity of flame propagation

## $CH_4$/air mixture




Predicted dependence of $U_n$ on ϕ for $CH_4$/air mixture at $[O_2(a^1\Delta_g)]/([O_2]+[O_2(a^1\Delta_g)])$= 0; 0.05 and 0.1 for $T_0$=300 K (a) and 450 K (b) and $P_0$=1 atm.

**At $T_0$=450 K the flame speed increase due to the presence of 10% singlet oxygen molecules in $O_2$ for fuel lean mixture (ϕ=0.45) may be ~70% and for fuel rich mixture (ϕ=1.9) ~30%.**

**For temperature ($T_0$=300 K) the flame speed growth is slightly smaller.**

# Clean combustion

CONTROL OF POLLUTANT FORMATION DURING COMBUSTION BY MEANS OF EXCITATION OF INTERNAL DEGREES OF FREEDOM OF MOLECULES

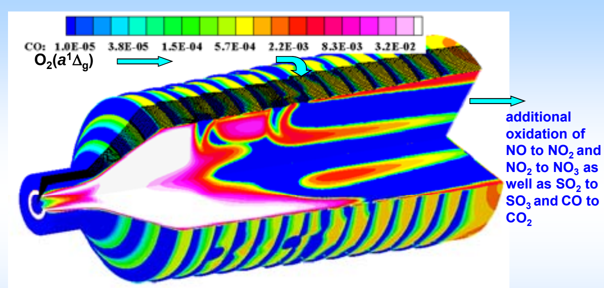
- **We can change the formation pathways of pollutant due to selective excitation of vibration or electronic states of molecules**

1. $H_2O(001) + NO = HNO + OH$
   $NH_3 + OH = NH_2 + OH$
   $NH_2 + NO = N_2 + H_2O$
   } Excitation of asymmetric mode of $H_2O$ molecules by laser radiation ($\lambda_l$ = 2.66 μm)
2. $O_2(X\,^3\Sigma_g^-) + h\nu(\lambda_l\text{=762 nm}) = O_2(b^1\Sigma_g^+)$
   $O_2(b^1\Sigma_g^+) + SO_2 = SO_3 + O(^3P)$
   $SO_3 + H_2O = H_2SO_4$
   } Laser-induced or electron impact excitation of $O_2$ molecules

- **The use of excited molecules to enhance the clusters formation and to stimulate the nucleation at relatively high temperature in the exhaust**

$SO_2 + O_3(001) = SO_3 + O_2$
$SO_3 + H_2O(001) = H_2SO_4$
$nH_2O(001) + H_2SO_4 = H_2SO_4(H_2O)_n$

# Aviation combustor




- Aero-engine test rig combustor configuration and CFD predicted CO mass concentration field inside the combustor. A one million cell sector geometry is used. The k-ε turbulence closure model is used.

## Summary

- Excitation of $O_2$ molecules makes it possible to initiate the detonation wave in a supersonic flow over the wedge at 1 m distance from the wedge apex for a small specific energy deposited to the gas -$3 \cdot 10^{-2}$ J/cm$^3$.
- The intensification of ignition and full-scale combustion is caused by the acceleration of the formation of highly reactive atoms and radicals mainly due to abundance of electronically excited oxygen molecules $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma^+_g)$ in the mixture and has a non-thermal character.
- For initiation of oblique detonation wave over a wedge, it is sufficient to activate molecular oxygen in a narrow near-axis region, i.e. in a thin layer adjacent to the wedge apex.
- The excitation of $O_2$ molecules in electrical discharge may be an efficient approach to initiate the diffusion combustion in a $H_2(CH_4)$+air mixture supersonic flow for small input energy ($E_s$=0.03J/cm$^3$) at extremely narrow $O_2$ excitation region (d=0.5 cm).
- The abundance of singlet oxygen molecules in the $H_2$-air and $CH_4$-air mixtures in amount of 5-10% of the total concentration of molecular oxygen, can considerably affect the speed of laminar flame propagation.

We certainly underhand that our researches are only a starting point in the solving the problem of combustion enhancement and development of novel combustion concepts, but we believe that we have found a true way to do it.

This work was supported by International Scientific Technical Center (ISTC), Russian Foundation for Basic Research (RFBR), the Research Program of Russian Academy of Science and INTAS.

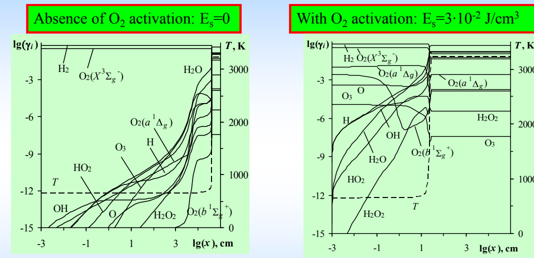
Also I am grateful to the co-workers of my Research Center “Physics of Non-equilibrium Processes and Novel Combustion Concepts”

Many thanks for your attention

## Plasma-chemical initiation of detonation in a supersonic flow of $H_2/O_2$ mixtures

Absence of $O_2$ activation: $E_s$=0

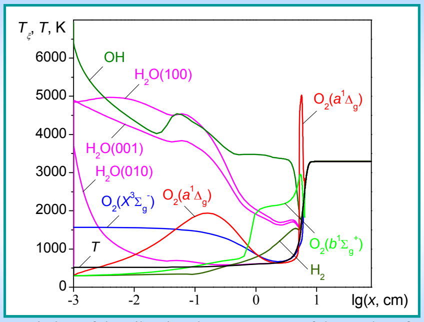
With $O_2$ activation: $E_s=3 \cdot 10^{-2}$ J/cm$^3$




Evolution of species mole fractions and temperature (solid and dotted curves) along the $H_2/O_2$=2/1 flow behind the shock front for $E_s$ = 0 (*a*); $3\times10^{-2}$ (*b*) J/cm$^3$ at $T_0$=300 K, $P_0=10^4$ Pa, $M_0$=6.5, β=25°.

**The $O_2$ activation by electrical discharge results in the formation of electronically excited oxygen molecules and O atoms that intensifies the chain mechanism of combustion.**

## Plasma-chemical initiation of detonation in a supersonic flow of $H_2/O_2$ mixtures




Variation of the vibrational temperatures of the modes of molecules, $T_\xi$, and tranlational temperature, $T$, downstream the shock front at deposited energy $E_s$=6·10$^{-2}$ J/cm$^3$.

Flow parameters;

β=20°

$M_0$=6

$P_0$=10$^4$ Pa

## Initiation of a detonation wave above a wedge:

### mathematical model

- **Set of equations:**

$$\frac{\partial \vec{E}}{\partial x} + \frac{\partial\left(\vec{F}+\vec{F}_v\right)}{\partial y} = \vec{G}$$

$$\vec{E} = \begin{pmatrix} \rho u \\ \rho u^2 + P \\ \rho uv \\ \rho u\left(H + V^2/2\right) \\ \|uN_i\| \end{pmatrix} \quad \vec{F} = \begin{pmatrix} \rho v \\ \rho uv \\ \rho v^2 + P \\ \rho v\left(H + V^2/2\right) \\ \|vN_i\| \end{pmatrix} \quad \vec{F}_v = \begin{pmatrix} 0 \\ \sigma_{yx} \\ \sigma_{yy} \\ q_y \\ \|J_i^y\| \end{pmatrix} \quad \vec{G} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ Q_I \\ \|q_{ch}^i + q_I^i\| \end{pmatrix}$$

- **Boundary conditions:**

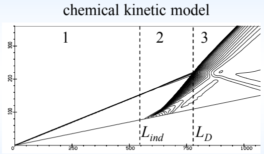
$x = 0$: $f=f_0$
$y = 0$: $v=0$, $\partial f / \partial y = 0$
$y = 70$ cm: the non-reflecting conditions

- **Numerical method**: the marching method based on a stationary analog of the Godunov method.

## The effect of non-equilibrium excitation of molecular vibrations behind shock front

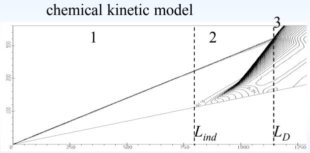
Pressure fields in the flow of $H_2/O_2$ = 2/1 mixture ($P_0$ = 5·10$^3$ Pa, $T_0$ = 600 K, $M_0$ = 6)

Thermally **equilibrium** chemical kinetic model




**$L_{ind}$=5.7 m, $L_D$=7.7 m**

Thermally **nonequilibrium** chemical kinetic model

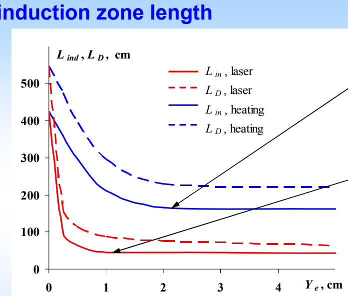



**$L_{ind}$=7.6 m, $L_D$=11.4 m**

❑ **In thermally non-equilibrium kinetic model the induction and transition zone lengths are essentially lager than those in the thermally equilibrium model.**

## Initiation of a detonation wave above a wedge:

### induction zone length

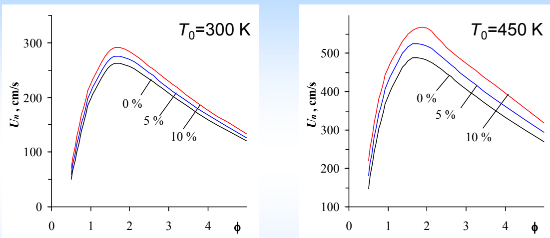



**Under heating the mixture detonation wave cannot be stabilized within 2.5 m from the tip at any $Y_e$.**

**At given value of $E_s$ there exists the quantity of critical transversal dimension $Y_e$ of the irradiation region, beginning of which the lengths of induction and detonation zones changes only slightly.**

Induction and detonation zone lengths vs. transversal dimension of the excitation region.
Flow parameters: $H_2/O_2$=2/1 mixture, $M_0$ = 6, $P_0$ = 10$^4$ Pa, $T_0$ = 600 K.
Laser radiation: $\lambda_I$ = 762 nm, $E_s$ = 0.05 eV/(molecule $O_2$).
Dashed lines - mere laser heating;
Continuous lines - laser excitation of $O_2$ molecules into $b^1\Sigma_g^+$ state .

# Velocity of flame propagation
## in $H_2$/air mixture

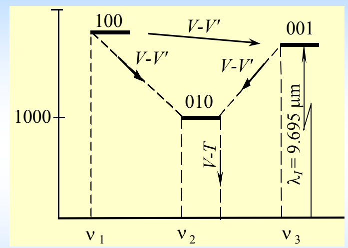



Predicted dependence of $U_n$ on ϕ for $H_2$-air mixture at $[O_2(a^1\Delta_g)]$= 0; 0.05 and 0.1 $[O_2]$ for $T_0$=300 K (a) and 450 K (b) and $P_0$=1 atm.

**An increase in the concentration of singlet oxygen molecules in the mixture and in the temperature leads to the growth of the flame speed.**

A.M. Starik, V.E. Kozlov, N.S. Titova. J. Phys. D: Applied Phys., 2008, V.41, 125206

# Laser-induced excitation of $O_3$ molecular vibrations




Excitation: $O_3$+hν($\lambda_l$≈9.7 μm)=$O_3$(001)
$000(12_{1,12})\rightarrow 001(11_{1,11})$
$\lambda_l$=9.69483 μm, $\lambda_{mn}$=9.69486 μm

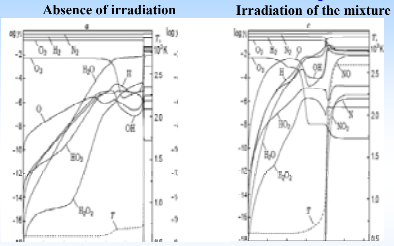
This transition is allowed in dipole approximation, $A_{mn}$=10.64 $s^{-1}$,
$P_0=10^4$ Pa, $I_0$=50 kW/cm$^2$
$\tau_l=10^{-6}$ s, $\tau_R=3\cdot10^{-5}$ s

$\tau_l < \tau_R$

**The scheme of low vibrational levels of $O_3$ molecule. Solid and dashed arrows depict the induced transition and collisional pathways of vibrational energy relaxation (V-V' and V-T processes).**

# Ignition of $H_2/O_2$(air)/$O_3$ quiescent mixture by laser-induced excitation of $O_3$ molecular vibrations

**Absence of irradiation** | **Irradiation of the mixture by laser photons at $\lambda_l$≈9.7 μm**



$P_0=10^4$ Pa, $T_0$=600 K

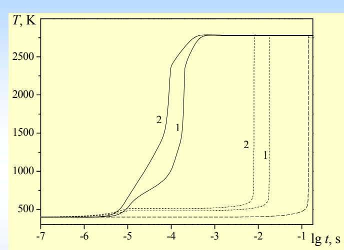
At $E_{in}$=0 ⟶ $\tau_{in}=9\cdot10^{-2}$ s

At $E_{in}$=5 J/cm$^2$ ($E_s=10^{-3}$ J/cm$^3$) ⟶ $\tau_{in}=10^{-3}$ s

Gas temperature (dashed curves) and molar fractions of the components versus time (solid curves) for ignition of a stoichiometric $H_2$/air/$O_3$ mixture with 0.5%, $O_3$ content in the case of absence of the radiation and in the case of laser-induced excitation of asymmetric vibrations of $O_3$ molecule by radiation for $E_0$=5 J/cm$^2$ and $\tau_p=10^{-5}$sec.

**Laser-induced excitation of $O_3$ molecular vibrations intensifies the thermal explosion mechanism of $O_3$ photolysis and chain-branching mechanism of $H_2$/air mixture combustion**

# Ignition of $C_2H_2$/air/$O_3$ quiescent mixture by laser-induced excitation of $O_3$ molecular vibrations




Initial parameters of $C_2H_2$/air+5%$O_3$ mixture: $T_0$ = 400 K; $P_0=10^4$ Pa

Pulse duration $\tau_p=10^{-5}$ sec

Dotted curves correspond to the heating of the gas by laser radiation
Solid curves correspond to excitation of $O_3$ molecular vibrations
1 – $E_{in}$ = 0.5 J/cm$^2$ ($E_s=5.5\cdot10^{-3}$ J/cm$^3$, $T_{v3}$=1370 K))
2 – $E_{in}$ = 1 J/cm$^2$ ($E_s=7.7\cdot10^{-3}$ J/cm$^3$, $T_{v3}$=1650 K)

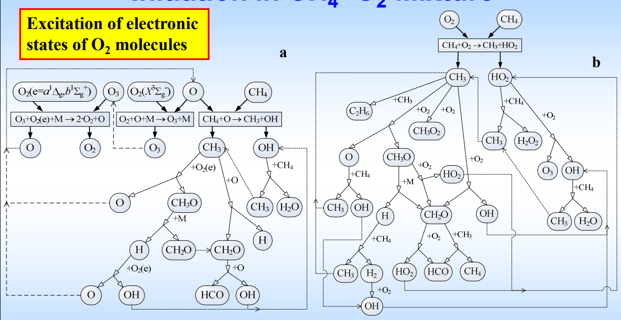
$$E_s = \int_0^{\tau_p} k_\nu I dt$$

Time evolution of the gas temperature during ignition of $C_2H_2$/air/stoichiometric mixture with 5% $O_3$ content upon exposure to radiation with $\lambda_l$=9.7 μm in the case when absorbed energy goes to the heating of the gas and when the absorbed energy goes to excitation of $O_3$ molecular vibrations dashed curve corresponds to pure stoichiometric $C_2H_2$/air mixture

**Excitation of $O_3$ molecular vibrations by laser radiation at 9.7 μm wavelength is more efficient (by a factor of $10^2$) in reduction of $\tau_{in}$ than the heating of the gas by laser radiation**

## Kinetic Mechanisms of Combustion Initiation in $CH_4$+$O_2$ Mixture

**Excitation of electronic states of $O_2$ molecules**




**The principal scheme of the chain mechanism development $CH_4$-$O_2$ mixture upon the activation of $O_2$ molecules by electrical discharge (*E/N*=1.1·10$^{-16}$ V·cm$^2$) (a) and at the heating the gas (b) at low temperature (T<1200K).**

## The effect of non-equilibrium excitation of molecular vibrations behind shock front

The reason of increase of the length at which ignition front forms for thermally **non-equilibrium** chemical kinetic model as compared to **equilibrium** model: