Physics and chemistry of the influence of excited molecules on combustion enhancement

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The paper addresses detailed analysis of kinetic processes in the $\text{H}_2$−$\text{O}_2$, $\text{CO}$−$\text{O}_2$ and $\text{CH}_4$−$\text{O}_2$ reactive systems upon the presence of singlet oxygen molecules $\text{O}_2(a^1\Delta_g)$ and $\text{O}_2(b^1\Sigma_g^+)$ and the influence of the activation of oxygen molecules in electric discharge on the acceleration of ignition in the $\text{H}_2$−$\text{O}_2$ and $\text{CH}_4$−$\text{O}_2$ mixtures. The possibility of the intensification of CO oxidation due to excitation of $\text{O}_2$ and $\text{N}_2$ molecule vibrations and generation of singlet oxygen molecules is also considered. It is shown that the effect of accelerating the ignition strongly depends on the reduced electric field and, as a consequence, on the composition of discharge plasma as well as on the features of chain mechanism development in oxy-fuel systems. It is revealed that the most effective approach for the intensification of CO oxidation both in the moist air and in the products of hydrocarbon combustion in air is the generation of $\text{O}_2(a^1\Delta_g)$ molecules by electric discharge. Computations showed that the presence of 1% $\text{O}_2(a^1\Delta_g)$ in the total oxygen allowed one to convert CO to CO$_2$ even at the temperature $T = 850$–$900$ K in the time of $10^{-2}$ s. The excitation of $\text{O}_2$ and $\text{N}_2$ molecule vibrations is less effective for such a conversion.

1. Introduction

A possibility of ignition and combustion enhancement in various mixtures by means of the excitation of reactive molecules was extensively discussed for the past years (e.g. [1–3]). Interest in this problem is due to the fact that both vibrationally and electronically excited molecules
react much faster than non-excited ones. Theoretical [4–9] and experimental [10–14] studies showed that the rate constants of reactions with excited molecules can be by a factor $10^2$–$10^4$ higher than those with ground state molecules. Both vibrationally and electronically excited molecules can be produced with rather high efficiency in tailored electric discharge [2,15–17].

Singlet delta oxygen (SDO) molecules $O_2(a^1 \Delta_g)$ have attracted the attention of researchers for a long time. SDO is an important intermediate in a number of chemical reactions of biological, medical and environmental significance [18]. It has been implicated in the photochemical transformations of air pollutants [19] and in the degradation of polymers [20]. Also, $O_2(a^1 \Delta_g)$ and $O_2(b^1 \Sigma_g^+)$ molecules play an important role in the photochemistry of ozone in the middle and upper atmosphere [21–23].

To date, there exist a lot of proofs that the presence of excited oxygen molecules in the reacting mixtures can substantially enhance ignition and combustion [1,4,24–33]. It is worth noting that, originally, the hypothesis for a strong influence of SDO on the combustion process in the $H_2$–$O_2$ mixture was proposed by Basevich & Belyaev [31]. On the basis of this hypothesis, they attempted to explain the increase in the flame speed in the low-pressure fuel-lean $H_2$–$O_2$ mixture observed after the activation of oxygen molecules in a glow discharge [32]. However, detailed analysis of the effect of the presence of SDO in the mixture on the combustion kinetics was not done in [31]. Comprehensive investigation of the influence of $O_2(a^1 \Delta_g)$ molecules on the flame speed and extending the flammability limits for the $H_2$–$O_2$ mixture with the use of a detailed reaction mechanism demonstrated that the major effect took place for the fuel-lean mixture [33]. Later, a similar tendency was predicted for the $CH_4$–$O_2$ mixture [24].

The numerical analysis of the influence of $O_2(a^1 \Delta_g)$ and $O_2(b^1 \Sigma_g^+)$ molecules on the ignition of $H_2$–$O_2$ (air) and $CH_4$–$O_2$ (air) mixtures in a supersonic flow behind the inclined shock wave was conducted in [26,28,34,35] on the basis of detailed kinetic mechanisms comprising a large set of reactions with $O_2(a^1 \Delta_g)$ and $O_2(b^1 \Sigma_g^+)$ molecules. However, in past years, novel kinetic data on reactions with $O_2(a^1 \Delta_g)$ and $O_2(b^1 \Sigma_g^+)$ molecules in the $H_2$–$O_2$, $CO$–$H_2$–$O_2$, $CH_4$–$O_2$ and $C_2H_6$–$O_2$ mixtures were obtained on the basis of accurate $ab$ initio calculations (herein and hereafter the term ‘accurate $ab$ initio calculations’ means the quantum-chemical calculations based on solving of the Schrödinger equation for multi-electron systems at a high level of theory), and novel numerical results on the influence of the activation of oxygen molecules by specially arranged electric discharge were reported.

The objectives of this paper are to make a critical review of the physics and chemistry of the influence of the activation of oxygen molecules by electric discharge on the chain mechanism development in different oxy-fuel systems and to consider the possibility of the reduction of CO concentration in moist air and combustion exhaust of hydrocarbons via activation of $O_2$ and $N_2$ molecules by tailored electric discharge.

2. Production of excited molecules by electric discharge

In past years, a number of different types of discharge were applied to enhance combustion both for hydrogen–air and for hydrocarbon–air mixtures. However, not all of them can produce excited molecules needed for combustion enhancement. It is known that the composition and parameters of plasma produced by electric discharge depends on the value of reduced electric field $E/N$ ($E$ is the electric field strength and $N$ is the number density of molecules), specific energy put into the gas and, certainly, on the composition of the mixture which is subjected to the discharge [2,15].

Depending on the $E/N$ value, the energy of electrons is spent on the excitation of different types of internal degrees of freedom of molecules (rotational, vibrational and electronic) or on the dissociation and ionization of molecules. So, in air, at a relatively low value of reduced electric field $E/N = 1$–$5$ Td ($1$ Td $= 10^{-17}$ V cm$^2$), mostly rotational and vibrational degrees of freedom of molecules are excited by electron impact. At higher $E/N$ magnitude ($E/N = 5$–$50$ Td), the energy of electrons is spent on the excitation of vibrations of $O_2$ and $N_2$ molecules as well as
Figure 1. Predicted values of gas temperature $T$, vibrational temperature $T_v$ of $O_2(X^3Σ^−_g)$ and $N_2(X^1Σ^+_g)$ molecules and mole fractions $γ_i$ of the main neutral and charged components of air plasma as a function of $E/N$ for the ‘ideal’ discharge with $E_s = 0.5 \text{ J cm}^{-3}$ at $T_0 = 800 \text{ K}$. (Online version in colour.)

... electronic states of $O_2$ molecules. At $E/N > 75 \text{Td}$, the processes of dissociation of molecules and the excitation of electronic states of $N_2$ molecules prevail.

This is clearly seen from figure 1, which plots the variation of vibrational temperatures of ground state oxygen and nitrogen molecules and mole fractions $γ_i$ of different species versus reduced electric field for the ‘ideal discharge’ with input specific energy $E_s = 0.5 \text{ J cm}^{-3}$. These results were obtained on the basis of numerical solving of a steady-state Boltzmann equation for electron energy distribution function, when the processes of the excitation of electronic and vibrational states of $O_2$ and $N_2$ molecules as well as dissociation and ionization by electron impact dominate over the other plasma chemical reactions. Note that the model of ‘ideal discharge’ assumes that the characteristic times of secondary plasma chemical reactions as well as quenching of excited atoms and molecules are much greater than those of the processes caused by electron impact. One can see that the yield of $O_2(\alpha^1Δ_g)$ molecules in such a mixture cannot be very high, because only 4.5% of the discharge energy reaches the excitation of singlet electronic states of $O_2$ molecules. However, at the conditions considered, the mole fraction of $O_2(\alpha^1Δ_g)$ can mount to $7 \times 10^{-3}$ at $E/N = 11 \text{Td}$. It is worth noting that, at such $E/N$ value, vibrationally excited $O_2$ and $N_2$ molecules also form, but vibrational temperatures of $O_2(X^3Σ^−_g)$ and $N_2(X^1Σ^+_g)$ do not exceed 1750 K. Because the ignition of both $H_2−O_2$ and $CH_4−O_2$ mixtures does not occur at temperatures smaller than $T = 800 \text{ K}$, this value for temperature was chosen as a basic one for discharge modelling. Also, such a value of air temperature is typical for gas turbine combustor.

A much higher energy percentage is spent on the excitation of vibrational and electronic states of $O_2$ molecules in pure oxygen or in the $CH_4−O_2$ mixture. In pure oxygen, approximately 45% of input energy reaches the excitation of $\alpha^1Δ_g$ and $\beta^1Σ^+_g$ states at $E/N = 11 \text{Td}$. Figure 2 depicts the variation of mole fractions of different species in the range of $E/N = 2−150 \text{Td}$ at $E_s = 0.5 \text{ J cm}^{-3}$ in ‘ideal’ discharge for pure oxygen with $T_0 = 800 \text{ K}$. One can see that at $E/N < 40 \text{Td}$, the most abundant species are $O_2(\alpha^1Δ_g)$ and $O_2(\beta^1Σ^+_g)$. At greater $E/N$ values, ground state atomic oxygen $O(^3P)$ dominates, and, at $E/N > 50 \text{Td}$, the concentration of excited atomic oxygen $O(^1D)$ becomes notable. The concentrations of ions are much smaller than the concentrations of excited oxygen molecules and O atoms.

In the $CH_4−O_2$ mixture (figure 3), at $E/N = 10−50 \text{Td}$, some part of the discharge energy is spent on the excitation of $CH_4$ molecule vibrations, and vibrational temperature of $CH_4(1000)$
mode can achieve 2200 K (at $E/N = 10$ Td). For such a mixture, at $E/N > 100$ Td, the concentrations of atomic hydrogen H and methyl radical CH$_3$ become higher than the concentration of O$_2(a^1 \Delta_g)$; however, their concentrations are notably smaller than that for atomic oxygen O($3P$).

Thus, different types of electric discharge operating with distinguishing $E/N$ values produce different plasma composition. For example, steady microwave discharge under high-pressure conditions and arc discharge provide an equilibrium plasma with rather high temperature ($T = 4000–8000$ K). The typical low-pressure direct current (DC) glow discharge occurs at $E/N = 40–80$ Td and can be used for the excitation of N$_2$ molecule vibrations in air and singlet electronic states $a^1 \Delta_g$ and $b^1 \Sigma_g^+$ of O$_2$ molecules in pure oxygen and in the CH$_4$–O$_2$ mixture.
However, in order to produce SDO in appropriate amounts at subatmospheric pressure, one needs to use non-self-sustaining discharge, for example combined high-voltage pulse-sustaining and DC crossed discharges [36,37] or micro cathode sustained discharge operating in DC mode [38]. It should be emphasized that depending on plasma composition, different processes are responsible for combustion enhancement owing to exposure of the reacting mixture to an electric discharge.

3. Key reactions and chain mechanism development upon production of singlet oxygen molecules in some important oxy-fuel systems

(a) H$_2$ − O$_2$ system

Historically, the investigations of key reactions responsible for the acceleration of chain process due to production of singlet oxygen molecules started, originally, for the H$_2$ − O$_2$ mixture. This is caused, firstly, by the fact that this system is the simplest one among the other combustible oxy-fuel systems and, secondly, that the kinetics of the oxidation process in such a mixture is on the basis of the reaction mechanisms of the ignition and combustion of different hydrocarbons.

As was revealed on the basis of ab initio calculations [7,39,40], the principal chain-initiation reaction in the H$_2$ − O$_2$ mixture is the reaction

$$ H_2 + O_2 = H + HO_2, \quad (3.1) $$

which produces highly reactive atomic hydrogen. Then, the H atom reacts with HO$_2$ and produces OH radical

$$ H + HO_2 = 2OH. \quad (3.2) $$

A very fast reaction is the reaction of the H atom with molecular oxygen

$$ H + O_2 = OH + O. \quad (3.3) $$

This process is one of the chain-branching reactions responsible for the chain mechanism development in the H$_2$ − O$_2$(air) mixture. The rise of O atoms initiates the second chain-branching reaction

$$ O + H_2 = OH + H. \quad (3.4) $$

The main reaction, responsible for energy release during the oxidation of hydrogen, is the recombination reaction

$$ H + OH + M = H_2O + M. \quad (3.5) $$

The reaction

$$ H + O_2 + M = HO_2 + M \quad (3.6) $$

is the principal chain termination reaction.

Note that, up to now, the set of reactions involved in the oxidation mechanism of hydrogen is established rather well, and the developed reaction mechanisms for the H$_2$ − O$_2$ (air) mixture (e.g. [41,42]) describe a large set of experimental data with rather high accuracy.

The presence of singlet oxygen molecules in the H$_2$ − O$_2$ mixture leads to the appearance of novel principal channels of the formation of highly reactive O and H atoms and OH radicals,
carriers of the chain mechanism [7]:

\[ \text{H}_2 + \text{O}_2(a^1 \Delta_g) = \text{H} + \text{HO}_2(A^\prime), \]  
\[ \text{H}_2 + \text{O}_2(b^1 \Sigma_g^+) = \text{H} + \text{HO}_2(A^\prime), \]  
\[ \text{H} + \text{O}_2(a^1 \Delta_g) = \text{OH} + \text{O}(3P), \]  
\[ \text{H} + \text{O}_2(b^1 \Sigma_g^+) = \text{OH} + \text{O}(1D) \]  

and

\[ \text{H} + \text{O}_2(a^1 \Delta_g) + M = \text{HO}_2(A^\prime) + M. \]

One can see that reactions with participation of an \( \text{O}_2(b^1 \Sigma_g^+) \) molecule lead to the formation of electronically excited an \( \text{HO}_2(A^\prime) \) molecule and an \( \text{O}(1D) \) atom.

Recent theoretical studies based on accurate \textit{ab initio} calculations [7,9,43] showed that the rate constants of reactions with SDO were much higher than those with ground state oxygen. Shown in figure 4 is the comparison of temperature-dependent rate constants for analogous reactions of chain initiation (processes (3.1) and (3.7); figure 4a) and chain-branching (processes (3.3) and

\[ \text{H}_2 + \text{O}_2(X^3 \Sigma_g^-) = \text{H} + \text{HO}_2(A^\prime) \]

\[ \text{H}_2 + \text{O}_2(a^1 \Delta_g) = \text{H} + \text{HO}_2(A^\prime) \]

\[ \text{O}_2(X^3 \Sigma_g^-) + \text{H} = \text{OH} + \text{O}(3P) \]

\[ \text{O}_2(a^1 \Delta_g) + \text{H} = \text{OH} + \text{O}(3P) \]

\[ \text{O}_2(a^1 \Delta_g) + \text{H} = \text{O}_2(X^3 \Sigma_g^-) + \text{H} \]
(3.9); figure 4b) with $O_2(X^3\Sigma_g^-)$ and $O_2(a^1\Delta_g)$ molecules. One can see that at a relatively low temperature, $T = 1100$ K, the rate constant of reaction (3.7) is by a factor of $3 \times 10^4$ greater than that for process (3.1). The rate constants of the analogous chain-initiation and chain-branching reactions with $O_2(b^1\Sigma_g^+)$ molecules (processes (3.8) and (3.10)) are only somewhat higher than those with ground state oxygen molecule.

It should be emphasized that potential energy surfaces (PESs) for the $H + O_2(X^3\Sigma_g^-)$ and $H + O_2(a^1\Delta_g)$ systems have some features. As is seen from the energy diagram shown in figure 5, the interaction of a H atom with an $O_2(X^3\Sigma_g^-)$ molecule can occur via both doublet $A''$ ($2TS_1$ transition state) and quartet $A'$ ($4TS$ transition state) PESs. For the quartet PES, there is no local minimum corresponding to the HO$_2$ structure. The interaction in the $H + O_2(a^1\Delta_g)$ system is associated with the second doublet PES $A'$ ($2TS_2$ transition state). There exists the intersection of the second doublet $A'$ and quartet surfaces. The intersection of these PESs can be associated with the process of electronic energy transfer. $H + O_2(a^1\Delta_g)$ reacting system can leave the $A'$ doublet term via the intersection point of this $A'$ term with the quartet $4TS$ term, and this process is associated with $O_2(a^1\Delta_g)$ quenching

$$O_2(a^1\Delta_g) + H = O_2(X^3\Sigma_g^-) + H.$$ \hspace{1cm} (3.12)

The reaction rates of this channel were calculated in [9] by using the quantum-mechanical approach of weak coupling approximation. It was revealed that the rate coefficient of quenching channel (3.12) did not exceed 0.1 of the rate coefficient of reacting channel (3.9) in the temperature range $T = 250$–$4000$ K. The value of probability of quenching channel (3.12) depends on temperature. The temperature-dependent rate constant of the quenching channel is depicted in figure 4b.

Note that the temperature-dependent rate constant of reaction (3.9), taking into account the probability of the non-adiabatic quenching transition, describes the existing experimental data [10,11,13,14,44] with high accuracy. This is clearly seen from figure 4b, where these experimental data are also depicted.

It is worth noting that up to recent times there was some speculation regarding the ratio of the rate constants of these channels. So, Hack & Kurzke [45] supposed, however, without any proofs, that the rate constant of quenching channel (3.12) was approximately by a factor of 10 higher than that for the reacting channel (3.9). Later, Popov [46], following this supposition, introduced an adjustable parameter $\beta = k(3.9)/(k(3.9) + k(3.12))$, where $k(3.9)$ and $k(3.12)$ are the rate constants of channels (3.9) and (3.12), respectively. He assumed that this parameter should be smaller than 0.2, i.e. quenching of the $O_2(a^1\Delta_g)$ molecule by the H atom occurs much faster than the reaction between the H atom and SDO. This value of the $\beta$ parameter was applied in [46] for the analysis...
of the impact of the presence of SDO on the oxidation process in the \( \text{H}_2 - \text{O}_2 \) mixture. The same \( \beta \)-value was taken in [47] for modelling ignition in the \( \text{H}_2 - \text{O}_2 \) mixture subjected to repetitively pulsed nanosecond discharge. However, direct calculations of \( k_{(3.9)} \) and \( k_{(3.12)} \) [9] exhibited that these suppositions were not valid.

From the energy diagram shown in figure 5, it follows that process (3.9) is a complex-forming reaction that proceeds via the formation of vibrationally excited \( \text{HO}_2 \) molecules in the excited electronic state \( \text{HO}_2(A')^* \). The excited intermediate complex \( \text{HO}_2(A')^* \) can be stabilized with the third body \( M \), and, as a result, the relatively stable \( \text{HO}_2(A') \) molecule can form in the course of reaction (3.11). The rate constant of this reaction was estimated in [7] using the Rice–Ramsperger–Kassel theory. It was shown that the total rate constant \( k_{\text{tot}} = k_{(3.9)} + k_{(3.12)} \) was pressure-dependent; however, such a dependence becomes notable only at pressure \( p \geq 100 \text{ atm} \). Therefore, the probability of the quenching channel does not depend on pressure at \( p < 100 \text{ atm} \).

The recommended rate constants for reactions (3.1), (3.3), (3.6)–(3.12) are listed in table 1. The rate coefficient of the \( \text{HO}_2 \) quenching channel \( \text{HO}_2(A') + \text{M} = \text{HO}_2(A'') + \text{M} \) is as large as approximately \( 10^{12} - 10^{13} \text{ cm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} \).

(b) \( \text{CO} - \text{O}_2 \) system

One of the promising synthetic fuels is the synthesis gas consisting mostly of \( \text{H}_2 \) and \( \text{CO} \). The analysis of the combustion enhancement of syngas in air due to the presence of SDO in the syngas–air mixture was performed recently in [27]. The principal reaction responsible for CO oxidation in the \( \text{CO} - \text{O}_2 \) system is the reaction

\[ \text{CO} + \text{O}_2(X^3 \Sigma^-) = \text{CO}_2 + \text{O}(^3\Pi). \]  

(3.13)

In the presence of \( \text{O}_2(a^1 \Delta_g) \) molecules in the mixture, the reaction

\[ \text{CO} + \text{O}_2(a^1 \Delta_g) = \text{CO}_2 + \text{O}(^1D) \]  

(3.14)

dominates. The rate constants of these reactions were estimated on the basis of accurate \textit{ab initio} calculations of PESs and non-variational transition state theory [6]. The obtained results exhibited that the rate constant of reaction (3.14) was by a factor of \( 10^3 - 10^4 \) higher than that for reaction (3.13) and, at \( T \geq 1000 \text{ K} \), was greater than the rate constant of \( \text{O}_2(a^1 \Delta_g) \) quenching by \( \text{CO} \) molecules

\[ \text{O}_2(a^1 \Delta_g) + \text{CO} = \text{O}_2(X^3 \Sigma^-) + \text{CO}. \]  

(3.15)

The rate coefficient of this channel is considered to be temperature-independent, and its value is equal to \( 5.4 \times 10^6 \text{ cm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} \) [48]. The rate constant of the reaction of \( \text{O}_2(b^1 \Sigma_g^+) \) with \( \text{CO} \)

\[ \text{CO} + \text{O}_2(b^1 \Sigma_g^+) = \text{CO}_2 + \text{O}(^1D), \]  

(3.16)

was also estimated in [27] using the modified model of vibronic terms (MMVT) approach [7]. It turned out that the value of \( k_{(3.16)} \) was only somewhat greater than the value of \( k_{(3.13)} \). The dependences of the rate constants of channels (3.13), (3.14) and (3.16) on temperature are shown in figure 6. The recommended rate constants for these reactions are listed in table 1.

As was demonstrated earlier [27], the process of the oxidation of pure CO in the presence of SDO occurs via following reactions:

\[ \text{CO} + \text{O}_2(a^1 \Delta_g) = \text{CO}_2 + \text{O}(^1D), \]

\[ \text{O}(^1D) + \text{M} = \text{O}(^3\Pi) + \text{M} \]

and

\[ \text{CO} + \text{O}(^3\Pi) + \text{M} = \text{CO}_2 + \text{M}. \]
Table 1. Recommended rate constants for the reactions with \(O_2(\chi^3 \Sigma_g^-), O_2(a^1 \Delta_g)\) and \(O_2(b^1 \Sigma_g^+)\) considered in the present work (cm\(^3\), mol, s, K).

<table>
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<tr>
<th>reaction</th>
<th>(k_+, (\text{cm}^3/\text{mol})^{n-1} \text{s}^{-1})</th>
<th>(A)</th>
<th>(n)</th>
<th>(E_a)</th>
<th>refs</th>
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<tr>
<td>(H_2 + O_2(\chi^3 \Sigma_g^-) = H + HO_2(A'''))</td>
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<td>2.43</td>
<td>26 926</td>
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<td>(H_2 + O_2(a^1 \Delta_g) = H + HO_2(A'''))</td>
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<td>1.88</td>
<td>17 070</td>
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<tr>
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<td>20 500</td>
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<td></td>
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<td>(H + O_2(\chi^3 \Sigma_g^-) = \text{OH} + 0)</td>
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<td>7705</td>
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<tr>
<td>(H + O_2(\chi^3 \Sigma_g^-) + M = HO_2(A'') + M^{a,b})</td>
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<td>-565</td>
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<td>(O_2(a^1 \Delta_g) + H = O_2(\chi^3 \Sigma_g^-) + H^\prime)</td>
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</tr>
<tr>
<td>(CH_3 + O_2(b^1 \Sigma_g^+) = CH_3O + OH)</td>
<td>6.62 \times 10^{10}</td>
<td>0</td>
<td>7094</td>
<td>[24]</td>
<td></td>
</tr>
<tr>
<td>(CH_3 + O_2(\chi^3 \Sigma_g^-) = CH_3O + 0)</td>
<td>2.11 \times 10^{13}</td>
<td>0</td>
<td>16 340</td>
<td>[24]</td>
<td></td>
</tr>
<tr>
<td>(CH_3 + O_2(a^1 \Delta_g) = CH_3O_2(A'))</td>
<td>1.66 \times 10^{17}</td>
<td>-2.71</td>
<td>4340</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>(CH_3 + O_2(a^1 \Delta_g) = CH_3O + OH)</td>
<td>3.47 \times 10^2</td>
<td>1.63</td>
<td>3475</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>(CH_3 + O_2(a^1 \Delta_g) = CH_3O + 0)</td>
<td>1.02 \times 10^{4}</td>
<td>2.68</td>
<td>3350</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>(C_2H_6 + O_2(\chi^3 \Sigma_g^-) = C_2H_5 + HO_2(A''))</td>
<td>2.92 \times 10^{15}</td>
<td>1.90</td>
<td>24 950</td>
<td>[8]</td>
<td></td>
</tr>
<tr>
<td>(C_2H_6 + O_2(a^1 \Delta_g) = C_2H_5 + H_2O_2)</td>
<td>5.47 \times 10^{-1}</td>
<td>3.66</td>
<td>5130</td>
<td>[8]</td>
<td></td>
</tr>
<tr>
<td>(O_2(a^1 \Delta_g) + C_2H_6 = O_2(\chi^3 \Sigma_g^-) + C_2H_6)</td>
<td>0.22</td>
<td>3.11</td>
<td>1970</td>
<td>[8]</td>
<td></td>
</tr>
<tr>
<td>(N + O_2(a^1 \Delta_g) = N + NO)</td>
<td>3.55 \times 10^{15}</td>
<td>1.21</td>
<td>15 927</td>
<td>[49]</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\text{Efficiency factors are } \varepsilon(\text{H}_2\text{O}) = 12.0, \varepsilon(\text{H}_2) = 2.5.\)

\(^b\text{Reaction is given as a true fit with } F_s(N_2) = 0.5.\)

\(^c\text{The rate constant is given as the sum of two Arrhenius dependencies.}\)
When the mixture additionally comprises H2 and H2O, even in small amounts, the oxidation process develops via the chain-branching mechanism, and its rate is much higher than that for the oxidation of pure carbon oxide [27]. The combustion enhancement is more pronounced in the case of the presence of SDO in the CO–O2 mixture with addition of H2 and H2O molecules [27].

(c) CH4–O2 system

The other important and widely applied fuel is natural gas consisting mostly of methane. It is believed that, at low temperatures ($T < 1400$ K), the reaction of methane with ground state oxygen molecule

$$\text{CH}_4 + \text{O}_2(X^3\Sigma_g^-) = \text{CH}_3 + \text{HO}_2(A'') \quad (3.17)$$

is the principal path of chain initiation in the CH4–O2(air) mixture.

Though this reaction was included in the known and widely applied reaction mechanism GRI-Mech 3.0 [51], until 2007 there were no direct measurements of its rate constant. Earlier, the backward reaction to path (3.17) was studied by Zhu & Lin [52] on the basis of ab initio calculations. With the usage of calculated PES and variational Rice, Ramsperger, Kassel, Marcu (RRKM) theory, the temperature-dependent rate constant for this reaction was determined in the temperature range $T = 300–2000$ K. The measurements of Srinivasan et al. [53], conducted at $T = 1655–1822$ K, coincide rather well with the calculations of Zhu & Lin [52]. Baulch et al. [54] recommended the expression for $k_{(3.17)}(T)$ on the basis of the calculations of Zhu & Lin [52]. It is worth noting that the rate constant for reaction (3.17) used in the popular reaction mechanism GRI-Mech.3.0 [51] differs substantially (by a factor of 8–10) from that obtained by Zhu & Lin [52].

Ab initio calculations, performed in [7,52,53,55], revealed that reactions of CH4 with excited molecules $\text{O}_2(a^1\Delta_g)$ and $\text{O}_2(b^1\Sigma_g^+) \: \text{occurred through the following paths:}$

$$\text{CH}_4 + \text{O}_2(a^1\Delta_g) = \text{CH}_3 + \text{HO}_2(A'') \quad (3.18)$$

and

$$\text{CH}_4 + \text{O}_2(b^1\Sigma_g^+) = \text{CH}_3 + \text{HO}_2(A'). \quad (3.19)$$

Analysis, conducted in [7], suggested that the most reliable temperature-dependent rate constant for reaction path (3.18) had been obtained by Zhu & Lin [52]. The rate constant of reaction channel (3.19) was estimated in [7] with the use of the MMVT approach. Figure 7 depicts the dependencies of $k_{(3.17)}(T)$, $k_{(3.18)}(T)$ and $k_{(3.19)}(T)$. One can see that, at low temperature ($T = 1000$ K), the rate
The rate constant of the reaction of CH4 with SDO is 10^4 times greater than that with ground state oxygen. The recommended temperature-dependent rate coefficients for reaction channels (3.17)–(3.19) are listed in table 1.

The rate constant of the quenching channel upon the collision of O2(a^1 Δg) molecules with CH4 was measured at T = 300 K [56] and equals 8.4 × 10^5 cm^3 mol^-1 s^-1. As was revealed in [9], the notable temperature dependence of the rate constant of the quenching channel for the electronically excited O2(a^1 Δg) molecule can exist in the case of the intersection of PESs for the reactions with excited and non-excited molecules. Because there is no intersection of PESs for CH4 + O2(a^1 Δg) and CH4 + O2(X^3 Σ^- g) systems, one can suppose that the rate constant of the quenching channel

\[ \text{O}_2(a^1 Δ_g) + \text{CH}_4 = \text{O}_2(X^3 Σ^- g) + \text{CH}_4 \]  

is independent on temperature or this dependence is very slight, and one can conclude that at T ≥ 1000 K the rate constant of reaction channel (3.18) is notably higher than that for quenching channel (3.20).

A very important reaction, responsible for the chain propagation in the CH4−O2 system, is the reaction of methyl radical CH3 with O2(X^3 Σ^- g) molecule. This process occurs through the following channels:

\[ \text{CH}_3 + \text{O}_2(X^3 Σ^- g) = \text{CH}_3\text{O}_2(A'') \]  
\[ \text{CH}_3 + \text{O}_2(X^3 Σ^- g) = \text{CH}_2\text{O} + \text{OH} \]  
and

\[ \text{CH}_3 + \text{O}_2(X^3 Σ^- g) = \text{CH}_3\text{O} + \text{O}. \]

The rate constants of these channels were reported by Baulch et al. [54]. In the presence of O2(a^1 Δ_g) molecules in the CH4−O2 mixture, the other channels can occur

\[ \text{CH}_3 + \text{O}_2(a^1 Δ_g) = \text{CH}_3\text{O}_2(A') \]  
\[ \text{CH}_3 + \text{O}_2(a^1 Δ_g) = \text{CH}_2\text{O} + \text{OH} \]  
and

\[ \text{CH}_3 + \text{O}_2(a^1 Δ_g) = \text{CH}_3\text{O} + \text{O}. \]

Note that in reaction path (3.24) the electronically excited CH3O2(A') complex forms. Ab initio analysis of PESs for CH3 + O2(X^3 Σ^- g) and CH3 + O2(a^1 Δ_g) systems was conducted in the works [4,57]. The resulting energy diagram for these systems is shown in figure 8. As is seen, there exists the intersection between doublet A'' and singlet A' PESs. The rate constants for (3.24)–(3.26)
Figure 8. Energy diagram for CH$_3$ + O$_2$(X$^3\Sigma_g^-$) and CH$_3$ + O$_2$(a$^1\Delta_g$) systems. (Online version in colour.)

(paths were, at first, estimated in [24] by using the MMVT approach which cannot take into account the PESs intersection. The more accurate calculations of the temperature-dependent rate coefficients of these channels were performed later by Lebedev et al. [4] with the use of RRKM theory. Recommended rate constants for these channels are listed in table 1. Shown in figure 9 is the comparison of the rate constants of corresponding reactions of CH$_3$ radicals with O$_2$(X$^3\Sigma_g^-$) and O$_2$(a$^1\Delta_g$) molecules.

Ethane, C$_2$H$_6$, is a constituent in natural gas and plays an important role in the oxidation chemistry of methane. So, one of the crucial processes leading to the delay in the chain mechanism development is the recombination reaction

\[
\text{CH}_3 + \text{CH}_3 + \text{M} = \text{C}_2\text{H}_6 + \text{M}.
\]

Therefore, at the ignition stage, notable amounts of C$_2$H$_6$ molecules can form. It is known [54] that the reaction of C$_2$H$_6$ molecules with ground state oxygen O$_2$(X$^3\Sigma_g^-$) results in the formation
of C$_2$H$_5$ and HO$_2$ molecules in the ground electronic state

$$C_2H_6 + O_2(X^3\Sigma_g^-) = C_2H_5 + HO_2(A''). \tag{3.27}$$

As is believed [54], the rate constant of this process at $T \leq 1000$ K is very small and does not exceed $10^2$ cm$^3$ mol$^{-1}$ s$^{-1}$. Comprehensive analysis of the processes in the C$_2$H$_6 + O_2(X^3\Sigma_g^-)$ and C$_2$H$_6 + O_2(a^1\Delta_g)$ systems was conducted recently in [8] with the accurate compound quantum-chemical approach. It was revealed that in the course of the reaction of C$_2$H$_6$ molecules with SDO, in contrast to the C$_2$H$_6 + O_2(X^3\Sigma_g^-)$ reaction, C$_2$H$_4$ and H$_2$O$_2$ molecules formed

$$C_2H_6 + O_2(a^1\Delta_g) = C_2H_4 + H_2O_2. \tag{3.28}$$

In the course of triplet and singlet PES investigations, it was found that there exists the intersection of these PESs (figure 10). The appropriate rate constants for channels (3.27) and (3.28) were estimated on the basis of variational transition state theory taking into account the tunnelling effect and intersystem crossing leading to the non-adiabatic transition process

$$O_2(a^1\Delta_g) + C_2H_6 = O_2(X^3\Sigma_g^-) + C_2H_6. \tag{3.29}$$

The rate constant of quenching channel (3.29) was estimated using the Landau–Zener theory [8]. Figure 11 depicts the temperature-dependent rate coefficients for paths (3.27)–(3.29). One can see that the rate constant of reaction (3.28) is much greater than that for reaction (3.27). At $T = 1000$ K, the ratio of these rate coefficients is as large as $3 \times 10^6$. The rate coefficient of quenching channel (3.29), at low temperature ($T \leq 500$ K), is notably higher than that of reactive channel (3.28). However, at higher temperatures ($T > 1000$ K), the rate constant of O$_2(a^1\Delta_g)$ quenching by C$_2$H$_6$ molecules is much smaller than that for reaction (3.28). Recommended rate constants for processes (3.27)–(3.29) are presented in table 1.

It should be emphasized that, nowadays, there are no experimental data on quenching of O$_2(a^1\Delta_g)$ by C$_2$H$_6$. At $T = 300$ K, the recommended approximation for $k_{(3.29)}(T)$ gives $k_{(3.29)} = 1.6 \times 10^4$ cm$^3$ mol$^{-1}$ s$^{-1}$. This value is notably lower than the rate constants of O$_2(a^1\Delta_g)$ quenching by H$_2$ ($2.35 \times 10^6$ cm$^3$ mol$^{-1}$ s$^{-1}$), CH$_4$ ($8.4 \times 10^5$ cm$^3$ mol$^{-1}$ s$^{-1}$), C$_2$H$_4$ ($1.2 \times 10^6$ cm$^3$ mol$^{-1}$ s$^{-1}$) and C$_3$H$_8$ ($1.4 \times 10^6$ cm$^3$ mol$^{-1}$ s$^{-1}$) [8].

The other important channel for chain mechanism development for CH$_4$ and C$_2$H$_6$ oxidation is the reaction of C$_2$H$_5$ with molecular oxygen. This process was studied in the past both theoretically [58,59] and experimentally [60]. However, it has not been studied completely, even when the O$_2$ molecule is in the ground electronic state. In modern kinetic mechanisms [24,61], it
C2H6 + O2(\textit{X}{3\Sigma^{-}}) = C2H5 + HO2

C2H6 + O2(\textit{a}{1\Delta}) = C2H4 + H2O2

\[ C2H6 + O2(\textit{a}{1\Delta}) = C2H6 + O2(\textit{X}{3\Sigma^{-}}) \]

\[ k \text{ (cm}^3\text{ mol}^{-1} \text{s}^{-1}) \]

\[ 0 \quad 1000 \quad 2000 \quad 3000 \]

\[ T \text{ (K)} \]

**Figure 11.** Temperature-dependent rate constants for C2H6 + O2(\textit{X}{3\Sigma^{-}}) and C2H6 + O2(\textit{a}{1\Delta}) reactions. (Online version in colour.)

is assumed that the main reaction pathway of C2H5 with ground state oxygen is the following:

C2H5 + O2(\textit{X}{3\Sigma^{-}}) = C2H4 + HO2.

Its activation energy $E_a$ is equal to approximately 2000–2500 K [24,61]. However, theoretical studies revealed three different products of this reaction: C2H4 + HO2, c−CH2CH2O + OH and CH3CHO + OH. Extensive theoretical analysis suggests that the two following channels prevail in the system under study:

\[ C2H5 + O2(\textit{X}{3\Sigma^{-}}) = C2H4 + HO2 \quad (3.30) \]

and

\[ C2H5 + O2(\textit{X}{3\Sigma^{-}}) = c−CH2CH2O + OH. \quad (3.31) \]

Nevertheless, accurate theoretical estimations of the rate constants for these channels have not been performed up to now.

As concerns the reaction of C2H5 with SDO, the available data are very scarce. Only Rienstra-Kiracofe et al. [58] obtained rather fragmentary data on the PES for the C2H5 + O2(\textit{a}{1\Delta}) system. From analysis of this PES, one can conclude that the interaction of C2H5 with O2(\textit{a}{1\Delta}) occurs without an activation barrier at the initial stage. Subsequently, the reaction proceeds via intermediate complex, transition state and hopping between PESs, resulting in the formation of C2H4 + HO2. Owing to the complex nature of the overall C2H5 + O2(\textit{a}{1\Delta}) = C2H4 + HO2 process involving non-adiabatic transitions, it is fairly difficult to estimate its rate constant; however, one can suggest that it is somewhat higher than that for process (3.30).

\( (d) \) N\(^{(4S)}\) + O\(_2\) system

The reaction of ground state atomic nitrogen N\(^{(4S)}\) with normal O\(_2(X^3\Sigma_{g}^{-})\) molecules is one of the principal channels involved in the Zeldovich mechanism of NO formation

\[ O + N_2 = N + NO \quad (3.32) \]

and

\[ N + O_2 = O + NO. \quad (3.33) \]

The rate constant of reaction (3.33) was established with rather high accuracy, and measurements of different researchers are in good consistency with each other [62]. During theoretical analysis of
this reaction, conducted in [63,64], it was established that the activation barrier of reaction (3.33) was about 3000 K.

The \( \text{O}_2(a^1 \Delta_g) + \text{N}(4S) \) reacting system has been much less studied, though the reaction of SDO with N atoms plays an important role in atmospheric and plasma chemistry as well as in plasma-assisted combustion. Qualitative features of \( \text{O}_2(a^1 \Delta_g) + \text{N}(4S) \) PES were established by Walch [62]. However, the extensive theoretical studies of this reaction were performed only recently in [49], where the rate constant of the path

\[
\text{O}_2(a^1 \Delta_g) + \text{N}(4S) = \text{O}(3P) + \text{NO}(X^2 \Pi)
\]

was estimated by using accurate \textit{ab initio} calculations of PES and non-variational transition state theory including tunnelling correction. It was revealed that the activation barrier for this process was about a factor of 5 higher than that for reaction (3.33). The comparison of the rate constants for reactions (3.33) and (3.34) is shown in figure 12. One can see that the reactivity of \( \text{O}_2(a^1 \Delta_g) \) molecules in the reaction with N atoms is much smaller than that of ground state oxygen.

A number of elementary reactions of singlet oxygen molecules with saturated hydrocarbons \( \text{C}_n \text{H}_{2n+2} \) \((n \geq 3)\), organic \( \text{C}_n \text{H}_m \text{O} \) molecules, their intermediates, unsaturated and aromatic hydrocarbons have not been studied yet and require special extensive theoretical and experimental investigations.

4. Mechanisms of the influence of excited molecules on the oxidation and ignition processes

Let us consider now the influence of the composition of plasma generated in the electric discharge on the ignition characteristic of some important oxy-fuel systems. As follows from the plots shown in figures 1–3, vibrationally excited \( \text{O}_2(V) \) and electronically excited \( \text{O}_2(a^1 \Delta_g) \) and \( \text{O}_2(b^1 \Sigma_g^+) \) molecules can be produced in notable amounts at low reduced electric field \((E/N = 1–5 \text{ Td} \) and \(5–20 \text{ Td}, \) respectively), while excited \( \text{N}_2(V) \) molecules form mainly at \(E/N = 20–75 \text{ Td}\).

In this case, for analysing the characteristics of plasma-assisted ignition and combustion, a thermally non-equilibrium kinetic model, taking into account the coupling of vibrational relaxation and chemistry, should be used. Such a model was developed on the basis of our previous works [27,30,35,65]. It involves 258 reversible reactions with 33 species including
excited $O_2(a^1 \Delta_g, V)$ and $O_2(b^1 \Sigma_g^+, V)$ molecules. The model also treats the channels of electronic-vibrational ($E-V$) exchange and elementary processes of intermode vibrational-vibrational ($V-V'$) exchange between the modes of $N_2$, $H_2$, CO, NO, $O_2(X^3 \Sigma_g^{-})$, $O_2(a^1 \Delta_g)$, $O_2(b^1 \Sigma_g^+)$, OH, $H_2O$, $HO_2$, $O_3$ and $CH_4$ molecules as well as the processes of vibrational-translational ($V-T$) relaxation.

Consider what happens when molecular oxygen is subjected to ‘ideal’ electric discharge with different $E/N$ values and, then, oxygen plasma is mixed with molecular hydrogen or methane. The characteristic mixing time is assumed to be significantly smaller than the time of vibrational relaxation of $O_2(X^3 \Sigma_g^{-}, V)$ molecules and the time of $O_2(a^1 \Delta_g)$ and $O_2(b^1 \Sigma_g^+)$ quenching. This assumption is valid for the initial pressure range $P_0 = 0.1–1$ atm, both for the $H_2-O_2$ and for the $CH_4-O_2$ systems.

Figure 13 shows the predicted dependence of induction time $\tau_{in}$ for stoichiometric $H_2-O_2$ and $CH_4-O_2$ mixtures on the $E/N$ value at $E_s = 0.5$ J cm$^{-3}$, $T_0 = 600$ K for $P_0 = 0.1$ and 1 atm.

For the analysis, different values of initial temperature $T_0$ for mixtures under study were taken: $T_0 = 600$ K for the $H_2-O_2$ mixture and $T_0 = 800$ K for the $CH_4-O_2$ one. This is due to the fact that hydrogen and methane possess distinguishing reactivity and ignition capability (for methane, these characteristics are notably worth than those for hydrogen). It should be emphasized that without activation of $O_2$ molecules in electric discharge there is practically no ignition in the $H_2-O_2$ and $CH_4-O_2$ mixtures at such $T_0$ and $P_0$ values, i.e. $\tau_{in}$ is very long. One can see that the behaviour of $\tau_{in}(E/N)$ dependence for the stoichiometric $H_2-O_2$ and $CH_4-O_2$ mixtures differs significantly. For the $H_2-O_2$ mixture, the value of $\tau_{in}$ shortens notably with increasing reduced
Figure 14. Temporal profiles of normalized CO mole fraction in the 1%CO–1%H2O–21%O2–77%N2 mixture ($T_0 = 900\text{ K}$, $P_0 = 1\text{ bar}$) at $E/N \approx 2\text{ Td}$ (solid curves) and $E/N \approx 30\text{ Td}$ (dashed curves) for $E_s = 0, 0.01, 0.03, 0.06\text{ J cm}^{-3}$ (curves 1–4) and when the energy of discharge is spent on heating the gas (dotted curves). (Online version in colour.)

electric field in the range $5\text{ Td} < E/N < 30\text{ Td}$. At $E/N \geq 30\text{ Td}$, $\tau_{\text{in}}$ varies only slightly at high pressure ($P_0 = 1\text{ atm}$) and remains virtually the same at lower pressure ($P_0 = 0.1\text{ atm}$). For the CH$_4$–O$_2$ mixture, one can see the existence of local minimum in the $\tau_{\text{in}}(E/N)$ dependence both for low ($P_0 = 0.1\text{ atm}$) and high ($P_0 = 1\text{ atm}$) pressures. This minimum is achieved at $E/N = 10\text{ Td}$. At higher $E/N$ values, the induction time increases notably. This means that the rise in the concentration of O atoms in the mixture and, consequently, the decrease in the concentration of O$_2(a^1\Delta_g)$ molecules results in slower development of the chain mechanism. The difference in $\tau_{\text{in}}$ value at $E/N > 100\text{ Td}$ compared to the minimal magnitude of $\tau_{\text{in}}$ attains a factor of 3 at $P_0 = 1\text{ atm}$.

The other interesting issue in the problem under study is the intensification of the oxidation of carbon oxide. CO is one of the key gaseous pollutants produced during combustion of organic fuels, coals, biomass, waste, etc. The presence of CO in the combustion exhaust is attributed to incomplete oxidation of fuels. The process of ‘dry’ CO oxidation is rather slow because of the high activation barrier of reaction (3.13) ($E_a \approx 24\ 000\text{ K}$). However, trace amounts of H$_2$O or H$_2$ accelerate CO oxidation. Nevertheless, even in moist air or in the combustion exhaust, the oxidation of CO at moderate temperatures ($T < 1000\text{ K}$) does not practically occur. Therefore, it would be very interesting to analyse the possibility to reduce significantly the concentration of CO in moist air or in the products of hydrocarbon combustion in the temperature range $T = 850–900\text{ K}$ by means of electric discharge with different values of $E/N$.

Let us consider processes in moist air containing 1% CO at $T_0 = 900\text{ K}$ and $P_0 = 1\text{ atm}$ subjected to ‘ideal’ discharge with $E/N \approx 2, 8$ and $30\text{ Td}$. As was mentioned above, at $E/N \approx 2\text{ Td}$ the major part of specific input energy $E_s$ reaches vibrational excitation of molecular oxygen (up to 90%). From the plots shown in figure 14, one can see that discharge with $E/N \approx 2\text{ Td}$ allows one to shorten CO oxidation time. So, at $E_s = 0.06\text{ J cm}^{-3}$, it is possible to convert 80% CO to CO$_2$ until the time instant $t = 10^{-2}\text{ s}$. At energetically equivalent heating of the gas, only 36% CO can be oxidized to the moment $t = 10^{-2}\text{ s}$. Analysis showed that the processes mainly responsible for this effect were the reactions with vibrationally excited oxygen molecules O$_2(V) + M = O + O + M$ and O$_2(V) + O_2(V) = O_3 + O$ that promote CO$_2$ formation in the recombination process CO + O + M = CO$_2$ + M.

At $E/N \approx 30\text{ Td}$, the efficiency of the excitation of N$_2$ molecule vibrations by an electron impact may be as high as 90%. As was shown previously [65], excitation of N$_2$ molecules can accelerate ignition in the CO–H$_2$–O$_2$ mixture due to fast resonance V–V’ exchange
Figure 15. Temporal profiles of normalized CO mole fraction in the 1%CO–1%H2O–21%O2–77%N2 mixture at $T_0 = 900\,\text{K}$, $P_0 = 1\,\text{bar}$ with different $O_2(a^1\Delta_g)$ content: $\gamma_{O_2(a^1\Delta_g)}^0 = 0\,(1);\,0.02\,(2);\,0.04\,(3)$ (solid curves) and when $O_2(a^1\Delta_g)$ excess energy is spent on heating the gas (dashed curves).

$N_2(V = 1) + CO(V = 0) = N_2(V = 0) + CO(V = 1)$. This process can also accelerate CO removal from moist air. The calculated profiles of normalized CO concentration for different $E_s$ values, in this case, are also presented in figure 14. One can see that the excitation of $N_2$ molecule vibrations in the discharge is less effective than that of $O_2$ ones. The analysis showed that, in spite of relatively high vibrational excitation of CO molecules at the time interval $t = 10^{-6}–10^{-5}\,\text{s}$, they reached thermal equilibrium with translational degrees of freedom to the time instant $t = 10^{-4}\,\text{s}$. As a result, the efficiency of the gas activation by discharge with $E/N \approx 30\,\text{Td}$ is only a little higher than that in the case of equivalent heating.

As was mentioned above, $O_2(a^1\Delta_g)$ molecules can be produced in notable amounts in pure oxygen by electric discharge with $E/N \approx 11\,\text{Td}$. Let us consider the influence of initial concentration of $O_2(a^1\Delta_g)$ molecules in moist air on CO oxidation. Figure 15 depicts the temporal profiles of normalized CO mole fraction in a 1%CO–1%H2O–21%O2–77%N2 mixture for different initial $O_2(a^1\Delta_g)$ mole fraction $\gamma_{O_2(a^1\Delta_g)}^0$ in normal oxygen. One can see that production of SDO allows one to shorten the time of CO oxidation substantially. So, at $\gamma_{O_2(a^1\Delta_g)}^0 = 0.04\gamma_{O_2}^0$ the time of CO conversion is 10-fold smaller than that in the case with $\gamma_{O_2(a^1\Delta_g)}^0 = 0$. It is of great importance that the abundance of 4% $O_2(a^1\Delta_g)$ in molecular oxygen allows us to convert 85% CO to CO$_2$ for the time of 0.2 s even at a low temperature $T_0 = 900\,\text{K}$. The analysis of reaction rates showed that the reactions of $O_2(a^1\Delta_g)$ with CO and H2O molecules came into play in the intensification of CO oxidation in this case.

Computations also demonstrated that the activation of air by electric discharge made it possible to reduce CO concentration in the combustion exhaust due to occurrence of low temperature oxidation of CO in the near wall region of the combustor, where the temperature is equal to approximately 850 K. Upon computations, we supposed that the fresh air, activated by electric discharge, was admixed to the combustion products of a stoichiometric CH4–air mixture with composition 2%O2–2%H2–5%CO–5%CO2–15%H2O–71%N2 and pressure $P_0 = 1\,\text{atm}$ with ratio 1 : 4. Note that the time of CO oxidation due to admixture of air is 4 s, i.e. there is practically no oxidation in the post combustor flow. In the case of activation of air by electric discharge with $E_s = 0.04\,\text{J cm}^{-3}$ and $E/N = 2$ and 30 Td, this time decreases to 0.05 and 0.3 s, respectively, i.e. the dominating excitation of $O_2$ vibrations is more effective than the excitation of $N_2$ ones. It was also shown that the presence of only 1% SDO in molecular oxygen allowed one to convert the whole amount of CO to CO$_2$ for the times shorter than $10^{-2}\,\text{s}$ even at $T_0 = 850\,\text{K}$ and $P_0 = 1\,\text{atm}$. An extra
generation of SDO results in only a slight acceleration of CO oxidation. Therefore, it is sufficient to produce only 1% of O$_2(a^1\Delta_g)$ molecules to provide the CO removal from combustion exhaust via admixture of air activated by electric discharge at $E/N = 8$ Td.

5. Conclusion

Today, there exist a number of experimental and rather accurate theoretical data on the rate constants for reactive and quenching channels in different reacting systems (not only for the H$_2$–O$_2$) that can be used to build the appropriate reaction mechanisms needed to describe the chain processes in the presence of excited O$_2(a^1\Delta_g)$ and O$_2(b^1\Sigma_g^+)$ molecules in the reacting mixtures. Both experimental data and theoretical calculations exhibit that the reactivity of O$_2(a^1\Delta_g)$ molecules is higher, in most cases, than that of ground state oxygen O$_2(X^3\Sigma_g^-)$, although for the reaction of atomic nitrogen with O$_2(a^1\Delta_g)$ molecule, the situation is inverted. It is remarkable that for all important reacting species there exists the temperature range where the rate constants of reaction channels with SDO are higher than those for the quenching channels. Nevertheless, a number of elementary reactions of singlet oxygen molecules with hydrocarbon and organic molecules and their intermediates have not been studied until now and require special extensive theoretical and experimental investigations.

The computations showed that the effect of shortening the ignition delay strongly depended on the value of the reduced electric field, i.e. on the type of discharge and, as a consequence, the composition of oxygen plasma. For instance, in the stoichiometric H$_2$–O$_2$ mixture with $T_0 = 600$ K and $P_0 = 0.1$ and 1 atm, the major shortening of ignition delay is achieved at $E/N = 100–150$ Td, whereas, for the CH$_4$–O$_2$ mixture with $T_0 = 800$ K and $P_0 = 0.1$ and 1 atm, the major reduction in $\tau_{in}$ value is ensured at much smaller $E/N$ values (approx. 10–12 Td) when the discharge produces mostly O$_2(a^1\Delta_g)$ and O$_2(b^1\Sigma_g^+)$ molecules.

It was revealed that the most effective approach to remove CO from moist air and combustion exhaust was the generation of SDO at reduced electric field $E/N \approx 8$ Td. The presence of even a small amount of SDO (0.01–0.02% of normal oxygen) in the mixture containing the impurity of carbon monoxide makes it possible for a rapid conversion of CO to CO$_2$ to even at low temperatures, $T = 850–900$ K. The excitation of O$_2$ molecules to the $a^1\Delta_g$ state is many times more effective as regards to accelerating the oxidation process and decreasing the ignition temperature than mere heating the mixture. The vibrational excitation of O$_2$ and N$_2$ molecules by discharge is less effective in regards to the acceleration of CO oxidation, than the generation of O$_2(a^1\Delta_g)$ molecules.

Authors' contributions. S.A.M. contributed to the conception and design of the paper and on the review and analysis of kinetic data on the processes with O$_2(a^1\Delta_g)$ and O$_2(b^1\Sigma_g^+)$ molecules. L.B.I. provided the numerical simulation of production of excited molecules by electric discharge and analysis of the influence of the activation of O$_2$ molecules at different values of reduced electric field $E/N$ on the ignition delay in the H$_2$–O$_2$ and CH$_4$–O$_2$ mixtures. S.A.S. contributed to the analysis of key reactions and chain mechanism development upon production of singlet oxygen molecules in oxy-fuel systems: H$_2$–O$_2$, CO–O$_2$, N–O$_2$ and to the analysis of the influence of excited molecules on the oxidation of CO–air mixture. T.N.S. contributed to the analysis of key reactions and chain mechanism development upon production of singlet oxygen molecules in H$_2$–O$_2$, CH$_4$–O$_2$ and N–O$_2$ systems. She also provided the acquisition of the available literature data and significant contribution to the design of the manuscript. All authors gave final approval for publication.

Competing interests. The authors declare that they have no competing interests.

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