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Modeling study of the acceleration of ignition in ethane–air and natural gas–air mixtures via photochemical excitation of oxygen molecules

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ABSTRACT

The paper addresses the study of the influence of laser-induced excitation of O_2 molecules to the $b^1\Delta_g{}^+$ electronic state and their photodissociation by laser photons on the ignition of ethane and natural gas in air. The extended reaction mechanism for the oxidation of CH_4–C_2H_6–air mixture comprising excited $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g{}^+)$ molecules and $O(^1D)$ atoms has been built. This mechanism includes recent *ab initio* data on the interaction of C_2H_6 with $O_2(a^1\Delta_g)$ molecule. The cross section of laser radiation absorption at given wavelength was calculated in a detailed manner by taking into account the effects of temperature, pressure and contribution of several nearest spectral lines. The computations have shown that both considered photochemical methods accelerated the ignition and decreased the ignition temperature. They are much more effective in the ignition enhancement than mere heating the mixture by equivalent input energy. It has been revealed that the photodissociation of O_2 molecules by laser photons with $\lambda_I = 193.3$ nm was somewhat more effective in accelerating the ignition of the C_2H_6–air mixture, especially, at low temperatures ($T_0 < 850$ K) and high pressure ($P_0 = 10$ atm). However, at smaller pressure ($P_0 = 1$ atm) both for ethane and for natural gas, the excitation of O_2 molecules to the singlet sigma state provides higher reduction in the induction time and ignition temperature compared to their photodissociation.

1. Introduction

Intensification of chain reactions in combustible mixtures via excitation of vibrational and electronic states of reacting molecules or generation of highly reactive atoms and radicals is one of the most promising ways to enhance the combustion in practical devices including automobile and air-breathing engines [1–10]. Excited molecules and active species, carriers of chain mechanism in the fuel–air mixture, can be produced with rather high efficiency by specially arranged electric discharge [6,8,10–13] or by resonance laser radiation [5,14–18]. As was demonstrated earlier [5,13,15,17], both the excitation of O_2 molecules to the electronic state $b^1\Sigma_g{}^+$ and photodissociation of O_2 molecules by laser radiation with 762.3 nm and 193.3 nm wavelength, respectively, can substantially accelerate chain reactions both in the H_2–air and in the CH_4–air mixtures and, as a consequence, can reduce the ignition temperature and shorten the ignition delay. Both these approaches are much more effective in accelerating the ignition than mere heating the mixture by laser radiation [1].

Advantages of one photochemical method over another were proved to be dependent on the composition of the combustible mixture and its pressure and temperature [5,17]. So, the computations showed that, for the H_2–air mixture, the photodissociation of O_2 molecules by 193.3 nm laser radiation was more effective for the reduction of ignition delay, whereas, for the CH_4–air mixture, the excitation of O_2 molecules to the $b^1\Sigma_g{}^+$ state was more preferable for the intensification of ignition. This difference is explained by the features of chain mechanism development in each oxy-fuel system.

Today, natural gas (NG), composed mostly of methane and ethane, is considered as a very promising fuel both for automobile and gas turbine engines [19,20]. However, natural gas possesses very worthy ignition characteristics compared to other hydrocarbons. It has longer ignition delay and higher ignition temperature. Therefore, it would be very fruitful to find an effective way allowing one to decrease the ignition temperature and to reduce the ignition delay in the NG–air mixture.

Because NG contains ethane in notable amount (up to 13%) [21], the features of chain mechanism development in the CH_4–C_2H_6–air mixture upon the activation of O_2 molecules by laser photons both with 762.3 nm and with 193.3 nm wavelength can

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differ substantially from those in the pure CH_4–air mixture. So, in recent theoretical study [22] it was revealed that the reaction of C_2H_6 with excited $O_2(a^1\Delta_g)$ molecule produced C_2H_4 and H_2O_2, while the reaction of ethane with ground state oxygen molecule $O_2(X^3\Sigma_g{}^-)$ gave rise C_2H_5 and HO_2 products.

This paper does address the study of accelerating the ignition in the C_2H_6–air and CH_4–C_2H_6–air mixtures upon photochemical activation of ground state O_2 molecules by laser radiation via their excitation to the singlet sigma $b^1\Sigma_g{}^+$ state or via their dissociation with production of atomic oxygen.

2. Methodology and basic assumptions

Let us analyze the initiation of combustion in quiescent homogeneous CH_4–C_2H_6–air mixture exposed to either UV laser radiation with wavelength $\lambda_I = 193.3$ nm or laser radiation with wavelength $\lambda_I = 762.346$ nm. The radiation with the wavelength 193.3 nm can be produced by ArF laser, whereas the radiation with $\lambda_I = 762.346$ nm is generated by diode or dye lasers as well as by solid laser with $Al_2O_3Ti^{3+}$ crystal.

It should be emphasized that the possibility of the ignition of combustible mixture due to exposure of the gas, being in heated cell, to resonance laser radiation with 193.3 nm wavelength was demonstrated experimentally at subatmospheric pressure by Lavid et al. [15]. The authors of that work used the focused radiation of eximer ArF laser with pulse duration of 10 ns and rather small energy of 170 mJ. The possibility of the photo-excitation of O_2 molecules to the singlet delta $a^1\Delta_g$ and singlet sigma $b^1\Sigma_g{}^+$ states by laser radiation with 1.063 µm and 762.3 nm wavelength was demonstrated experimentally in [23] and [24,25], respectively.

At low temperatures ($T \leq 300$ K), the UV laser radiation with $\lambda_I = 193.3$ nm is absorbed by O_2 molecules in the Schumann–Runge bands, mostly at the transition

$$O_2(X^3\Sigma_g^-, V', J', K') \to O_2(B^3\Sigma_u{}^-, V'', J'', K'')$$

with vibrational quantum numbers $V' = 0$, $V'' = 4$ and following rotational quantum numbers $J' = 17$, $K' = 17$ and $J'' = 16$, $K'' = 17$ [15,26]. The excited $O_2(B^3\Sigma_u{}^-$, $V'' = 4)$ molecule dissociates very rapidly either via fast intramode vibrational–vibrational exchange with the formation of ground state $O(^3P)$ and excited $O(^1D)$ atoms or via predissociation through the $^3\Pi_g$ state with the formation of two $O(^3P)$ atoms.

Laser photons with $\lambda_I = 762.346$ nm are absorbed at the center of the spectral line of the transition

$$O_2(X^3\Sigma_g^-, V', J'', K') \to O_2(b^1\Sigma_g{}^+, V'', J'', K'')$$

with vibrational quantum numbers $V' = V'' = 0$ and rotational quantum numbers $J' = 9$, $J'' = 8$ and $K' = K'' = 8$.

Following to our previous work [27], consider the photochemical processes at the center region of the laser beam with the Gaussian distribution of the radiation intensity I along the radius

$$I(r, t) = I_0(t)\exp\left(-\frac{r^2}{R_b^2}\right).$$

Here R_b is the characteristic radius of the beam and $I_0(t) = I_0$ at $0 < t \leq \tau_p$ and $I_0(t) = 0$ at $t > \tau_p$, where τ_p is the radiation pulse duration. Upon modeling, we supposed that $\tau_p = 10^{-5}$ s.

The rate of photodissociation W_{ph} and the rate of induced transition W_I are determined by the identical equation

$$W_{ph(I)} = \sigma_I I / h\nu_I,$$

where ν_I is the radiation frequency, σ_I is the absorption cross section at the frequency of exerting radiation and h is the Planck constant. Note that, nowadays, modern UV lasers operates with the pulse duration of tens nanoseconds, while the diod laser generates the radiation with 762.3 nm during much longer time $\tau_p \sim 10^{-5}$–10^{-3} s. Therefore, the value of pulse duration $\tau_p = 10^{-5}$ s was chosen as a basic one. In the case of using the UV eximer ArF laser with 193.3 nm wavelength such a duration of radiation action can be achieved via the repetition of shorter pulses (~10 with duration of 10 ns).

As was demonstrated earlier [17,27], for narrow beam with $R_b \approx 0.1$–0.5 cm in the pressure and temperature ranges of interest: $P_0 = 0.1$–10 atm and $T_0 = 600$–1200 K (herein and hereafter, subscript "0" denotes the parameters of the undisturbed gas), there was the following hierarchy of the characteristic times $\tau_a < \tau_p \sim \tau_I \sim \tau_{ph(I)} < \tau_d \leq \tau_\lambda$. Here, τ_a is the time of acoustic vibration propagation across the beam, τ_d is the characteristic time of diffusion (it is governed by the diffusion of the lightest carriers of the chain mechanism – hydrogen or oxygen atoms), $\tau_{ph(I)} = W_{ph(I)}^{-1}$ is the characteristic time of photodissociation (induced transition) and τ_λ is the characteristic time of heat conduction. In this case, the processes of diffusion and heat conduction can be ignored. In addition, upon the absorption of the radiation both with $\lambda_I = 193.3$ nm and with $\lambda_I = 762.346$ nm, the condition $R_b \ll L_\nu$, where L_ν is the characteristic absorption length of collimated laser beam, is valid. Hence, for both cases, the approximation of a thin optical layer can be applied. Let us assume that translational, rotational and vibrational degrees of freedom of molecules are in thermodynamic equilibrium. In this case, the system of governing equations involves the differential equations for the variation of species concentrations and the equation for the variation of energy at $P =$ const. Concrete form of these equations was reported in [27].

The absorption cross section at the 193.3 nm wavelength was calculated taking into account the contribution of the nearest spectral lines that can be significant even at atmospheric pressure due to their overlap as follows

$$\sigma_I = \sum_i \sigma_i(\nu_I) + \sigma_H(\nu_I),$$

where $\sigma_i(\nu_I)$ is the cross section at frequency ν_I for the ith absorption line belonging to the Schumann–Runge bands and $\sigma_H(\nu_I)$ is the cross section at the frequency ν_I in the Herzberg continuum. The values of $\sigma_i(\nu_I)$ was calculated in the same manner as in [26] with the usage of matrix elements $\langle\Omega'|\hat{H}|\Omega\rangle$ for the electronic transition $X^3\Sigma_g{}^- \to B^3\Sigma_u{}^-$ borrowed from [28]. In line with this methodology, the cross section $\sigma_i(\nu_I)$ at the center of ith spectral line is determined through the integral absorption cross sections S_i in line with the formula reported in [26]

$$\sigma_i(\nu_k) = \frac{S_i}{\frac{b_V}{c}\left[1.065 + 0.447\left(\frac{b_c}{b_V}\right) + 0.058\left(\frac{b_c}{b_V}\right)^2\right]}$$

The value of S_i was calculated in according to the expressions

$$S_i = \frac{\pi e^2}{mc^2} \cdot f_i \cdot F_i(v'', J'', N''),$$

$$f_i = f_i(J', N', v', J'', N'', v'') = f_{v'v''} \cdot \frac{S(J', N', J'', N'')}{2N'' + 1},$$

where b_c and b_V are the collisional and Voigt linewidths, respectively, e is the elementary charge, m is the mass of the electron, c is the velocity of light, $F_i(V'', J'', N'')$ is the relative population of the low level of absorption transition, $f_{v'v''}$ is the band oscillator strength for the transition $(X^3\Sigma_g{}^-, V') \to (B^3\Sigma_u{}^+, V'')$ and $S(J', N', J'', N'')$ is the Hönl–London factor. It was calculated in line with the formulas reported in [29]. The values of $f_{v'v''}$ were taken from [26].

Figure 1 depicts the spectrum in the range of $\lambda = 193.2$–193.8 nm for pure O_2 at the temperatures $T_0 = 300$ and 700 K and pressure $P_0 = 1$ atm. One can see that, at $T_0 = 300$ K, the laser radiation with $\lambda_I = 193.3$ nm is absorbed not exactly in the center