



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



A.M. Starik*, A.V. Pelevkin, N.S. Titova

Central Institute of Aviation Motors, Scientific Educational Centre "Physical and Chemical Kinetics and Combustion", Aviamotornaya st. 2, Moscow, 111116, Russia

ARTICLE INFO

Article history:

Received 20 May 2016

Revised 29 July 2016

Accepted 10 October 2016

Available online 11 November 2016

Keywords:

Ethane

Natural gas

Ignition

Laser-induced excitation

Photodissociation

Kinetic mechanism

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 $\lambda_l = 193.3$ 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.

© 2016 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

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

* Corresponding author.

E-mail address: star@ciam.ru (A.M. Starik).

differ substantially from those in the pure CH₄–air mixture. So, in recent theoretical study [22] it was revealed that the reaction of C₂H₆ with excited O₂(*a*¹Δ_g) molecule produced C₂H₄ and H₂O₂, while the reaction of ethane with ground state oxygen molecule O₂(*X*³Σ_g[−]) gave rise C₂H₅ and HO₂ products.

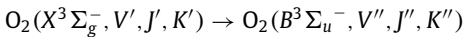
This paper does address the study of accelerating the ignition in the C₂H₆–air and CH₄–C₂H₆–air mixtures upon photochemical activation of ground state O₂ molecules by laser radiation via their excitation to the singlet sigma *b*¹Σ_g⁺ state or via their dissociation with production of atomic oxygen.

2. Methodology and basic assumptions

Let us analyze the initiation of combustion in quiescent homogeneous CH₄–C₂H₆–air mixture exposed to either UV laser radiation with wavelength λ_l = 193.3 nm or laser radiation with wavelength λ_l = 762.346 nm. The radiation with the wavelength 193.3 nm can be produced by ArF laser, whereas the radiation with λ_l = 762.346 nm is generated by diode or dye lasers as well as by solid laser with Al₂O₃Ti³⁺ crystal.

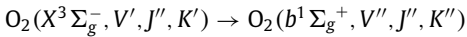
It should be emphasized that the possibility of the ignition of combustible mixture due to exposure of the gas, being in heated cell, to resonance laser radiation with 193.3 nm wavelength was demonstrated experimentally at subatmospheric pressure by Lavid et al. [15]. The authors of that work used the 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 O₂ molecules to the singlet delta *a*¹Δ_g and singlet sigma *b*¹Σ_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* ≤ 300 K), the UV laser radiation with λ_l = 193.3 nm is absorbed by O₂ molecules in the Schumann–Runge bands, mostly at the transition



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 O₂(*B*³Σ_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 ³Π_g state with the formation of two O(³P) atoms.

Laser photons with λ_l = 762.346 nm are absorbed at the center of the spectral line of the transition



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* ≤ τ_{*p*} and *I*₀(*t*) = 0 at *t* > τ_{*p*}, where τ_{*p*} is the radiation pulse duration. Upon modeling, we supposed that τ_{*p*} = 10^{−5} s.

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

$$W_{ph(l)} = \sigma_l I / h\nu_l,$$

where ν_{*l*} is the radiation frequency, σ_{*l*} 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 τ_{*p*} ~ 10^{−5}–10^{−3} s. Therefore, the value of pulse duration τ_{*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* ≈ 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 τ_{*a*} < τ_{*p*} ~ τ_{*l*} ~ τ_{*ph(l)*} < τ_{*d*} ≤ τ_{*λ*}. 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), τ_{*ph(l)*} = *W_{ph(l)}*^{−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 λ_{*l*} = 193.3 nm and with λ_{*l*} = 762.346 nm, the condition *R_b* ≪ *L_v*, where *L_v* 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

$$\sigma_l = \sum_i \sigma_i(\nu_l) + \sigma_H(\nu_l),$$

where σ_{*i*}(ν_{*l*}) is the cross section at frequency ν_{*l*} for the *i*th absorption line belonging to the Schumann–Runge bands and σ_{*H*}(ν_{*l*}) is the cross section at the frequency ν_{*l*} in the Herzberg continuum. The values of σ_{*i*}(ν_{*l*}) was calculated in the same manner as in [26] with the usage of matrix elements ⟨Ω'|*H*|Ω⟩ for the electronic transition *X*³Σ_g[−] → *B*³Σ_u[−] borrowed from [28]. In line with this methodology, the cross section σ_{*i*}(ν_{*l*}) at the center of *i*th 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

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

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

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_{ν''ν'}* is the band oscillator strength for the transition (*X*³Σ_g[−], *V*') → (*B*³Σ_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_{ν''ν'}* were taken from [26].

Figure 1 depicts the spectrum in the range of λ = 193.2–193.8 nm for pure O₂ 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 λ_{*l*} = 193.3 nm is absorbed not exactly in the center

Download English Version:

<https://daneshyari.com/en/article/6468419>

Download Persian Version:

<https://daneshyari.com/article/6468419>

[Daneshyari.com](https://daneshyari.com)