

Ozone recovery in the presence of CO and N₂O

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Abstract. Extremely reactive vibrationally excited ozone O₃(v) molecule is formed in excess of O₂ in particular in air-fuel mixture, however there is a lack of kinetic data on O₃(v) reactions with combustion products. The time-resolved absorption spectroscopy method was applied for measurements of the O₃ recovery rates after 266 nm photolysis in the presence of O, CO and nitrous oxides. It was revealed that reaction O₃(v) + O results in an incomplete ozone recovery. In the reaction O₃(v) + O stabilization channel dominates the reactionary one. In the presence of N₂O, ozone does not restore to its initial level.

1 Introduction

Active oxygen species (AOS – ozone O₃, molecular singlet oxygen O₂(a) (0.98 eV) and O₂(b) (1.63 eV), atomic oxygen O(³P) and O(¹D) (1.97 eV)) play an important role in the combustion, especially when it is initiated by plasma [1, 2]. In recent years, a wide interest to them is because the processes involving AOS can be used to expand the limits of combustion and ignition. In order to reduce harmful emissions, primarily nitrogen oxides NO_x, requires reduction of the maximum gas temperature in the combustion chamber. For this purpose, the use of lean air-fuel mixture is preferable, as this also leads to a reduction in fuel consumption. Expanding the limits of combustion and ignition with the increase in the ratio "air/fuel" is one of the most pressing problems in the theory of combustion. These limits can be extended by external impact: plasma, chemical or the light (laser).

Creation of non-equilibrium plasma with high levels of reduced electric field, E/N, and a significant level of energy load may provide a high yield of oxygen atoms at O₂ plasma dissociation. The oxygen atoms enter into rapid chemical reactions with hydrocarbons and cause initiation of the combustion process. The possibility of using an electric discharge has been experimentally demonstrated in terms of thermal engines, such as in [1, 3]. Selective excitation of internal degrees of freedom of ozone and oxygen molecules by laser radiation can also increase the limits of the ratio "air/fuel".

With an excess of O₂ (the atmosphere, the air-fuel mixture, oxygen-containing plasma), oxygen atoms are effectively removed in the three-body recombination process



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This forms a vibrationally-excited ozone molecule $O_3(v)$ which, together with the atomic oxygen may play an important role in the initiation of combustion, recovery of ozone in the atmosphere, etc. These processes were not previously included in the kinetic scheme of planetary atmospheres, combustion and oxygen-containing plasma. The vibrational excitation of ozone greatly accelerates the rate of reactions with O and $O_2(a)$ [4]. To determine the role of the reaction pathways to the dynamics of ozone in the atmosphere, in the combustion and in oxygen-containing plasma, new kinetic data are required that are not currently available in the literature and databases.

2 Experimental approach

The ozone kinetics was studied using the absorption spectroscopy method [4]. Ozone photolysis was performed by UV laser pulses at a wavelength of 266 nm (radiation of the 4th harmonic of the Solar Laser Systems, model LQ829 solid-state laser with a pulse duration of 10 ns) in a photolysis cell.

Pulsed laser photolysis of O_3/O_2 mixtures, in the presence of various buffer gases, was used for these kinetic measurements. A schematic diagram of the apparatus used is shown in Fig. 1. The photolysis radiation at 266 nm was provided by the fourth harmonic of a Nd:YAG laser (Solar Systems LQ829; 10 ns pulse duration; repetition rate 10 Hz). The diameter of the laser beam was 8 mm. The photolysis cell constructed from a solid brass block with 1-cm diameter channels for the flow of gases, the passage of the photolysis and probe laser beams, and the observation of emission from the photolysis zone. The gas velocity in the photolysis zone was typically 50–100 cm/s, which was fast enough to ensure that a fresh sample of gas was photolyzed on each pulse. A mass flowmeter and needle valves were used to control the gas flow rates. The cell was evacuated by a rotary pump, and the pumping rate was adjusted using a ball valve.

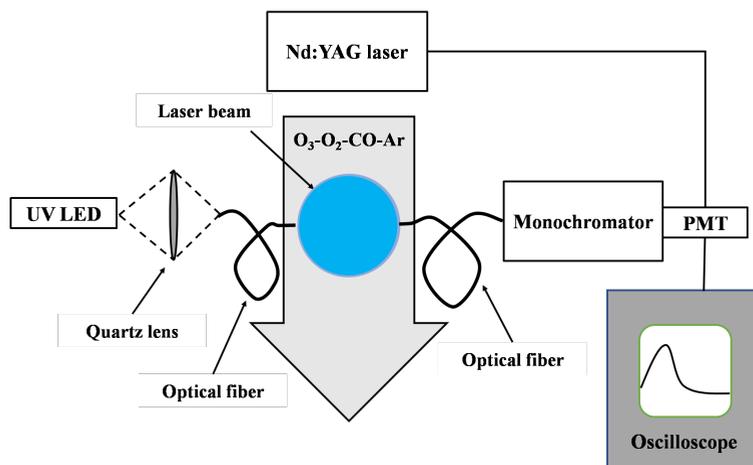


Fig. 1. Schematic diagram of the experimental setup for measuring the ozone concentration in the photolysis zone, based on time-resolved absorption spectroscopy.

Time-resolved absorption spectroscopy at $\lambda=258$ nm was employed for O_3 concentration measurements in the photolysis zone. A light-emitting diode (LED; UVTOP255) was used as a source of UV light. A quartz lens ($f = 1.5$ cm) was used to collect the light from the LED and focus this light into a quartz optical fiber. The light transmitted by this fiber traversed the photolysis zone, and a fraction of this light was collected by a second fiber. The ends of the optical fibers were positioned such that all of the O_3 between them was

exposed to the photolysis radiation. The light transmitted by the collection fiber was dispersed by a monochromator and detected by a photomultiplier (PMT). Time-resolved emission signals from the PMT were averaged and stored using a digital oscilloscope (Agilent DSO1022A; 200 MHz response).

3 Results and analysis

3.1 Ozone recovery in the presence of O₂

Figure 2 shows the example of time dependences of ozone concentrations after laser photolysis of O₃-O₂-Ar mixture by radiation with a wavelength of 266 nm at the specific laser pulse energy $E = 70 \text{ mJ/cm}^2$, total gas pressure $P_{\text{tot}} = 712 \text{ Torr}$, and initial ozone pressure $P_{\text{O}_3} = 0.85 \text{ Torr}$. The gas mixture temperature was $T = 300 \text{ K}$. The total mixture pressure and the total gas flow rate were maintained constant. Partial argon P_{Ar} and oxygen P_{O_2} pressures were varied so that the equality $P_{\text{O}_2} + P_{\text{Ar}} = P_{\text{tot}}$ would be satisfied.

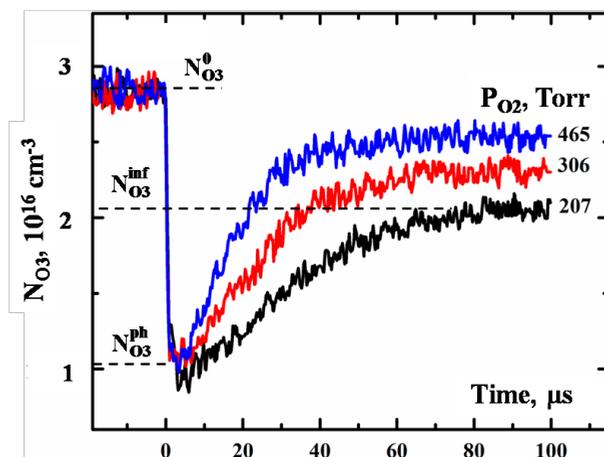


Fig. 2. Temporal profiles of the O₃ concentration at $E = 70 \text{ mJ/cm}^2$, $P_{\text{tot}} = 712 \text{ Torr}$, $T = 300 \text{ K}$, and various O₂ pressures.

As seen in Fig. 2 the rate and degree of ozone recovery strongly depend on the mixture composition. We can see that the ozone concentration does not reach initial values $N_{\text{O}_3}^0$ and tend at $t \rightarrow \infty$ to certain values of $N_{\text{O}_3}^{\text{inf}}$. This phenomenon was called the incomplete ozone recovery effect [5]. An addition of components quenching vibrationally excited ozone to the mixture increases the degree of ozone recovery, determined from the expression

$$\eta_{\text{rec}} = \frac{N_{\text{O}_3}^{\text{inf}} - N_{\text{O}_3}^{\text{ph}}}{N_{\text{O}_3}^0 - N_{\text{O}_3}^{\text{ph}}}$$

where $N_{\text{O}_3}^{\text{ph}}$ – ozone concentration after laser photolysis. Ar is a less weak relaxant for O₃(v) than O₂, therefore, its addition to the mixture led to a decrease in the degree of O₃ recovery. The effect of incomplete ozone recovery is caused by the process O₃(v)+O with the branching factor $\gamma_r = 0.81 \pm 0.13$ for the chemical channel of reaction products.

3.2 Ozone recovery in the presence of CO

Figure 3 shows the typical time dependences of the ozone concentration after laser photolysis of mixture O₂-O₃-Ar-CO at a wavelength of 266 nm for specific pulse energy E = 70 mJ/cm², total gas pressure P_{tot} = 720 Torr, oxygen pressure P_{O₂} = 180 Torr, gas mixture temperature T = 300 K, and initial ozone pressure P_{O₃} = 0.85 Torr.

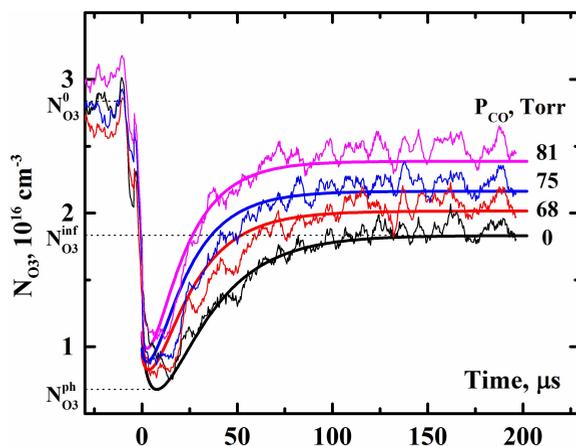
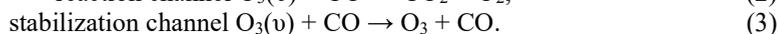


Fig. 3. Temporal profiles of the O₃ concentration at E = 70 mJ/cm², P_{tot} = 720 Torr, P_{O₂} = 180 Torr, T = 300 K, and various CO pressures. Smooth curves are time profiles calculated by kinetic modeling.

The reaction of vibrationally excited ozone with carbon monoxide at moderate temperatures can proceed in two possible channels:



The experimental results clearly show that an increase in the CO concentration leads to an increase in the degree of ozone recovery. This indicates that the stabilization channel dominates over the reaction one. Kinetic modeling of processes in the photolysis cell during experiments was performed. The best agreement with experimental data was achieved at the process (3) rate constant of $(1.5 \pm 0.2) \cdot 10^{-13}$ cm³/s. The method used in this study does not allow an accurate conclusion about the contribution of the reaction channel to the general kinetics of changes in the ozone O₃ concentration, except for the estimate of the upper boundary of the reaction (2) rate constant not exceeding 10^{-14} cm³/s.

3.3 Ozone recovery in the presence of nitrous oxides

Typical temporal profiles of the ozone concentration after laser photolysis of mixture O₃-O₂-N₂O at a wavelength of 266 nm for specific pulse energy E = 70 mJ/cm², total gas pressure P_{tot} = 807 Torr, oxygen pressure P_{O₂} = 600 Torr, gas mixture temperature T = 300 K, and initial ozone pressure P_{O₃} = 0.85 Torr are presented in Fig. 4.

Reaction of vibrationally excited ozone with nitrogen oxide NO produced in the secondary processes



has more probability than reaction with thermalized ozone with the rate constant 1.8×10^{-14} cm³/s [6]. Reaction (4) competes with the relaxation process



for which there is no any kinetic information.

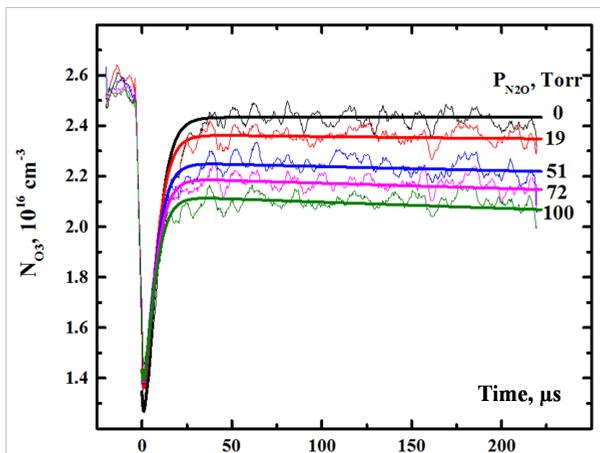


Fig. 4. Temporal profiles of the O_3 concentration at $E = 70 \text{ mJ/cm}^2$, $P_{\text{tot}} = 807 \text{ Torr}$, $P_{\text{O}_2} = 600 \text{ Torr}$, $T = 300 \text{ K}$, and various N_2O pressures. Smooth curves are time profiles calculated by kinetic modeling.

The experimental results in Fig. 4 show that addition of N_2O into the gas mixture significantly decreases the degree of ozone recovery. Unfortunately the method used in this study does not allow to separate processes (4) and (5) because NO is actively produced due to reactions of N_2O with photolysis products. Thus we used kinetic modeling to estimate the orders of magnitude of the rate constants for the processes (4) and (5) which amounted to $\sim 10^{-11} \text{ cm}^3/\text{s}$ and $\sim 10^{-13} \text{ cm}^3/\text{s}$, respectively.

Summary

The vibrationally excited ozone molecule $\text{O}_3(\text{v})$ plays an important role in oxygen containing mixtures, thus processes involving it should be included into combustion and atmosphere databases. The degree of ozone recovery depends on the medium composition. An addition of components quenching $\text{O}_3(\text{v})$, such as carbon monoxide CO , to the gas mixture increases the degree of ozone recovery. The reverse situation is observed with increasing the N_2O pressure which indicates the course of reactions between $\text{O}_3(\text{v})$ and nitrous oxides. Accurate measurements of the rate constants for processes (4) and (5) require further investigation.

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