Measurements of Vibrationally Excited Oxygen Produced in Recombining O₂-Ar Mixtures

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Abstract

Kinetics of O₂ vibrational excitation is studied during the O atom recombination in an O₂-Ar mixture partially dissociated by a burst of ns discharge pulses in a flow reactor, at T = 380-650 K. Time-resolved vibrational level populations of molecular oxygen in the ground electronic state, O₂(X,v=8-20), are measured by ps Laser Induced Fluorescence on the O₂ Schumann Runge bands, with absolute calibration by NO LIF in a NO-N₂ mixture with a known composition, at quenching-free conditions. O atom number density in the same mixture is measured by ps Two-Photon absorption LIF (TALIF). The discharge generates a diffuse volumetric plasma, without well-pronounced filaments. The temperature in the plasma is measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS) of excited Ar atoms. The results indicate a rapid initial decay of the O₂(X,v=8-20) molecules generated by electron impact in the discharge, on ~ 100 µs time scale, due to the V-V exchange and V-T relaxation. This decay is followed by a much slower decay, on the time scale much longer compared to the characteristic time for V-V relaxation, up to several ms. This indicates an additional process of O₂(v) generation by chemical reactions initiated by the O atom recombination. This effect is observed both in the non-preheated and preheated O₂-Ar mixtures. However, comparison of the time-resolved O₂(v=8-13,17-20) vibrational level populations after the burst excitation of non-preheated and preheated exhibits significant differences. In the preheated mixtures, peak O₂(v) populations during the slow decay following the excitation are significantly lower, suggesting a significant effect of O atom recombination via the reaction pathways involving ozone. Additional data need to be taken in preheated mixtures with the low O₂ mole fraction, ~1%, and at higher pressures, at the conditions when the discharge excitation would result in dissociation of most of O₂ molecules in the mixture.
1. Introduction

The critical role of vibrational excitation of oxygen and nitrogen during their dissociation in nonequilibrium high-enthalpy flows (primarily behind the hypersonic shock waves), has been recognized for a long time [1]. However, accurate experimental quantification of this effect is difficult. Although significant O$_2$ vibrational populations and O atom number density can be generated at pulsed hypersonic flow facilities, such as shock tubes [2-6], nonequilibrium dissociation measurements necessitate acquiring the state-specific data during a single shot experiment, on ~1-100 µs time scale. In spite of the remarkable recent progress in laser diagnostics, paving the way to the low-uncertainty measurements of the nonequilibrium dissociation factor in shock tubes [4-6], state-specific measurements of molecular dissociation from high vibrational levels remain extremely challenging.

In the present work, we use a different approach, where the vibrational levels of molecular oxygen in the ground electronic state, O$_2$(X$^3$Σ$_g^-$,v), populated during the recombination of O atoms, are monitored in an O$_2$-Ar mixture partially dissociated by a ns pulse discharge burst in a flow reactor. Comparison of the experimental data with the predictions of a kinetic model, incorporating the state-specific rate coefficients of O atom recombination,

$$O + O + M \rightarrow O_2(v) + M,$$

(1)

as well as the rates of vibrational-translational (V-T) and vibrational-vibrational (V-V) relaxation [7-10], is expected to yield insight into the kinetics of vibrationally-enhanced O$_2$ dissociation, since the recombination rates, $k_r(\rightarrow v)$, are related to the dissociation rate, $k_d(v \rightarrow)$, via the detailed balance,

$$k_d(v \rightarrow, T) = k_r(\rightarrow v, T) \cdot \frac{n_o(T)}{n_{O_2(v)}(T)}.$$  

(2)

In Eq. (2), $n_o(T)$ and $n_{O_2(v)}(T)$ are the number densities of O(^3P) atoms and O$_2$(X$^3$Σ$_g^-$,v) molecules in thermal equilibrium. This approach can be used if the reactants (O atoms) are generated in significant amounts at well-characterized conditions, and if the number densities of the reactants and the products (e.g. O atoms and O$_2$(X,v) molecules, respectively), as well as the gas temperature, are measured at the same time. Figure 1 plots the kinetic modeling predictions of O$_2$(X,v) vibrational populations in a recombining O-O$_2$-Ar mixture at T = 500 K and P = 100 Torr, illustrating the formation of a quasi-steady-state “tail” in the O$_2$ vibrational distribution function, produced by the O atom recombination.

In the present experiments, oxygen atoms are produced in a repetitive ns pulse discharge in an O$_2$-Ar mixture, which generates a diffuse, spatially uniform plasma at high pressures and high reduced electric fields [11]. This is critical for the efficient O$_2$ dissociation by electron impact, and by quenching of excited electronic states of Ar atoms. O atom recombination is monitored on a long time scale after the discharge burst, up to of several milliseconds, much longer compared to the time scales for O$_2$ vibrational relaxation and collisional quenching of excited electronic states of O$_2$, O, and Ar generated in the discharge. At these conditions, oxygen recombination is dominated by the reactions of O atoms in the ground electronic state. Although the present measurements are done at relatively low temperatures T = 380-650 K, this approach can be also extended to higher temperatures, up to T ~ 1500 K, such that the predictive capability of the kinetic model may be assessed over a wide temperature range.
2. Experimental

A schematic of the experimental apparatus is shown in Fig. 2. The electric discharge cell is a 22 mm x 10 mm rectangular cross section, 20 cm long quartz channel fused to 1 inch diameter quartz tubes, attached to 1 inch diameter quartz endpieces with Brewster’s angle optical access windows made of fused silica, using Ultra-Torr vacuum fittings. The total length of the cell is 60 cm. A 20% O\textsubscript{2} / 80% Ar mixture flows through the cell at the flow rate of 2 SLM, through the ¼ inch diameter inlet port and 1 inch diameter exit port, connected to the gas delivery and exhaust lines by the Ultra-Torr fittings. The mixture components are pre-mixed and delivered from a single gas cylinder. The flow rates of the mixture components are regulated and monitored by the mass flow controllers (MKS1179A). The pressure in the cell is maintained at 100 Torr by throttling the flow in the vacuum exhaust line. The flow is preheated several cm upstream of the discharge electrodes, using a heating tape wrapped around the flow channel and insulated on the outside by fiberglass wrapping sleeves around the heating tape (see Fig. 2). Preheating the flow serves both to improve the discharge plasma uniformity and to suppress ozone formation during the O atom recombination in the flow dissociated by the electric discharge. The temperature of the heating tape, up to \( T = 270 \, ^\circ\text{C} \), is measured by a thermocouple placed between the cell and heating tape.

The flow in the cell is excited by a diffuse double dielectric barrier, ns pulse discharge between two parallel rectangular plate copper electrodes 60 mm long and 14 mm wide, mounted to the top and bottom walls in the middle of the quartz channel, as shown in Fig. 2. The electrodes are held in place by ceramic brackets and screws, and are embedded in RTV high temperature silicone sealant. The discharge is sustained by a positive polarity MegaImpulse NPG-18/100k high-voltage pulse generator, with the pulse peak voltage up to 16.7 kV and pulse duration of approximately 14 ns FWHM. The pulse generator is operated in burst mode, at a pulse repetition rate of 100 kHz, burst duration of 100 pulses (1 ms), and burst repetition rate of 10 Hz. Energy coupled to the plasma is determined by measuring the pulse voltage and current waveforms using custom-made, high bandwidth capacitive voltage probes and shunt current probes [12]. No corona discharge was detected on the electrodes at the present conditions. After the pulse burst, O atoms generated by the electron impact dissociation of O\textsubscript{2}, and by the reactive quenching of electronically excited Ar atoms by O\textsubscript{2} recombine to form the vibrationally excited O\textsubscript{2} molecules. The discharge bursts are repeated at 10 Hz, allowing the O atom recombination between the bursts, and the data are integrated over multiple bursts.

Time resolved populations of vibrational levels of molecular oxygen in the ground electronic state, O\textsubscript{2}(X^3\Sigma_g^-,v) and ground state O atoms, O(3P), are measured in the recombining O\textsubscript{2}-O-Ar flow by ps single-photon Laser Induced Fluorescence (LIF) and ps Two-photon Absorption LIF (TALIF), respectively. For both of these diagnostics, we use a ps Optical Parametric Oscillator (OPO, Ekspla PG401), pumped by the 3\textsuperscript{rd} harmonic of a 10 Hz ps Nd:YAG laser (Ekspla PL2143A, nominal pulse duration 30 ps), at the pulse energy of 5 mJ at 355 nm. In the present work, the OPO produces output at 225-450 nm, with the pulse energy of 15-190 \( \mu \text{J} \) and the linewidth of 2.0-3.5 cm\textsuperscript{-1}, tunable in 0.05 nm increments below 420 nm, and 0.1 nm increments above 420 nm. The OPO output beam is focused into the center of the discharge cell by a plano-convex lens with the focal distance of 50 cm. A beam reflection off a fused silica plane window is used to monitor the OPO output pulse energy, using a photodiode (see Fig. 2). The OPO output linewidth is measured by an Acton SpectraPro-500i 0.5 m spectrometer with a 2400 lines/mm grating and a Princeton Instruments PI-Max ICCD camera as a detector, using a beam reflection from another fused silica plane window (see Fig. 2). Where possible, spectra from higher orders
of the grating were recorded, to maximize the spectral resolution. Line shapes up to 230 nm were measured in the 3rd order, between 230 nm and 330 nm in the 2nd order, and above 330 nm in the 1st order. The fluorescence signal is collected by a 2 inch diameter, 10 cm focal distance fused silica lens and detected by a gated PMT (Hamamatsu R3996), to isolate the signal from the plasma emission, as shown in Fig. 2. A narrow bandpass filter (12 nm FWHM, centered at 340 nm) placed in front of the PMT is used to isolate one of the fluorescence transition bands, and to block laser scattering and plasma emission.

Vibrational level populations of molecular oxygen, \(O_2(X^3\Sigma_g^-, v')\), formed during the recombination of O atoms in the recombining flow, are monitored by LIF on the \(O_2(B^3\Sigma_u^+, v' \leftarrow X^3\Sigma_g^-, v'')\) Schumann Runge bands, as shown schematically in Fig. 3. This approach is similar to the one used in Ref. [13], where a narrow linewidth tunable dye laser was used to probe \(O_2(X^3\Sigma_g^-, v=8-22)\) vibrational level populations formed by the photodissociation of ozone. During the measurements, the vibrational level of the upper state was kept the same, \(v'=0\), since this resulted in the highest Franck-Condon factor for the pump transition. Because the \(B^3\Sigma_u^+\) state is strongly predissociated, as shown schematically in Fig. 3, the decay of the upper state is dominated by predissociation rather than emission or collisional quenching [14], and therefore assumed to be independent of the mixture composition, pressure, and temperature. For every \(O_2\) vibrational level probed, the overlapping rotational transitions \(N'' = R7\) and \(N'' = P3\) are selected, since they are close to the peak rotational level population at the relatively low temperatures in the plasma.

A portion of the synthetic excitation spectrum for the \(v'=0 \leftarrow v'=13\) pump transition is shown in Fig. 4. Due to the relatively broad OPO output linewidth of 2.0-3.5 cm\(^{-1}\), it may produce excitation on other rotational transitions in the vicinity of the target \(R7\) and \(P3\) transitions. This is accounted for during the data reduction. A bandpass filter in front of the PMT isolates the \(v'=0 \rightarrow v'=14\) fluorescence transition band back to the \(X^3\Sigma_g^-\) state, such that \(v''=14\) is not accessible to present LIF measurements. Additionally, levels \(v''=15\) and \(v''=16\) cannot be accessed since the OPO does not produce the output in this range, near the pump laser wavelength of 355 nm.

Absolute calibration of the LIF measurements using the known \(O_2(X^3\Sigma_g^-, v)\) populations at thermal equilibrium is challenging, since it needs to be done at relatively high temperatures in the reactor cell and requires the excitation transitions in vacuum UV. In the present work, we use the NO LIF signal from a reference 100 ppm NO-N\(_2\) mixture at room temperature, following the pump transition \(NO(A^3\Sigma, v'=0 \leftarrow X^3\Pi, v''=0)\) at 225-227 nm for absolute calibration. The schematic of the pump and fluorescence transitions in O\(_2\) and NO molecules is shown in Fig. 5. The advantage of using the NO \(\gamma\) bands for calibration is that the fluorescence on the \(v'=0 \rightarrow v''=8\) band is entirely within the pass band of the 340 nm bandpass filter used for the \(O_2\) fluorescence measurements. This removes the need for the comparison of the collection optics and the PMT response at two different wavelengths. The calibration has been done at the quenching-free conditions in a low-pressure NO-N\(_2\) mixture, at \(P = 10.3\) Torr, when the fluorescence is controlled by the spontaneous radiative decay of the \(NO(A^3\Sigma, v'=0)\) state. A computer code predicting the synthetic O\(_2\) fluorescence spectrum, based on LIFBASE [15], is used to relate the NO number density in the calibration mixture to \(O_2(X^3\Sigma_g^-, v)\) vibrational level populations in the discharge afterglow. Figure 6 compares the synthetic NO LIF excitation spectrum (line) with the experimental NO LIF spectrum (symbols), obtained by the stepwise tuning of the OPO, showing good agreement.

The O atom number density in the recombining flow is measured using the two-photon absorption LIF transition at 225.65 nm, which corresponds to the \(J''=2\) component of the triplet ground electronic state, \(O(3P)\). The fluorescence is detected by the same PMT, using a 840 nm
bandpass filter with the FWHM of 40 nm. For absolute calibration, the TALIF signal in the O₂-Ar afterglow is compared to that of xenon excited at 224.35 nm, using the calibration technique described in detail in Ref. [16]. During the measurements, the OPO is maintained within the quadratic TALIF signal range.

The temperature of the flow excited by the discharge in the cell is measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS) of electronically excited Ar atoms [17]. For this, a c.w. diode laser beam (New Focus Model 6312, linewidth <300 kHz), producing tunable output from 765 nm to 781 nm, is directed along the cell, and the absorption line profile is measured on the 1s₃ → 2p₇ transition in the 3p⁵s state of Ar. Due to the rapid quenching of excited argon atoms by oxygen, the absorption line shape is measured only at the end of the discharge burst, after pulse #100. The pressure broadening coefficient for this absorption transition is available only for pure Ar [17], so at the present conditions it is determined by measuring the absorption line shape over a range of pressures, from 20 to 120 Torr. During these measurements, the number of discharge pulses in the burst was limited to 3 to keep gas heating to a minimum. The inferred pressure broadening coefficient, \( K = 22.85 \text{ MHz/Torr} \), is 30% higher compared to the value reported for pure Ar. The collisional (Lorentzian) broadening linewidth, \( \Delta \nu_L \), is calculated as follows, \( \Delta \nu_L = K \cdot P \text{Torr} \left( \frac{300}{T} \right)^{0.7} \). The temperature is inferred from the best fit synthetic absorption line shape (Voigt profile).

3. Results & Discussion

Figure 7 plots the ns pulse discharge voltage, current, and coupled energy waveforms, taken in a 20% O₂-Ar mixture, both initially at room temperature and preheated mixtures, at a pressure of 100 Torr. At these conditions, the coupled discharge pulse energy remains nearly the same during the burst, 1.1 mJ/pulse. In contrast to measurements taken earlier in a 2% H₂ - 2% O₂ - Ar mixture at similar conditions (plane-to-plane ns pulse discharge at \( P=100 \text{ Torr} \) and \( T = 300-600 \text{ K} \)) [18], we observe that the coupled energy remains roughly the same at preheated conditions compared to non-preheated conditions. Figure 8 shows the plasma emission images taken at these conditions, with and without preheating. It can be seen that in a non-preheated mixture, several filaments are formed in the plasma during the discharge burst, due to the ionization instability development. As expected, in a preheated mixture the plasma is diffuse, with no sign of well-defined isolated filaments. As shown in our previous work [19], preheating suppresses the ionization instability development in the plasma, most likely by enhancing the transport (ambipolar diffusion and thermal conductivity) from the incipient filaments. The plasma remains diffuse during the entire discharge pulse burst, and images taken in the preheated mixture are similar. This justifies the use of the line-of-sight averaged TDLAS temperature measurements, as well as a quasi-zero-dimensional kinetic model for the interpretation of the results.

Figure 9 compares the experimental and best fit synthetic Ar* absorption line shapes measured during the last pulse of the discharge burst in the initially room temperature and preheated O₂-Ar flows. The temperatures inferred from the synthetic line shapes at these conditions are \( T = 360 \pm 30 \text{ K} \) and \( T = 610 \pm 30 \text{ K} \), respectively. Preheating the flow is essential for reducing the effect of ozone chemistry on the O atom recombination process, due to the following reactions,

\[
O + O_2 + M \rightarrow O_3 + M. \quad (3)
\]

5
\[ O + O_3 + M \rightarrow O_2(v) + O_2. \]  

(4)

Note that the reaction of Eq. (4) may also contribute to \( O_2 \) vibrational excitation [20], such that its effect needs to be reduced, to isolate that of reaction of Eq. (1). By increasing the temperature, the thermal decomposition of ozone, i.e. the reverse reaction of Eq. (3), is enhanced, such that the contribution of both reactions on the net rate of \( O \) atom recombination is reduced.

At the present conditions, two different kinetic processes contribute to the vibrational excitation of oxygen in the ground electronic state. The first process is vibrational excitation by electron impact during the discharge burst. Although the energy fraction going to vibrational excitation of molecules in dielectric barrier ns pulse discharges is low, due to very high peak reduced electric field, modest vibrational excitation of \( N_2 \) in ns pulse discharges in air and nitrogen has been measured previously [19,21]. Following the electron impact excitation, \( O_2(X^2\Sigma_g^+,v) \) vibrational level populations decay, both by the “downward” V-V exchange with the non-excited \( O_2 \) in the ground vibrational state, \( w=0 \) [13],

\[ O_2(v) + O_2(w = 0) \rightarrow O_2(v - 1) + O_2(w = 1), \]

(5)

and by the rapid V-T relaxation by \( O \) atoms, which may include multi-quantum energy transfer [22].

\[ O_2(v) + O \rightarrow O_2(v - \Delta v) + O. \]

(6)

The second process is the vibrational excitation produced during the \( O \) atom recombination, isolating which is the objective of the present work. Based on the V-V rates for \( O_2-O_2 \) measured in Ref. [13], the characteristic time for the V-V exchange at the present conditions is estimated to be approximately 20 \( \mu s \). Therefore detecting the vibrationally excited molecules on a significantly longer time scale would indicate \( O_2 \) vibrational excitation generated during the \( O \) atom recombination.

In the present work, the vibrational populations are monitored after the discharge burst excitation for time delays ranging from 4 \( \mu s \) to 20 ms, i.e. significantly longer compared to the characteristic time for the V-V relaxation. The results are summarized in Figs. 10-15. Figure 10 plots the absolute \( O_2(X^2\Sigma_g^+,v) \) vibrational level populations in a 20% \( O_2-Ar \) mixture, initially at room temperature, at different delay times after the excitation by the discharge burst. It can be seen that vibrational levels ranging from \( v=8 \) to \( v=19 \) are populated, creating an extended “plateau” in the \( O_2 \) vibrational distribution function. As discussed in Section 2, vibrational levels \( v=14-16 \) are not accessible to the present LIF diagnostics. It is also apparent that the \( O_2(v) \) populations decay on a long time scale, over 10 ms, which exceeds considerably the characteristic time for the V-V relaxation. The results measured in the preheated mixture, also plotted in Fig. 10, are similar.

Time-resolved \( O_2(X^2\Sigma_g^+,v) \) vibrational level populations after the discharge burst excitation, plotted in Figs. 11-13, provide additional insight into the kinetics of their excitation, based on the time scales of their decay. From Fig. 11, showing the data for \( v=8 \), it is clear that the \( O_2(v) \) population before the discharge burst is near the detection limit. The initial rapid decay of \( O_2(v) \) molecules excited during the discharge, due to the downward V-V exchange and V-T relaxation, is readily apparent. The apparent \( O_2(v=8) \) initial decay rate coefficient inferred from the data taken at \( t = 4-20 \mu s \) at room temperature, \( 1.3 \cdot 10^{-13} \text{ cm}^3/\text{s} \), is consistent with the \( O_2-O_2 \) V-V rate coefficient measured in Ref. [13] (in the present work, the decay rate is higher by a factor of 2). However, on a ms time scale the decay slows down considerably, clearly indicating an additional source of \( O_2(v) \)
generation after the discharge burst is over. Since the characteristic time scales for electron-ion recombination, electron attachment, and ion-ion recombination are much shorter, this source can be attributed only to the reactions of the neutral species, initiated by the O atom recombination. The decay of \( \text{O}_2(v) \) molecules on a very long time scale, \( \sim 10 \text{ ms} \), may also be affected by the excited flow residence time between the electrodes, estimated to be 15 ms.

Comparing the data taken in non-preheated and preheated \( \text{O}_2\)-Ar mixtures, at \( T = 360 \pm 30 \text{ K} \) and \( T = 610 \pm 30 \text{ K} \), respectively, it can be seen that the \( \text{O}_2(v=8) \) population during a extended “plateau” formed by the slow decay in the preheated mixture is significantly lower. This may indicate a slower recombination of O atoms at the lower total number density, but may also be due to the contribution of the reactions of Eqs. (3,4) involving ozone. These reactions accelerate the net rate of O atom decay and may enhance the rate of \( \text{O}_2(v) \) formation after the discharge burst. Therefore isolating the \( \text{O}_2(v) \) generation in the reaction of Eq. (1) requires taking data in the preheated \( \text{O}_2\)-Ar mixtures.

The results for \( v=13, \) plotted in Fig. 12, indicate the transient rise of the \( \text{O}_2(v) \) population in a non-preheated mixture on a ms time scale, following the initial rapid decay due to V-V and V-T relaxation, suggesting that the state-specific rate of O atom recombination may be higher compared to that for \( v=8 \). This rise becomes less pronounced in the preheated mixture, although the rate of \( \text{O}_2(v) \) decay becomes significantly slower, such that it is not clear to what extent this effect may be influenced by the possible contribution of the ozone chemistry. Finally, Fig. 13 plots the results for \( v=19, \) which indicate the same trend as Figs. 11-12, i.e. a rapid initial decay of the \( \text{O}_2(v) \) molecules generated during the discharge burst, followed by a much slower decay of \( \text{O}_2(v) \) molecules produced by the chemical reactions after the excitation. The apparent \( \text{O}_2(v) \) initial decay rates for \( v=13 \) and \( 19 \), \( 1.7 \times 10^{-13} \text{ cm}^3/\text{s} \) and \( 4.9 \times 10^{-13} \text{ cm}^3/\text{s} \), respectively, are significantly higher compared to the room temperature V-V rate coefficients for \( \text{O}_2\)-\( \text{O}_2 \) observed in Ref. [13]. This is most likely due to the contribution of the rapid V-T relaxation by O atoms.

As can be seen, in all three cases shown in Figs. 11-13, i.e. \( v=8, 13, \) and \( 19, \) preheating the mixture (a) results in the lower vibrational level populations during the long-term decay after the discharge burst, and (b) reduces the trend for a transient rise on a ms time scale, most pronounced at \( v=8 \). The data taken for other \( \text{O}_2 \) vibrational levels, \( v=9-12 \) and \( v=17-20, \) exhibit similar behavior. These results suggest a significant effect of the ozone chemistry on the mechanism of \( \text{O}_2(v) \) formation after the burst excitation at the low-temperature (non-preheated) conditions. To minimize this effect, additional measurements need to be taken at higher temperatures and higher \( \text{O}_2 \) dissociation fractions generated by the discharge burst, at the conditions where the recombination of O atoms and \( \text{O}_2 \) molecules (i.e. the reaction of Eq. (3)) would become a minor pathway.

Figure 14 plots the time-resolved, absolute O atom number density measured by ps TALIF in non-preheated and preheated 20% \( \text{O}_2\)-Ar mixtures, after the excitation by the discharge burst. It can be seen that the O atom number densities at these conditions are comparable. As expected, preheating the mixture reduces the rate of the O atom decay, due to the lower total number density, negative temperature dependence of the recombination rate coefficient, and possibly due to more rapid thermal decomposition of ozone.
4. Summary

In the present work, partial dissociation of an O₂-Ar mixture by a burst of ns discharge pulses in a flow reactor is used to study the kinetics of O₂ vibrational excitation during the O atom recombination. Vibrational level populations of ground electronic state molecular oxygen, O₂(X,v=8-20) in the partially dissociated, recombining 20% O₂-Ar mixture, initially at room temperature or preheated up to T = 610 K, is monitored by ps Laser Induced Fluorescence on the O₂ Schumann Runge bands, with absolute calibration by NO LIF in a NO-N₂ mixture with the known composition, at quenching-free conditions. O atom number density in the O₂-Ar mixture dissociated by the discharge burst is measured by ps Two-Photon absorption LIF (TALIF). The discharge generates a diffuse volumetric plasma, without well-pronounced filaments. The temperature in the plasma is measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS) of excited Ar atoms. The results indicate a rapid initial decay of the O₂(X,v=8-20) molecules generated by electron impact in the discharge, on ~ 20 µs time scale, due to the V-V exchange and V-T relaxation. This decay is followed by a much slower decay, on the time scale much longer compared to the characteristic time for V-V relaxation, up to several ms. This indicates an additional process of O₂(v) generation by chemical reactions initiated by the O atom recombination.

The effect is observed both in the non-preheated and preheated O₂-Ar mixtures. However, comparison of the time-resolved O₂(v=8-13,17-20) vibrational level populations after the burst excitation of non-preheated and preheated mixtures exhibits significant differences. In the preheated mixtures, peak O₂(v) populations during the slow decay following the excitation burst are significantly lower, suggesting a significant effect of O atom recombination via the reaction pathways involving ozone at near-room temperatures. Preheating the mixture likely reduces the ozone number density in the discharge afterglow. To estimate the contributions of different reaction pathways of O atom recombination into the generation of the vibrationally excited O₂(v) molecules, O atom recombination in a partially dissociated O – O₂ – O₃ – Ar mixture is analyzed at T = 380-1000 K, using a simple zero-dimensional chemical kinetics model. The results indicate that at T = 380 K, over 90% of the O atoms recombine into O₂ via the reactions of Eq. (3,4), rather than via the reaction of Eq. (1). In a mixture preheated to T = 1000 K, this fraction is reduced to approximately 80%, but still remains very significant. This estimate indicates that additional data need to be taken in preheated mixtures with a low O₂ mole fraction, ~1%, and at higher pressures, at the conditions when the discharge excitation results in dissociation of most of the initial O₂ molecules in the mixture, and recombination occurs on the time scale shorter than the flow residence time in the discharge cell.

5. Acknowledgments

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Figure 1. Kinetic modeling predictions of O$_2$(X,v) vibrational populations in a recombining O-O$_2$-Ar mixture, at T = 500 K and P = 100 Torr. 20% O$_2$-Ar mixture, complete O$_2$ dissociation into O atoms is assumed at t=0. A quasi-steady-state "tail" produced by the O atom recombination is apparent.

Figure 2. Schematic of the experimental setup showing excitation laser, discharge cell, and detection apparatus.
Figure 3. Schematic of LIF excitation & fluorescence transitions, and vibrational excitation due to recombination.

Figure 4. OPO line shape and $O_{v'}(B^3\Sigma_u^+, v' = 0, N' \leftrightarrow X^3\Sigma_g^-, v'' = 13, N'')$ pump transitions lines at $T = 300$ K. The pump transitions (blue lines) are shown as narrow peaks since the absorption linewidth is negligible compared to the OPO linewidth. The OPO line shape (Voigt profile, red line) is inferred from the line shape measured by a spectrometer.
Figure 5. Schematic of O₂ and NO pump and fluorescence transitions.

Figure 6. Comparison of the experimental NO(A^2Σ, v''=0 ← X^2Π, v''''=0) LIF excitation spectrum, taken in a 100 ppm NO-N₂ calibration mixture at room temperature at P = 10.3 Torr, with the synthetic spectrum.
Figure 7. Discharge pulse voltage, current, and coupled energy waveforms. 20% O₂-Ar mixture, initially at room temperature (left) and at preheated conditions (right). P = 100 Torr, pulse #100 in the burst.

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Figure 8. Single-shot, broadband plasma emission images taken during a 100-pulse discharge burst, in non-preheated (initially at room temperature) and preheated flows. 20% O₂-Ar mixture, P = 100 Torr, pulses #1-100 in the burst, camera gate 10 ns.
Figure 9. Experimental Ar* absorption line shapes, measured during pulse #100 of the discharge burst in a 20% O₂-Ar mixture, with and without preheating (red and blue dots, respectively). Temperatures inferred from the best synthetic fit of the line shapes (black solid curve) are T = 360 ± 30 K and T = 610 ± 30 K, for non-preheated and preheated flows, respectively.

Figure 10. **Left:** O₂(X²Σg⁻, v=8-19) vibrational level populations in the 20% O₂-Ar mixture, initially at room temperature, at different delay times after the excitation by the discharge burst. **Right:** same data measured in the preheated 20% O₂-Ar mixture.
Figure 11. Time-resolved $O_2(X^3Σ_g^+,v=8)$ vibrational level populations in the non-preheated and preheated 20% $O_2$-Ar mixtures vs. delay time after the excitation by the discharge burst, plotted on two different time scales. The shaded bar indicates the discharge burst excitation 1 ms long. The dashed black line shows an exponential fit to the data in the non-preheated flow up to 100 μs, along with the inferred decay rate coefficient.

Figure 12. Time-resolved $O_2(X^3Σ_g^+,v=13)$ vibrational level populations in the non-preheated and preheated 20% $O_2$-Ar mixtures vs. delay time after the excitation by the discharge burst, plotted on two different time scales. The shaded bar indicates the discharge burst excitation 1 ms long. The dashed black line shows an exponential fit to the data in the non-preheated flow up to 100 μs, along with the inferred decay rate coefficient.
Figure 13. Time-resolved $O_2(X^2\Sigma_g^+, v=19)$ vibrational level populations in the non-preheated and preheated 20% $O_2$-$Ar$ mixtures vs. delay time after the excitation by the discharge burst, plotted on two different time scales. The shaded bar indicates the discharge burst excitation 1 ms long. The dashed black line shows an exponential fit to the data in the non-preheated flow up to 100 μs, along with the inferred decay rate coefficient.

Figure 14. Time-resolved, absolute $O$ atom number density in non-preheated and preheated 20% $O_2$-$Ar$ mixtures, plotted vs. delay time after the excitation by the discharge burst.