RESONANCE-ENHANCED MULTIPHOTON IONIZATION OF MOLECULAR OXYGEN
AT THE 222 nm KrCl LASER WAVELENGTH

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Abstract
We study the photo-ionization mechanism of molecular oxygen at the 222 nm KrCl laser wavelength within a laser pulse intensity range of $10^8$ – $10^{10}$ W/cm$^2$, using 14 ns laser pulses. We experimentally observe (2+1) resonance-enhanced multiphoton ionization (REMPI) of molecular oxygen with the effective ionization cross-section

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\sigma^{(2)}_{O_2} = (3.2 \pm 1.3) \cdot 10^{-18} \text{ cm}^4 \cdot \text{s}^{-1} \cdot \text{W}^{-2}
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at an intensity range of $10^9$ – $10^{10}$ W/cm$^2$ and linear ionization due to gas impurities at an intensity range of $10^8$ – $10^9$ W/cm$^2$.

Keywords: KrCl laser, (2+1) REMPI, molecular oxygen, photoionization cross-section.

1. Introduction

Interaction of UV radiation with air and its components has been actively studied over the past decades. High-energy UV photons are capable of initiating important photochemical processes that are hardly triggered by longer-wavelength radiation. For example, UV radiation shorter than 242 nm (belonging to the so-called UVC 200–280 nm range) is known to cause the single-photon dissociation of molecular oxygen [1,2], which leads to the formation of ozone in the atmosphere [3,4]. High energy of UVC quantum, being small compared to the ionization potentials of the main components of air, is big enough to allow efficient low-order excitation of high-lying Rydberg states; providing a resonance condition, it leads either to resonance enhanced multiphoton ionization (REMPI) [5], dissociation [6], or fluorescence [7]. There are several established experimental techniques based on resonant nonlinear absorption (NLA) of UV radiation, such as REMPI spectroscopy [8] and two-photon absorption laser-induced fluorescence (TALIF) [9,10]. Because of resonant interaction, there may be quite unexpected outcomes of main mechanism of multiphoton ionization (MPI) and NLA in atmospheric air. For example, for the 248 nm radiation, the dominant MPI process in air is (2+1) REMPI of water vapor molecules naturally contained in the air [11]. Similar situation is observed at the 266 nm radiation for NLA [12].

The emission of KrCl excimer molecule brought a lot of attention in the recent years, primarily because the 222 nm radiation inactivates airborne human corona-viruses, being safe for human skin and eyes [13–15]. Thus, KrCl lamps are considered to be an efficient and safe way for disinfection of air, water, and surfaces. The subject of the UVC light interaction with air and related photochemistry is
also extensively studied. Even though the UVC radiation interaction with molecular oxygen has been a subject of dozens of papers over the last several decades [1–10, 16, 17], many parameters such as MPI and NLA cross-sections for particular wavelengths are not available in the literature. In this paper, we examine multiphoton ionization of molecular oxygen with a high-power 222 nm laser source.

2. Experiment

We perform our experiments with KrCl excimer laser (Lambda Physik LPX200) operated at the 3.3 atm total pressure of an optimum mixture [18] of HCl/Kr/Ne = 0.1%/10%/89.9%. It is equipped with external 1.5 m long Cassegrain-type unstable cavity with the magnification factor $M = 11$. In Fig. 1, we show the experimental setup.

The laser delivers the 222 nm pulses with an output energy of $E \sim 100–200$ mJ and the FWHM pulse length $\tau_p = 14$ ns. The laser pulse energy can be varied two orders of magnitude by means of diffractive variable attenuator (DVA). UV light is focused by $F = 1$ or 0.6 m lens into a photoelectric sensor described earlier [11]. The basic idea of the sensor is that the photoionization plasma closes the electric loop between the high voltage and collecting tubular electrodes, and the current (measured by a TDS 3054C 500 MHz oscilloscope) can be used to monitor the charge particle density produced by the laser pulse. Since the electron mobility is three orders of magnitude larger than that of ions, the measured current provides the time-resolved electron density integrated over the laser pulse cross-section. The sensor allows a temporal resolution of $\sim 2$ ns. Typical oscilloscope traces are given in Fig. 2a.

![Fig. 1. Layout of the experimental setup.](image)

![Fig. 2. Typical oscilloscope traces of the laser pulse (the solid curve) and photoelectric current (the dashed curve) in O$_2$ (a) and the measured KrCl laser spectrum (b).](image)
The photoelectron current increases over the first \( \sim 20 \) ns of the laser pulse, then starts to decrease, and completely vanishes after the laser pulse end. All the experiments are performed in a vacuum chamber with an UV fused silica entrance window evacuated to \( 10^{-2} \) Torr, flushed and filled with the gas to be investigated at room temperature, \( T = 21^\circ C \).

The ionization data for \( O_2 \) (99.999\% purity) are presented in Fig. 3. Each measurement point is an average of several dozen laser shots. Here, \( I_0 = E \left( \int f(x, y) \, dx \, dy \int g(t) \, dt \right)^{-1} \) is the peak laser intensity over normalized spatial \( f(x, y) \) and temporal \( g(t) \) intensity distribution functions. The electron density \( N_e^0 = \sigma_{\text{max}} / e \mu_e \) derived from the experimental data is a maximum over the spatial distribution attained during the laser pulse, where \( e \) is elementary charge and \( \mu_e = 1200 \) cm\(^2\)/V\( \cdot \)s is the electron mobility in oxygen; specific plasma conductivity is \( \sigma_{\text{max}} = u_m L/U_{\text{ch}} R_{\text{osc}} \int_{0}^{\infty} f^K(x, y) \, dx \, dy \), where \( K \) is the photo-ionization order, \( u_m \) is measured photocurrent amplitude, \( L = 0.8 \) cm is the inter-electrode gap, \( U_{\text{ch}} = 2 - 3 \) kV is charging voltage on the HV electrode, and \( R_{\text{osc}} = 50 \) \( \Omega \). At low incident laser intensities, \( I_0 < 10^9 \) W/cm\(^2\), the ionization yield appears to be linear but then obeys \( \sim I^2 \) power law within the \( 2 \cdot 10^9 - 2 \cdot 10^{10} \) W/cm\(^2\) intensity range. Both linear and square dependences, obviously, do not fit into direct three-photon ionization of molecular oxygen.

Our effort to attain multiphoton ionization in the other (not oxygen) air components failed. In the pure nitrogen, we observed linear dependence \( N_e(I_0) \), and the electron density produced by the laser pulse was significantly lower than estimated gas contamination level. We performed additional experiments in order to test, if the presence of minor air components, such as Argon or \( H_2O \), has significant impact on the air ionization. Additives of both 1–5\% of Ar and up to 2.3\% \( H_2O \) (corresponds to a relative humidity of 95\% at 21\(^\circ\)C) to air proved to have negligible effect on the air photoionization at \( \lambda = 222 \) nm.

3. Discussion

Now we review possible resonances that can be involved in our experiment. Our laser produces radiation centered at \( \lambda = 222.6 \) nm with a spectral width of \( \Delta \lambda_{\text{FWHM}} = 0.6 \) nm; see Fig. 2b. Two photons can cover an energy range of \( \sim 11.12 - 11.17 \) eV. Molecular oxygen Rydberg states that can fit into the two-photon resonance with UV radiation are well known [16]. The closest Rydberg states that are slightly below \( 2 \hbar \nu \) energy and fit the selection rules are a pair of \( 3d\pi_g \) states \( ^1\Sigma_{0^+} \) and \( ^3\Sigma_{0^+} \), and \( \hbar \nu X^3\Sigma_g^- \).
that can be reached from the ground state into $\nu = 2$ level at 11.083 eV and from the $4s\sigma_g$ state into $3\Pi_g \xrightleftharpoons{2h\nu} X^3\Sigma_g^-$ level at 11.045 eV. It should be noted, that these levels can be viewed as absorption continues due to the line broadening and the presence of overlapping rotational absorption bands.

Thus, we refer the observed second-order ionization nonlinearity to (2+1) REMPI through the $1\Sigma_{0g}^+$, $3\Sigma_{0g}^-$, or $3\Pi_g^-$ intermediate states. The nature of the linear part of the dependence can have multiple explanations. Oxygen has linear absorption at $\lambda = 222$ nm that leads to dissociation through the Hertzberg continuum [1]. However, it definitely will not contribute into the electron density since both photodissociation products will be oxygen atoms in $3p$ ground state requiring another 13.62 eV for ionization [19]. Two-photon dissociation is proposed [20] for $O_2$ at 226 nm wavelength, slightly longer than employed in our experiment, though the cross-section of this process is unknown. Such dissociation can lead to production of excited oxygen atom that can be ionized by a single KrCl photon.

To address linear part in more details, we turn to the theory of noncoherent (2+1) REMPI ionization [21,22]. For a pulse length $\tau_p$ longer than the transverse relaxation time $T_2$ of the intermediate state, the REMPI can be described by a set of kinetic equations for the population of the states involved,

$$\frac{\partial N_1}{\partial t} = -\mu \frac{\gamma + 1/T_2}{(\gamma + 1/T_2)^2 + (\Delta \omega)^2} (N_1 - N_2),$$

$$\frac{\partial N_2}{\partial t} = \mu \frac{\gamma + 1/T_2}{(\gamma + 1/T_2)^2 + (\Delta \omega)^2} (N_1 - N_2) - 2\gamma N_2,$$

$$\frac{\partial N_i}{\partial t} = 2\gamma N_2.$$

Here, $N_1$, $N_2$, and $N_i$ are the populations of the ground state (1), excited state (2), and ionized (i) state, respectively, $\mu = (1/2) (r_{12}/\hbar)^2 |E|^2 \propto I^2$ is spectral detuning of the incident radiation from the resonant state, $\gamma = (1/2) (r_{12}/\hbar)^2 |E|^2 \propto I^1$ is the two-photon transition rate, $r_{12}$ is a two-photon transition matrix element, $\gamma \propto |E|^2 \propto I$ is the single-photon ionization rate from the excited state, and $|E|$ is the laser field envelope.

Depending on the relations between the variables, this set of equations can have several extreme cases [22]. Of our particular interest is the one of low density plasma, $N_2 \ll N_1$.

(I) For relatively low intensities $\gamma \ll 1/T_2$ (the single-photon ionization is much slower than polarization relaxation), the population of the excited state $N_2 \approx \frac{1}{2} \frac{\mu}{\gamma} \frac{T_2}{1 + \Delta \omega T_2} \propto I$. Thus, the ionization rate has the second-order nonlinearity of the laser intensity, $\frac{\partial N_i}{\partial t} \propto I^2$.

(II) For high intensities, if the single-photon ionization rate is higher than polarization relaxation ($\gamma \gg 1/T_2$) and detuning from the resonance is large ($\gamma \ll \Delta \omega$), then $N_2 \approx \frac{\mu}{2(\Delta \omega)^2} \propto I^2$. In this case, $\frac{\partial N_i}{\partial t} \propto I^3$.

(III) Assuming that $\gamma \gg 1/T_2$ and $\gamma \gg \Delta \omega$, the population of the excited state saturates, namely, $N_2 \approx \frac{1}{2} \frac{\mu}{\gamma^2} \propto \text{const}(I)$, and thus the ionization rate becomes a linear function of laser intensity, $\frac{\partial N_i}{\partial t} \propto I$.

Summing up, the theory can justify any degree of ionization nonlinearity $N_e \sim I^K$, from $K = 1$ to $K = 3$. But if we compare it with experimental data, it does not fully match it. For instance, we observed the linear dependence at low intensities and the second-order dependence at high intensities. It contradicts with the theory that linear ionization (case III) refers to high intensity condition ($\gamma \gg 1/T_2$).
In the experiment, the linear part at lower intensity is caused, most probably, by the single-photon ionization or photoelectric effect of some minor organic gas impurity. The peak electron density on the linear part of the curve in Fig. 3 corresponds to $N_e \sim 10^{12}$ cm$^{-3}$ or $\sim 10^{-7}$ ionization degree, while typical major contaminant density in employed O$_2$ is on a ppm scale or $\sim 10^{-6}$.

From the experimental data obtained, we calculate the effective (2+1) REMPI cross-section to be

$$\sigma^{(2)}_{O_2} = (3.2 \pm 1.3) \cdot 10^{18} \text{ cm}^4/\text{s} \cdot \text{W}^2$$

as the best $N_e^0 = N_{O_2} \sigma^{(2)}_{O_2} I_0 \int_0^t g^2(t) \, dt$ fitting of the measured $N_e^0(I_0)$ data points shown as the solid line in Fig. 3, where $N_{O_2} = 2.5 \cdot 10^{19}$ cm$^{-3}$ is the concentration of molecular oxygen. If we compare the measured cross-section with our previous work [11,23] done with the 248 nm KrF laser radiation and using the same technique, (2+1) REMPI of oxygen at 222 nm provides significant, one–two orders of magnitude increase in the ionization yield compared to direct three-photon ionization of oxygen at the 248 nm wavelength. In turn, $\sigma^{(2)}_{O_2}$ is almost two–three orders of magnitude smaller compared to $\sigma^{(2)}_{H_2O}$ of (2+1) REMPI of the water vapor. To guide the eye, the calculated ionization curves are shown in Fig. 3 for direct three-photon ionization of O$_2$ at $P = 1$ atm and (2+1) REMPI of H$_2$O for the 248 nm radiation (2.2% H$_2$O diluted in $P = 1$ atm air or O$_2$) for the same pulse shape as in our current experiment.

4. Summary

In conclusion, we investigated multiphoton ionization of molecular oxygen with the 222 nm KrCl laser wavelength in the intensity domain $10^8 \sim 10^{10}$ W/cm$^2$. We observed the (2+1) REMPI through the intermediate $^3\Pi_g - ^1\Sigma_u^+$, $^3\Sigma_g^-$, and $4s\sigma_g^3\Pi_g$ resonance states with quadratic dependence on the laser intensity. The measured (2+1) REMPI cross-section is $\sigma^{(2)}_{O_2} = (3.2 \pm 1.3) \cdot 10^{-18}$ cm$^4 \cdot s^{-1} \cdot W^{-2}$. We estimate the absolute accuracy of the $\sigma^{(K)}$ measurements to be about 40%, mainly because of the high-order nonlinearity, resulting in a strong effect of small errors.

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