NONLINEAR PHOTOIONIZATION OF AIR IN THE SPECTRAL INTERVAL 355–200 nm

L.L. Losev and V.I. Soskov

P.N. Lebedev Physics Institute,
Academy of Sciences of the USSR, Moscow
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The nonlinear photoionization of air was investigated with the help of a UV laser, discretely tunable in the range 355–200 nm. *It was found that two-step ionization of nitrogen and oxygen occurs at wavelengths in the range* 355–200 nm *while two-photon ionization of oxygen occurs at wavelengths* $\lambda < 205$ nm. *It is shown that in the case of the two-step process the cross section for photoionization decreases as the gas pressure increases.*

INTRODUCTION

In many practical problems it is necessary to produce a definite density of free carriers in a gaseous medium, in particular, in air, and, in addition, it must be possible to vary the free-carrier density continuously over wide limits. Radiation from a gas discharge, *x*-ray sources, or charged-particle beams is usually employed for these purposes. Each of these sources has a number of characteristic properties, which determine the area of application of the source. As shown in Ref. 1, nonlinear ionization with UV laser radiation makes it possible to produce in gas media extended, partially ionized volumes. In Ref. 1 the fourth harmonic of the Nd:YAG laser ($\lambda = 266$ nm) was used as the source of UV radiation to ionize air, and it was established that when the intensity of the laser radiation is increased from 10^8 up to 10^{10} W/cm^2 the photodetection density increases from 10^8 up to 10^{13} cm^{-3} according to a power law with an exponent of ~2.

In order to increase the efficiency of nonlinear ionization, i.e., to reduce the intensity of the laser radiation required to produce the required density of ions, we investigated in this work the nonlinear ionization of air in the spectral range 355–200 nm.

EXPERIMENTAL APPARATUS

To investigate the ionization of gases we employed the apparatus illustrated schematically in Fig. 1. The radiation from a Nd: YAG laser, operating in the passive mode-locking regime with separation of a single pulse, was amplified and converted with the help of two KDP crystals into the fourth or third harmonic with wavelengths $\lambda_{4\omega} = 266$ nm and $\lambda_{3\omega} = 355$ nm. The pulse width was equal to ~ 35 ps and the maximum energy per pulse was equal to 10 mJ.

A lens with a focal length of 1 m focused the radiation into a cell filled with hydrogen or methane up to a pressure of 10 atm. In the cell the radiation was converted in the process of stimulated Raman scattering into the Stokes and anti-Stokes components, which were then collimated with a lens and separated with the help of a dispersion prism. The required component of the radiation was directed into the cell holding the gas under study. Thus the source of radiation, whose spectrum is shown in Fig. 2, was created. In order to obtain a more uniform distribution of the intensity, a central region was separated from a 15 mm in diameter light beam with the help of a 3.8 mm in diameter diaphragm.

The free carriers produced when the gas under study is ionized were detected with the help of the ionization chamber described in Ref. 1. The chamber operated in the complete charge-collection regime. The energy of the radiation was measured at the output of the ionization chamber. It is well known that the width of the Stokes and anti-Stokes components is reduced by the nonstationary nature of the stimulated Raman scattering. Based on existing experimental data, it was assumed to be equal to 10 ps. It should also be noted that variation of the pump energy in the course of the experiments can cause the width of the pulses of the converted radiation to change. Under the conditions of our experiments this change was equal to 50%.

SPECTRAL INVESTIGATIONS OF THE NONLINEAR PHOTOIONIZATION OF AIR

Since air is a multicomponent mixture of gases, the concentrations, ionization cross sections, and ionization potentials of whose separate components are different, it is quite difficult to say in advance which component makes the largest contribution to the nonlinear ionization. Only mass-spectrometric investigations of the products of ionization can give an accurate answer to this question. Information about which components determine the nonlinear ionization in certain sections of the spectrum can also be obtained by studying the dependence of the process of ionization of air on the frequency and intensity of the laser radiation.

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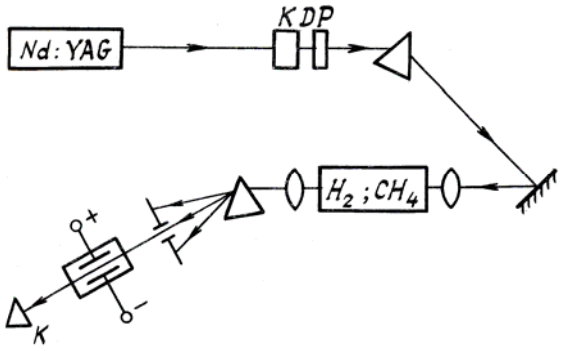

FIG. 1. Diagram of the experimental apparatus.

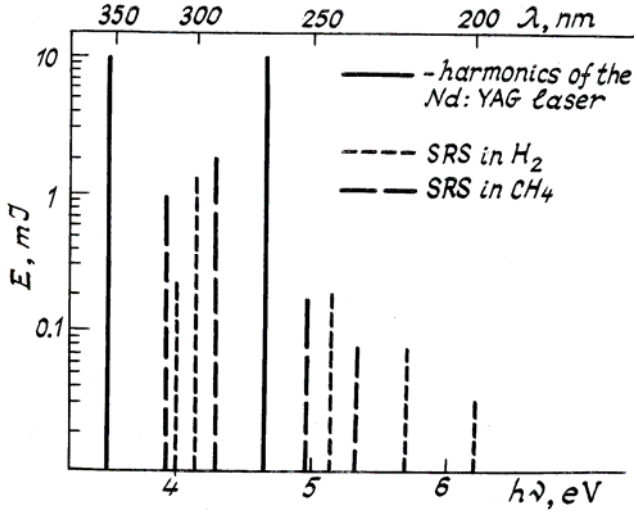

FIG. 2. The spectrum of the laser source.

In the general case, electrons can be produced in the gas in the process of nonlinear photoionization both by means of direct multiphoton ionization of the molecules and by means of a resonance multistep process — with a transition of the molecule to an intermediate energy level.[3] In this case the expression for the density n_e of the photoelectrons produced can be represented in the absence of saturation in the form $n_e = \sum_j n_j^0 \sigma_j(\omega) I^{mj} \tau$, where n_j^0 is the density of the component of air; $\sigma_j(\omega)$ is the photoionization cross section for the given component; I is the intensity of the ionizing radiation; m_j is the degree of nonlinearity of the photoionization process; and, τ is the width of the radiation pulse. The summation is performed over all components. As one can see from this expression, if m_j is the same for several components, then the contribution of each component will be determined by the product $n_j^0 \sigma_j(\omega)$. If the component with the low initial concentration and therefore large $\sigma(\omega)$ makes the main contribution to ionization, then by increasing the intensity of the radiation we achieve a regime when the product $\sigma_j(\omega) I^{mj} \tau$ becomes comparable to unity, i.e., saturation starts to appear. This must be reflected as a decrease in the degree of nonlinearity m_j. By determining the photoelectron density at which saturation appears the concentration of the component that makes the largest contribution to ionization can be determined. As shown in Ref. 1, for λ = 266 nm in the range of intensities (10^7–10^{10} W/cm^2 the degree of nonlinearity does not change and remains equal to ~ 2, while photoelectron density reaches ~ 5 ·10^{13} cm^{-3}. It can therefore be concluded that the component of air whose concentration is greater than (10^{14}–10^{15}) cm^{-3} ionizes. In air N_2, O_2, Ar, and CO_2 present in such concentrations.[4]

Our investigations showed that when air is ionized by radiation in the spectral range from 299 nm (the first Stokes component in H_2) to 200 nm (the third anti-Stokes component in H_2) (see Fig. 2) a quadratic dependence $m = 2.0 \pm 0.2$ is observed. In the case of ionization by radiation with wavelength λ = 355 nm (the third harmonic of the Nd: YAG laser) the degree of nonlinearity becomes equal to 3.0 ± 0.3. Since the ionization potentials of N_2, O_2, Ar, and CO_2 are equal to 15.58, 12.08, 15.8, and 13.77 eV, respectively, with the exception of radiation with λ = 200 nm, for which direct two-photon ionization of O_2 is possible, a two-step process of ionization, occurring according to the following

scheme, apparently occurs at the other wavelengths: 1) $M + 2h\nu \rightarrow M^*$; 2) $M^* + h\nu \rightarrow M^+ + e$. Saturation of a single-photon transition at the second stage can result in the experimentally observed nonlinearity of the process ~ 2.

The scheme of energy levels of the Ar atom is well known.[5] It follows from this scheme that under the conditions of our experiment this process is impossible in Ar. In the case of CO_2, when air is cooled to temperatures of ~ 100 K the CO_2 concentration in air can be reduced to ~10^{10} cm^{-3}. However the experiment performed showed that prefreezing of air does not affect the yield of photoelectrons. Therefore CO_2 also does not play a significant role in our case. We are thus left with the gases nitrogen and oxygen.

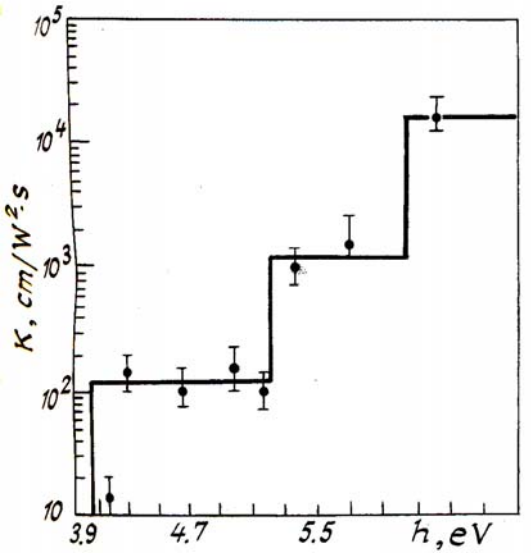

FIG. 3. K versus the photon energy.

Figure 3 shows the obtained wavelength dependence of the coefficient K in the expression $n_e = KI^2\tau$. The coefficient K is equal to the sum $\sum_j n_j^0 \sigma_j(\omega)$ over all ionizing components. As one can see from the dependence obtained, the coefficient K varies sharply in the range of photon energies ~ 6, 5.25, and 4 eV. This dependence can be explained by comparing the ionization potentials of nitrogen and oxygen with the photon energies. Doing so shows that the change in K near 6 eV is well correlated with the transfer to direct two-photon ionization of O_2. The change in the region of 5.25 eV coincides with the photon energy at which the sum of three quanta is equal to the ionization energy of N_2. In this case, two quanta are realized. This follows from the structure of the energy levels of the nitrogen molecule.[6] Analogously, the change In K near 4 eV corresponds to photon energy which in the case of tripling is equal to the ionization potential of O_2. In this case two-step ionization is also possible (this can be seen from the structure of the energy levels of O_2).[6] In addition, for photons with energy less than 4 eV at the first step three quanta are absorbed, while for energies exceeding 4 eV two photons are absorbed; this is reflected in the change in the degree of nonlinearity of the process. Based on this it can be concluded that under the conditions of nonlinear ionization of air in the wavelength range 355–238 nm and for radiation with $\lambda < 205$ nm the main ionizing component is oxygen, while in the range 238–205 nm the main ionizing component is nitrogen and because the UV spectra of N_2 and O_2 are continuous[6] this conclusion should be true for all wavelengths In the range investigated.

INVESTIGATION OF THE DEPENDENCE OF THE CROSS SECTION OF NONLINEAR PHOTOIONIZATION ON THE GAS PRESSURE

As was shown in the preceding paper,[1] whose results were confirmed in Ref. 7, in the case of nonlinear ionization of air by radiation with $\lambda = 266$ nm for fixed radiation intensity the free-carrier density produced remains approximately constant for air pressures ranging from 10^2 to 10^3 torr. As pointed out in Ref. 1, such a dependence cannot be explained by the recombination of free carriers. The dependence obtained was interpreted based on the quenching of autoionization states in inelastic collisions. However the results of Investigations presented in this paper showed that this character of the dependence is observed for all wavelengths (with the exception of $\lambda = 200$ nm) at which nonlinear ionization occurs by means of a two-step cascade process. In the case of direct multiphoton ionization of oxygen (radiation with $\lambda = 200$ nm) the dependence of the photoelectron density on the gas pressure changes and becomes linear. An analogous dependence at $\lambda = 200$ nm was obtained for Xe (whose ionization potential is equal to 12.1 eV), in which direct two-photon ionization also occurs.

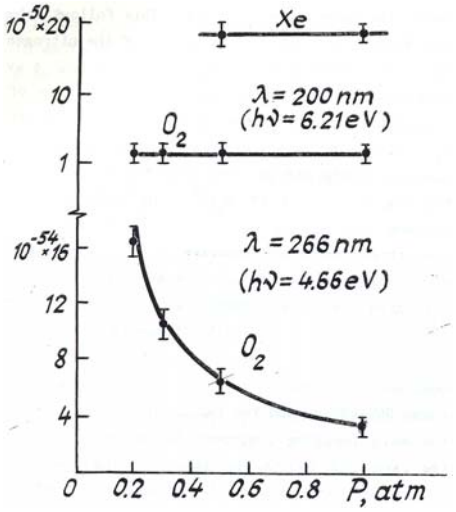

FIG. 4. The cross section for nonlinear ionization versus the gas pressure.

A linear dependence of the photoelectron density on the Xe pressure was also observed[8] under conditions

of direct two-photon ionization (λ = 193 nm). Therefore it can be conjectured that the dependence observed in Ref. 1 is connected with the existence of an intermediate resonance. Collisions can broaden the resonance level, and this in turn results in a reduction of the ionization cross section σ as the pressure increases,[3] and as a result the increase in the electron density is no longer proportional to the pressure. The experimentally obtained pressure dependence of σ for O_2 at λ = 266 nm is shown in Fig. 4. The values of σ obtained for O_2 and Xe at λ = 200 nm, which do not depend on the pressure, are also presented in Fig. 4.

CONCLUSIONS

Thus we have obtained the following results:

1. We have established that under the conditions of nonlinear ionization of air for wavelengths in the range 299–200 nm the photoelectron yield depends quadratically on the intensity of the laser radiation, while for λ = 355 nm a cubic dependence is observed.

2. The wavelength dependence of the coefficient $K = n_e/I^2\tau$ was obtained. Based on the dependence obtained, it was found that in the spectral range studied N_2 and O_2 make the main contribution to the nonlinear ionization of air.

3. The pressure dependence of the cross section for nonlinear ionization of O_2 was measured under the conditions of both direct two-photon ionization (λ = 200 nm) and two-step ionization (λ = 266 nm). It was shown that in the case when an intermediate resonance exists the cross section for multiphoton ionization decreases as the gas pressure increases.

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