NONLINEAR CHANGES IN THE INDEX OF REFRACTION OF AIR ACCOMPANYING PHOTODISSOCIATION OF OZONE AND THEIR EFFECT ON THE ANGULAR SPECTRUM OF THE RADIATION

A.N. Starodumov and A.V. Shipulin

Institute of General Physics
of the Academy of Sciences of the USSR, Moscow

Received September 5, 1989

The effect of changes in the chemical composition of the medium and heating accompanying photodissociation of ozone on the real part of the index of refraction was studied. The results of numerical calculations of the distortions of the beam profile are presented. It is shown that the concentration and thermal nonlinearities make a significant contribution to the change in the angular spectrum of the radiation passing through the ozone layer.

The interaction of optical radiation with atmospheric ozone has been studied only from the viewpoint of the extinction of the radiation by the ozone layer. The absorption spectra and the products of dissociation of O_3 have been studied in a large number of theoretical and experimental works,[1–3] but the propagation of UV and visible radiation, taking into account the self-action owing to decomposition of O_3 molecules, has not been studied as carefully. The theory of the propagation of waves of photodissociation of ozone (waves of self-bleaching of the stratosphere) under the action of powerful UV pulses is described in detail in Refs. 4 and 5, and the effect of the decomposition of ozone on the change in the concentrations of the hydrogen-oxygen-nitrogen components of the stratosphere is described in Ref. 6. The change in the angular spectrum of the radiation connected with nonlinear refraction and induced thermal and concentration scattering have almost not been studied. In this paper the effect of the changes in the chemical composition of the medium and heating accompanying dissociation of O_3 on the index of refraction and, therefore, the appearance of nonlinear refraction of the beam are analyzed for the first time.

We shall study the basic processes occurring when near-UV and visible radiation interacts with the ozone layer. Photons with energy $h\nu > 1.09$ ev photodissociate ozone into molecular and atomic oxygen:

$$O_3 + h\nu \Rightarrow O_2 + O\,(^1D), \qquad \lambda < 310\text{nm}; \tag{1}$$

$$O_3 + h\nu \Rightarrow O_2 + O\,(^3P), \qquad \lambda > 310\text{nm}. \tag{2}$$

The quantum yield of the reaction (1) equal to unity for $\lambda = 300$ nm, it decreases to $\varphi = 0.4$ for $\lambda = 308$ nm, and it is practically equal to zero for $\lambda > 310$. Atomic oxygen in tl excited state (reaction (1)) is deactivated quit rapidly by the reaction

$$O(^1D) + M \Rightarrow O(^3P) + M^*. \tag{3}$$

The characteristic deactivation time $\tau \simeq 10^{-7} \div 10^{-9}$ s.[1]

The increase in the concentration of atomic oxygen accompanying dissociation of ozone in the laser beam channel will change the dynamics of the concentrations of atmospheric gases, such as OH, HO_2, etc.[1] For the pulse widths studied $t_p \le 10^{-5}$ s, however, these processes have no effect on the propagation of the radiation because the concentrations of the reacting components are low or the reaction rates are slow. Ozone is formed only in three-body collisions

$$O + O^2 + M \Rightarrow O_3 + M^*, \tag{4}$$

where M is the ozone molecule or oxygen, which in a collision acquires kinetic energy equivalent to 1.09 eV. The reaction constant of the recombination reaction (4) is

$$k_1 = 8.2 \cdot 10^{-35} \exp\left(\frac{890}{RT}\right)\left[\frac{\text{cm}^6}{\text{s}}\right].$$

The change in the concentrations of O_3, O_2, $O(^1D)$, and $O(^3P)$ during the photochemical reactions is described by the following system of equations:

$$\frac{d[O_3]}{dt} = k_1 \cdot [O_2] \cdot [M] \cdot [O] - \sigma(\lambda) \cdot \frac{I}{h\nu} \cdot [O_3]; \tag{5a}$$

$$\frac{d[O_2]}{dt} = -k_1 \cdot [O_2] \cdot [M] \cdot [O] + \sigma(\lambda) \cdot \frac{I}{h\nu} \cdot [O_3]; \tag{5b}$$

$$\frac{d}{dt}[O(^1D)] = -k_2\cdot[M]\cdot[O(^1D)] + \sigma(\lambda)\cdot\varphi(\lambda)\cdot\frac{I}{h\nu}\cdot[O_3]; \quad (5c)$$

$$\frac{d}{dt}[O(^3P)] = -k_1\cdot[O_2]\cdot[M]\cdot[O(^3P)] + k_2\cdot[M]\cdot[O(^1D)] + \sigma(\lambda)\cdot\frac{I}{h\nu}\cdot[O_3]\cdot(1-\varphi), \quad (5d)$$

where

$k_2 = 10^{-10}\ \frac{cm^3}{s}$ for $M = O_2$ and

$k_2 = 2.2\cdot10^{-11}\ \frac{cm^3}{s}$ for $M = N_2$; I is the intensity of the radiation [W/cm^2]; and, σ is the cross section for absorption of radiation by O_3 molecules.

Since $[O_2(t=0) \gg [O_3(t=0)], [O(t=0)]$, in what follows the O_2 concentration is assumed to be constant. The insignificant changes in the concentration of molecular oxygen $\left(\frac{\Delta(O_2)}{[O_2(t=0)]} : 10^{-6}\right)$ will be taken into account with the help of the relation $\Delta[O_2] = -\Delta[O_3]$ in the analysis of the concentration effects.

We shall study the propagation of radiation with wavelength $\lambda = 308$ nm. In this case the change in the concentration of $O(^1D)$ can be neglected for pulses whose width $t_p \geq 10^{-7}$ s. Then the heating in the beam channel is determined by the exothermal reaction (1). We shall assume that when a single O_3 molecule dissociates the amount $h\nu \sim E_d$ of energy is transformed into heat instantaneously ($\nu_c^{-1} \sim 10^{-9}\div10^{-8}$ s, ν_c is the collision frequency), and energy E_d is acquired during recombination. For the specific heating power $\frac{\partial Q}{\partial t}$ we obtain the relation

$$\frac{\partial Q}{\partial t} = (h\nu - E_D)\frac{\sigma I}{h\nu}[O_3] - E_D k_1[O_2]\cdot[M]\cdot[O].$$

Heating of the air changes the gas density and, correspondingly, the index of refraction δn_T. The second mechanism for the nonlinear change in the index of refraction is connected with the different polarizabilities of the ozone molecules and the products of dissociation of ozone. The polarizabilities of the ozone molecule α_{O_3} is greater than the sum of the polarizability of molecular oxygen α_{O_2} and atomic oxygen α_O. Since the change in the concentration of O_3 depends on the intensity of the radiation there arises an additional nonlinear change in the index of refraction δn_c:

$$\delta n_k(t) = \left(\alpha_{O_2} + \alpha_O - \alpha_{O_3}\right)\cdot\left([O_3(t)] - [O_3(t=0)]\right).$$

To study numerically the effect of the concentration and thermal nonlinearity on the angular divergence of the laser beam we constructed a program in which the system of kinetic equations (5) and the parabolic equation for the complex amplitude of the field E with the nonlinear corrections δn_k and δn_T to the index of refraction was solved:

$$\left(2ik\frac{\partial}{\partial z} + \Delta_\perp + \frac{2k^2}{n_0}\delta n_{c,T}\right)E = 0,\quad n_0 \simeq 1. \quad (6)$$

The data on the altitude dependence of the initial concentrations of O, O_2, and O_3 were taken from Ref. 1. The radial distribution of the intensity over the aperture was assumed to be of the form ($a = 15$ cm)

$$I(x) = I_0 \exp\left[-\left(\frac{x}{a}\right)^2\right].$$

The equation (6) was solved using a six-point explicit-implicit scheme with a weight of 1/2; this gave convergence $\sim O(h_x^2 + h_t^2)$, where h_x and h_t are the coordinate and time steps. The nonlinear refraction of a beam in the ozone layer was investigated.

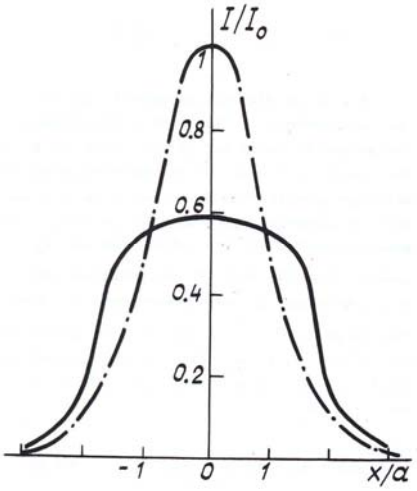

FIG. 1. The transverse profile of the beam intensity at the point of entry into (dot-dashed curve) and after passage through the ozone layer (solid line). The concentration nonlinearity $z = 0.3\ L_g$, $\varepsilon = 1.3$ J/cm^2, and $t_p = 10^{-7}$ s.

Figures 1 and 2 shows the results of the calculation of the change in the beam profile as a function of the traversed distance for the case of concentration and thermal nonlinearity, respectively. Depending on the pulse width, either the concentration nonlinearity ($t_p < 10^{-5}$ s) or the thermal nonlinearity ($t_p \geq 10^{-5}$ s) makes the main contribution to the nonlinear changes in the index of refraction. For the two types of nonlinearity we

studied regimes in which the nonlinear refraction starts to distort the beam profile significantly.

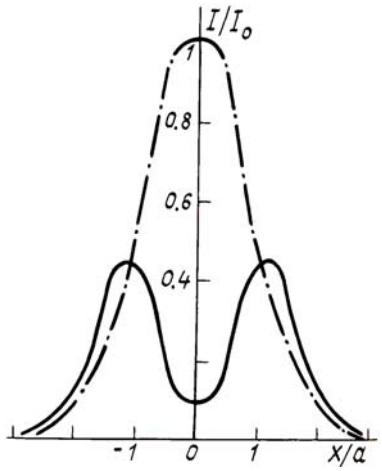

FIG. 2. The transverse profile of the bean' intensity at the point of entry into (dot-dashed line) and after passage through the ozone layer (solid line). The thermal nonlinearity $z = 0.3L_g$, $\varepsilon = 1.3$ *J/cm, and* $t_p = 10^{-4}$ *s.*

We found that the effect plays an appreciable role only for energy densities ≥ 1 J/cm^2. We note that if the intensity exceeds the saturation intensity $I_{sat} = h\nu/\tau_r\sigma$, where τ_r is the recombination time of ozone, then nonlinear spreading is suppressed and the axial part of the beam is relatively stabilized. Figures 1 and 2 show the changes in the initial beam profile at the inlet (dot-dashed line) and after propagating along an inclined path in the ozone layer (solid line) over a distance $z = 0.3\ L_d$, where L_d is the diffraction length. The energy density was equal to 1.3 J/cm^2. The concentration nonlinearity caused the radius of the beam to increase by a factor of 1.5. After passing through the ozone layer the beam continues to expand owing to distortions of the phase front which were accumulated in the ozonosphere. The nonlinear distortions caused by the thermal nonlinearity in the case of wide pulses $t_p \geq 10^{-5}$ s are even more significant (Fig. 2). The calculations were performed for the same energy density and path length as in the case of the concentration nonlinearity. One can see that some of the energy was transferred into the wings and a deep dip formed on the axis of the beam.

It should be noted that in thus work we neglected the effect of rotational SRS in the atmosphere on the angular spectrum of the radiation. The combined effect of rotational SRS and photodissociation of ozone will make the nonlinear distortions even stronger. Thus in this work we have predicted theoretically new mechanisms for nonlinear refraction of laser beams in the atmosphere which significant change the angular spectrum of the radiation.

REFERENCES

1. A.Kh. Khrgian *Physics of Atmospheric Ozone,* (Gidrometeoizdat, Leningrad, 1973).
2. M.J. Griggs, Chem. Phys. **49**, No. 2, 857 (1968).
3. J.C. Brock and R.T. Watson, Chem. Phys., **46**, 477 (1980).
4. I.M. Kopylova and A.P. Sukhorukov, Izv. Vyssh. Uchebn. Zaved., Fiz., No. 2 (1983).
5. I.M. Sizova and A.P. Sukhorukov in: *Proceedings of the All-Union Conference on Ozone*, Dolgoprudnyi (1977).
6. I.M. Sizova and A.P. Sukhorukov, Izv. Akad. Nauk SSSR, FAO, **16**, No. 9, 917 (1980).