Ozone photodissociation at excitation within the Hartley absorption band. Analytical description of quantum yields $O_2(a^1\Delta_g, v = 0–3)$ depending on the wavelength

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In modern photochemical model of ozone dissociation excited in the Hartley absorption band (V.A. Yankovskii, R.O. Manuilova, Atmos. Oceanic Opt. **16**, No. 7, 536–540 (2003)), it is necessary to take into account the formation of metastable oxygen molecules in excited electron state $O_2(a^1\Delta_g, v)$ with a high-level vibrational excitation. In this paper, we propose an analytical approximation to describe wavelength dependence of the quantum yields of molecules in excited electron and vibrational states $O_2(a^1\Delta_g, v = 0–3)$ of the singlet channel of ozone photolysis in the Hartley band. We have derived a unified analytical formula for all quantum yields of the molecules $O_2(a^1\Delta_g, v)$ in excited electron and vibrational states. This formula allows for both the threshold of the corresponding vibrational level formation of an $O_2(a^1\Delta_g, v)$ molecule and the photon energy. The formula derived agrees with the experimental data available.

Introduction

The generally accepted model of ozone photodissociation in the Hartley, Huggins, and Shappuis bands and that of molecular oxygen dissociation in the Schumann–Runge continuum considers only three electron levels of oxygen molecule excitation ignoring the vibrational excitation, namely: the ground and two low singlet states $O_2(X^3\Sigma_g^-)$, $O_2(a^1\Delta_g)$, and $O_2(b^1\Sigma_g^+)$.[1] This simplified assumption is untenable in view of the experimentally proved facts that at ozone photodissociation in the Hartley, Huggins, and Shappuis bands an overwhelming fraction of products are in the excited electron and vibrational states. The modern photochemical model of ozone and oxygen dissociation takes into account formation of oxygen molecules excited to high-level electron and vibrational states not only at the O_3 and O_2 photolysis, but also in the processes of energy exchange between the photolysis products.[2]

Ozone photolysis in the Hartley band passes through two channels:

$$O_3 + h\nu \rightarrow O_2(X^3\Sigma_g^-, v = 0–35) + O(^3P), \quad (1)$$

$$O_3 + h\nu \rightarrow O_2(a^1\Delta_g, v) + O(^1D), \quad (2)$$

where (1) is the triplet channel and (2) is the singlet channel.

As the wavelength of photolytic radiation shortens, the products of ozone photolysis change: the higher vibration levels are excited ($O_2(X^3\Sigma_g^-, v)$ in the triplet and $O_2(a^1\Delta_g, v)$ in the singlet channels, respectively).

The wavelength dependence of quantum yields $O_2(X^3\Sigma_g^-, v)$ in the triplet channel has been statistically investigated in Ref. 3. The table of discrete values for the quantum yields for $O_2(X^3\Sigma_g^-, v = 0–35)$ has been obtained as a function of wavelength. It is necessary to emphasize that the tabulated values are inconvenient for analytical calculations and require subsequent interpolations. For the singlet channel, the experimental data have been measured, at the fixed wavelengths of photolytic radiation, since the beginning of 1980.[4–7] However, the data were not numerous and systematic. Yield of the vibrationally excited products of ozone photolysis was not taken into account in the calculations, though at the wavelength of 254 nm (peak of the Hartley band), a fraction of the vibrationally excited products in the channel (2) can reach 70%.

Table 1 presents the threshold values of wavelengths, starting from which an excitation of the indicated level of the O_2 molecule occurs.

Table 1. Threshold values of the wavelengths for the product formation of ozone photolysis in the Hartley band (200–310 nm) through the singlet channel

Products of ozone photolysis	$O_2(a^1\Delta_g, 0)$	$O_2(a^1\Delta_g, 1)$	$O_2(a^1\Delta_g, 2)$	$O_2(a^1\Delta_g, 3)$
Threshold values λ, nm	310	296	284	273

1. Quantum yields of the $O_2(a^1\Delta_g, v)$ molecule formation through the singlet channel of the ozone photolysis

For realization of the ozone photodissociation model in the Hartley band, it is necessary to know the wavelength dependence of the quantum yields $F(a^1\Delta_g, v)$ through the singlet channel of ozone photolysis. In such a formulation, this problem has never been solved. By the present time, we have collected rather a large experimental material on the quantum yields $F(a^1\Delta_g, v)$ of the vibrationally excited molecules $O_2(a^1\Delta_g, v)$, formed at ozone photolysis in the Hartley band. The quantum yields $F(a^1\Delta_g, v)$ have been obtained for the fixed wavelengths λ in the interval from 235 up to 293 nm and for the values of v = 0–3. All the known experimental data are presented in Table 2.

Table 2. Quantum yields of the excited vibrational energy levels of $O_2(a^1\Delta_g, v)$, forming at ozone photolysis in the Hartley band depending on the wavelength

λ, nm	$v = 0$	$v = 1$	$v = 2$	$v = 3$	Reference
235	0.30	0.24	0.15	0.07	7
240	0.64	0.15	0.08	0.04	5
245	0.34	0.23	0.20	0.08	7
248	0.49	0.15	0.15	0.08	6
248.5	0.60	0.18	0.09	0.05	5
255	0.39	0.30	0.14	0.10	7
265	0.44	0.32	0.14	0.10	7
266	0.57	0.24	0.12	0.07	4
266.5	0.52	0.27	0.14	0.07	7
275	0.59	0.26	0.15		7
275.5	0.61	0.27	0.12		6
280	0.70	0.30			6
280.5	0.70	0.22	0.08		5
285	0.71	0.29			7
285.5	0.76	0.24			6
293	0.76	0.24			5

It is necessary to note that in the papers cited the quantum yield $F_{a,v}$ of the $O_2(a^1\Delta_g, v)$ molecules was measured for the fixed wavelengths, indicated in the first column of the Table 2, depending on the vibrational level v, while for calculating the quantum yield efficiency the $F_{a,v} = F_{a,v}(\lambda)$ dependence at a fixed v value is needed. Recently, new data on the quantum yields have been published in Refs. 7 and 8, and therefore, we turned to the problem of $F_{a,v} = F_{a,v}(\lambda)$ approximation.

In the Ref. 8, an attempt was made calculate $F_{a,v}(v)$ theoretically for the fixed values of λ within the framework of classical and quantum-mechanical approaches. Results of this investigation for v = 0–3 are presented in Fig. 1.

A typical feature of the experimental data is the quantum yield $O_2(a^1\Delta_g, v)$ fall at increasing vibrational number v. The monotonic fall of $F_{a,v}$ at decreasing λ is observed only for $v = 0$, but for $v \geq 1$, the values of $F_{a,v}$ have weakly pronounced maxima at some wavelengths of the photolytic radiation.

Theoretical calculations carried out in the Ref. 8, are in a good agreement with the experimental data only for v = 0. For other values of v, theoretical calculations both in classical and in quantum-mechanical approaches, do not only agree with the experiment, but also among themselves, as we can see from Fig. 1.

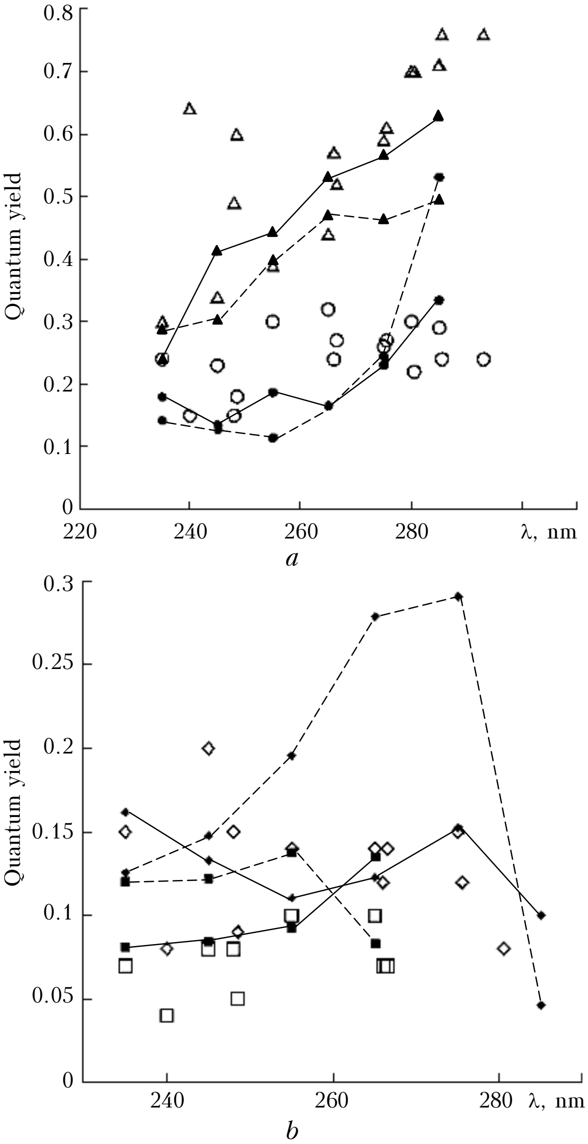

Fig. 1. Quantum yields of the $O_2(a^1\Delta_g$, v = 0–3) molecules, calculated within the framework of classical and quantum-mechanical approaches[8]: $v = 0$ and 1 (*a*); $v = 2, 3$ (*b*). Symbols are the experimental data (see Table 2): triangles ($v = 0$), circles ($v = 1$), rhombuses ($v = 2$), squares ($v = 3$), curves with the corresponding symbols are the theoretical calculation from Ref. 8 (solid lines represent the classical approach, dashed lines the quantum-mechanical approach).

Since the theory poorly agrees with the experimental data and cannot be used for calculating integrated quantum yields in the Hartley band, we have formulated a task to obtain approximations of the $F_{a,v}$ dependence on the wavelength for various vibrational quantum numbers.

2. Analytical description of the $F_{a,v}$ dependence on the wavelength

The specific feature of the photodissociation process is the threshold wavelengths, from which the next vibrational level $O_2(a^1\Delta_g, v)$ (see Table 1) starts to be excited.

Energy deficit of the reaction (2) is expressed by the formula

$$\Delta E = E - E_{DO_3} - E_{1D} - E_{a0}, \tag{3}$$

here E is the photon energy; E_{DO_3} is the energy of the ozone molecule dissociation (1.05 eV); E_{1D} is the excitation energy of $O(^1D)$ atom from the ground state of the oxygen atom (1.97 eV); E_{a0} is the energy of the $O_2(a^1\Delta_g, v = 0)$ level excitation relative to the ground state of the oxygen molecule (0.98 eV).

Hence, the quantum yield of $O_2(a^1\Delta_g, v = 0)$ is determined by the fraction of energy, necessary for excitation of this level, and corresponds to the physically obvious expression

$$F_{a,0}(x) = C_0 x, \tag{4}$$

where the parameter

$$x = \exp\left(-\frac{\Delta E}{E_{a0}}\right) \tag{5}$$

determines the fraction of $O_2(a^1\Delta_g, v = 0)$ molecules with energy higher than the excitation threshold of this level of the oxygen molecule (here ΔE was taken from Ref. 3).

Normalization coefficient C_0 is calculated so that the quantum yield of all vibrationally excited molecules in the singlet channel (2) is equal to unity and is numerically found from the normalization condition (4) in proximity of the long-wavelength threshold of the Hartley band:

$$C_0 = F_{a,0}(x_0)/x_0. \tag{6}$$

The next vibrational level of the $O_2(a^1\Delta_g, v = 1)$ molecule will be involved starting from the threshold energy for $v = 1$, as a fraction of molecules remaining after the $O_2(a^1\Delta_g, v = 0)$ excitation. Then the quantum yield $F_{a,1}$ will physically correspond to the obvious expression

$$F_{a,1}(x) = C_1 x(1 - x). \tag{7}$$

Normalization coefficient C_1 is calculated from the threshold excitation energy for $O_2(a^1\Delta_g, v = 1)$, but allowing for the constant of the preceding channel C_0:

$$\sum_{i=0}^{v} F_{a,i}(x_i) = 1. \tag{8}$$

It follows from Eq. (8) that

$$C_1 = \frac{1 - C_0 x_1}{x_1(1 - x_1)}. \tag{9}$$

As stated above, approximation of $F_{a,1}$ is valid for the values of energy higher than excitation threshold of $O_2(a^1\Delta_g, v = 1)$.

As follows from Fig. 2, the analytical formulas for $F_{a,v}$ well describe the experimental data for $v = 0$ and $v = 1$. It is typical that for $v = 0$, the value of $F_{a,0}$ monotonically falls with the decreasing λ, but for $v = 1$, $F_{a,1}$ has a maximum near 265 nm that well agrees with the known experimental data.

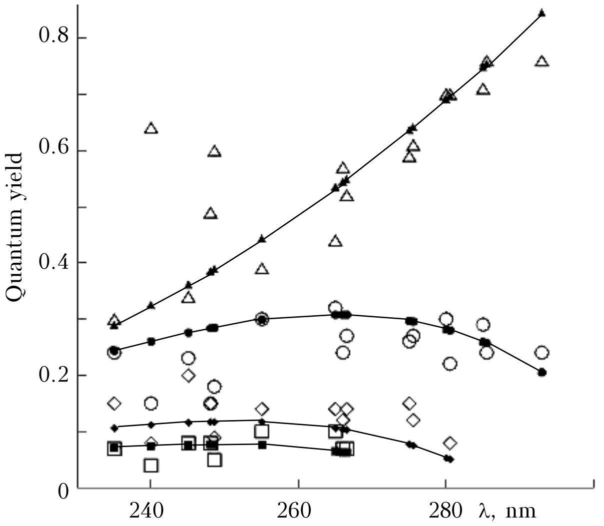

Fig. 2. Quantum yields of the $O_2(a^1\Delta_g, v = 0–3)$ molecules, calculated by the approximating formulas (14). Symbols are the experimental data (see Table 2): triangles ($v = 0$), circles ($v = 1$), rhombuses ($v = 2$), squares ($v = 3$), curves with corresponding symbol represent the data calculated by formula (14).

It is difficult to give simple physical interpretation for the higher vibrational quantum numbers, but analysis has shown that formulas for higher v can be formally constructed according to the principle analogous to that in Eqs. (4) and (7).

For the quantum yield of $O_2(a^1\Delta_g, v \geq 2)$

$$F_{a,2}(x) = C_2 x(1 - x - x^2/2), \tag{10}$$

where

$$C_2 = \frac{1 - C_0 x_2 - C_1 x_2(1 - x_2)}{x_2\left(1 - x_2 - \frac{x_2^2}{2}\right)}; \tag{11}$$

$$F_{a,3}(x) = C_3 x\left(1 - x - \frac{x^2}{2} - \frac{x^3}{4}\right), \tag{12}$$

and

$$C_3 = \frac{1 - C_0 x_3 - C_1 x_3(1 - x_3) - C_2 x_3\left(1 - x_3 - \frac{x_3^2}{2}\right)}{x_3\left(1 - x_3 - \frac{x_3^2}{2} - \frac{x_3^3}{4}\right)}. \tag{13}$$

And the general formula

$$F_{a,v}(x) = C_v x\left(1 - x - \frac{x^2}{2} - \frac{x^3}{2^2} - \frac{x^4}{2^3} - \ldots - \frac{x^v}{2^{v-1}}\right), \tag{14}$$

where

$$C_v = \left[1 - C_0 x_v - C_1 x_v(1 - x_v) - C_2 x_v\left(1 - x_v - \frac{x_v^2}{2}\right) - \ldots -\right.$$

$$-C_{v-1}x_v\left(1-x_v-\frac{x_v^2}{2}-\ldots-\frac{x_v^{v-1}}{2^{v-2}}\right)\Bigg]\Bigg/$$

$$\Bigg/x_v\left(1-x_v-\frac{x_v^2}{2}-\ldots-\frac{x_v^{v}}{2^{v-1}}\right) \qquad (15)$$

taking into account the normalization (8).

For calculating the normalization coefficient C_0 for $v = 0$, it was necessary to use the threshold value $\lambda = 310$ nm (see Table 1), however the quantum yield of such a level reaches its maximum value starting from $\lambda = 305$ nm, therefore, for calculating the normalization coefficient of this level, we used just this value of λ.

For calculation of the C_1 normalization coefficient for the $v = 1$ level, a threshold value of the vibrational level $v = 2$ was used, since the quantum yield of $F_{a,1}$ reaches its maximum value just at the moment, when the next vibrational level starts to be involved. Normalizations of the C_v coefficients for $v = 2$–3 were carried out according to the principle analogous to that in the case with C_1.

As follows from Fig. 2, the curves of the quantum yields approximations of $F_{a,v}$, on the whole, well agree with the known experimental data for all values of $v = 0$–3. Table 3 presents the used values of x_v and the normalization factors C_v (see Eq. (15)) for the corresponding vibrational levels of $O_2(a^1\Delta_g, v)$.

Table 3. Constants for calculation of the normalization coefficients

v	0	1	2	3
x_v	0.936	0.688	0.575	0.482
C_v	1.069	1.232	0.564	0.376

The analytical formulas proposed quite satisfactorily describe known experimental data and for higher values of $v = 4$–7 (see Ref. 7), but the available data are insufficient for statistical analysis.

3. Error in the calculated quantum yields $F_{a,v}$

Table 4 presents the root-mean-square deviations from the experimental data of quantum yields $F_{a,v}$, calculated by the approximating formulas (14) and within the framework of the classical and quantum-mechanical approaches from Ref. 8. Root-mean-square deviations $\sigma(F_{a,v})$ are calculated for all experimental points investigated at the present moment (parameter n in Table 4) depending on the wavelength. As follows from Table 4, the analytical expressions proposed in this paper essentially better describe the experimental data available by now.

Conventionally, in the models of ozone photolysis, the quantum yield is taken to be the same throughout the entire Hartley band, independent of the wavelength of photolytic radiation λ. Approximations of $F_{a,v}$ derived in this paper have allowed the integration of the quantum yields of ozone photolysis products over the wavelength λ to be performed within the framework of the model.[2]

Table 4. Root-mean-square deviations of the calculated quantum yields $F_{a,v}$ from the experimental data for all approximation models: the classical approach (*a*), the quantum-mechanical approach (*b*); *n* is the number of the experimental points used

$\sigma(F_{a,0})$	$\sigma(F_{a,1})$	$\sigma(F_{a,2})$	$\sigma(F_{a,3})$	Note
0.027	0.015	0.012	0.007	Given paper
0.029	0.020	0.011	0.014	Ref. 8 (*a*)
0.045	0.035	0.032	0.016	Ref. 8 (*b*)
16	16	13	9	*n*

4. Discussion and conclusions

At ozone photolysis in the Hartley band (2) through the singlet channel, the $O(^1D)$ atoms are formed along with the $O_2(a^1\Delta_g, v)$ molecules. Quantum yield of the $O(^1D)$ atoms is equal to the total quantum yield of the $O_2(a^1\Delta_g, v)$ molecules summed over all vibrational quantum numbers v.

Figure 3 presents the experimental data on the quantum yields of the $O(^1D)$ atoms, taken from Ref. 9 for $\lambda = 230$–310 nm. Besides, we have presented the experimental data from Ref. 10 on the quantum yields of the $O(^1D)$ atoms for the interval $\lambda = 193$–230 nm. The errors are shown in the figure by the vertical bars. Abnormally high errors of these experimental data are connected with the absence of systematic measurements in this region. For comparison, Fig. 3 also presents the total quantum yield of the $O_2(a^1\Delta_g, v)$ molecules calculated by the approximating formulas (14).

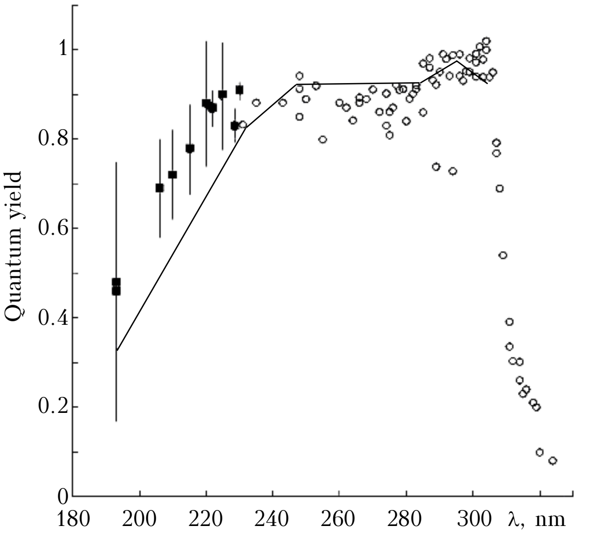

Fig. 3. Experimental data on quantum yields of the $O(^1D)$ atoms: squares together with the values of errors (Ref. 9), circles (Ref. 10); line is the total quantum yield of the $O_2(a^1\Delta_g, v)$ molecules, calculated by the approximating formulas.

The analytical formulas for description of the quantum yields $F_{a,v}$, proposed in this paper, are not the polynomial interpolation of the experimental data, therefore, it is possible to state the problem on extrapolation of the $F_{a,v}$ values to the interval of wavelengths $\lambda \leq 230$ nm. As follows from Fig. 3, such an extrapolation is close to the experimental data in the region of $\lambda = 193$–230 nm.[10] Moreover, the extrapolated values of the total quantum yield of the $O_2(a^1\Delta_g, v)$ molecules have the same dependence on wavelength, as the experimental data. We consider this a positive, though unexpected, result that confirms correctness of the approximation (14) chosen. Note also that the total quantum yield of the $O_2(a^1\Delta_g, v)$ molecules in this diagram is normalized to the quantum yield of the singlet channel of the ozone photolysis in the Hartley band in the interval of wavelengths from $\lambda = 230$ to 305 nm.

Acknowledgments

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