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Model of daytime emissions of electronically-vibrationally excited products of O₃ and O₂ photolysis: application to ozone retrieval

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Abstract. The traditional kinetics of electronically excited products of O₃ and O₂ photolysis is supplemented with the processes of the energy transfer between electronically-vibrationally excited levels O₂(a¹Δ_g, v) and O₂(b¹Σ_g⁺, v), excited atomic oxygen O(¹D), and the O₂ molecules in the ground electronic state O₂(X³Σ_g⁻, v). In contrast to the previous models of kinetics of O₂(a¹Δ_g) and O₂(b¹Σ_g⁺), our model takes into consideration the following basic facts: first, photolysis of O₃ and O₂ and the processes of energy exchange between the metastable products of photolysis involve generation of oxygen molecules on highly excited vibrational levels in all considered electronic states – b¹Σ_g⁺, a¹Δ_g and X³Σ_g⁻; second, the absorption of solar radiation not only leads to populating the electronic states on vibrational levels with vibrational quantum number v equal to 0 – O₂(b¹Σ_g⁺, v=0) (at 762 nm) and O₂(a¹Δ_g, v=0) (at 1.27 μm), but also leads to populating the excited electronic-vibrational states O₂(b¹Σ_g⁺, v=1) and O₂(b¹Σ_g⁺, v=2) (at 689 nm and 629 nm). The proposed model allows one to calculate not only the vertical profiles of the O₂(a¹Δ_g, v=0) and O₂(b¹Σ_g⁺, v=0) concentrations, but also the profiles of [O₂(a¹Δ_g, v≤5)], [O₂(b¹Σ_g⁺, v=1, 2)] and O₂(X³Σ_g⁻, v=1–35). In the altitude range 60–125 km, consideration of the electronic-vibrational kinetics significantly changes the calculated concentrations of the metastable oxygen molecules and reduces the discrepancy between the altitude profiles of ozone concentrations retrieved from the 762-nm and 1.27-μm emissions measured simultaneously.

Keywords. Atmospheric composition and structure (Airglow and aurora; Middle atmosphere – composition and chemistry; Thermosphere – composition and chemistry)

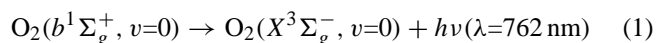
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1 Introduction

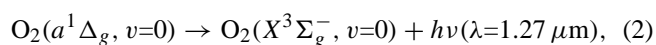
Measurements of radiation of electronically excited molecular oxygen in the Atmospheric band O₂(b¹Σ_g⁺, v=0→X³Σ_g⁻, v=0) at 762 nm and in the Infrared Atmospheric band O₂(a¹Δ_g, v=0→X³Σ_g⁻, v=0) at 1.27 μm are used for retrieving the altitude profile of ozone concentration (e.g. Thomas et al., 1984; Mlynarczyk et al., 2001). Interpretation of the measurements of emission at 1.27 μm is a well known method of determination of the altitude profile of ozone concentration, and emission at 762 nm was also suggested for this goal in Sica and Lowe (1993a, b). Both methods were realized in Mlynarczyk et al. (2001). Nowadays, interest in the models of these emissions grows due to the measurements in which both emissions were measured simultaneously in a rocket (Mlynarczyk et al., 2001) and especially in a satellite experiment (Murtagh et al., 2002).

Metastable molecules and atoms of oxygen are formed in the processes of photodissociation of ozone and oxygen molecules at absorption of ultra-violet radiation of the Sun. These excited products of O₃ and O₂ photolysis play an important role in the electronic-vibrational kinetics of O₂ molecules and in the heating of the middle atmosphere. The first commonly accepted model of electronic kinetics of these products was developed by Thomas (1984) and Harris and Adams (1983) and was significantly improved by Mlynarczyk et al. (1993). At present, the model of the electronic kinetics of the products of O₃ and O₂ photolysis, developed by Mlynarczyk et al. (1993), is used. Let's describe briefly the processes which were taken into account in this model. Photolysis of oxygen in the Schumann-Runge continuum and in the Lyman alpha (Lyman-α) line leads to the formation of the atomic oxygen in the first excited electronic state O(¹D). Photolysis of ozone in the Hartley band also leads to the formation of the O(¹D) atom and of the oxygen molecule in the first excited electronic singlet state O₂(a¹Δ_g). The processes of energy transfer from the O(¹D) state to the second

excited electronic state of the O₂ molecule O₂(b¹Σ_g⁺) and, further, to the first electronic excited state O₂(a¹Δ_g), play an important role in populating these two electronic states. All these excited states of atomic and molecular oxygen O(¹D), O₂(b¹Σ_g⁺), and O₂(a¹Δ_g) radiate. The corresponding O₂ emissions take place in the Atmospheric band:



and in the Infrared (IR) Atmospheric band:



where *v* is vibrational quantum number. These emissions are observed using a modern experimental technique. With the use of the kinetic scheme, suggested in Mlynchak et al. (1993), vertical profiles of the ozone abundance are retrieved from the observations of vertical profiles of these emissions (Mlynchak et al., 2001). At photolysis of ozone in the Hartley band, O₂(a¹Δ_g) is formed with the quantum yield about 90%. It seems evident that the Infrared Atmospheric band of O₂ at 1.27 μm (2), that is formed by transition from O₂(a¹Δ_g), is preferable for retrieving the profiles of ozone abundance. This point of view is traditional up to present. However, simultaneously with the production of O₂(a¹Δ_g), the O(¹D) atom is formed with the same quantum yield. Therefore, the ozone abundance retrieval could also be carried out using the emission from the state O₂(b¹Σ_g⁺) at 762 nm (Eq. 1). In the framework of the kinetic model suggested in Mlynchak et al. (1993), it is impossible to determine which method of retrieval is more accurate.

Beginning with the publications of the studies of Sparks et al. (1980), Valentini et al. (1987), Thelen et al. (1995), it has been known that the products of O₃ photolysis must also be vibrationally excited. Besides that, energy transfer from O(¹D) to O₂ leads to the formation of electronically-vibrationally excited molecules O₂(b¹Σ_g⁺, *v*) (Streit et al., 1976; Lee and Slinger, 1978). Mlynchak et al. (1993) supposed that vibrational kinetics can be neglected, which is possible only if the processes of vibrational-vibrational (V-V) and vibrational-translational (V-T) energy transfer between vibrational sublevels of electronic states are much faster than collisional deactivation of electronically excited states. However, the present laboratory and theoretical data on the kinetics of the excited products of ozone and oxygen photolysis (Hwang et al., 1999; Slinger and Copeland, 2003; Dylewski et al., 2001; Kalogerakis et al., 2002; Pejakovic et al., 2005) have given new information about the processes of energy exchange between electronic-vibrational levels, which are fast enough to compete with the processes of V-V and V-T energy exchange. These works made it necessary to create a model of electronic-vibrational kinetics of the excited products of O₃ and O₂ photolysis because the fast processes of energy exchange between electronically-vibrationally excited levels could not be considered in the framework of only electronic kinetics. It should also be

noted, that transitions O₂(b¹Σ_g⁺, *v*→X³Σ_g⁻, *v*') have also been observed in atmospheric experiments. Skinner and Hays (1985), analyzing the brightness of the Atmospheric band of O₂ in the daytime thermosphere measured by the Dynamic Explorer 2 in the altitude interval 60–300 km, took into account the contributions of transitions O₂(b¹Σ_g⁺, *v*→X³Σ_g⁻, *v*') for bands (0-0), (1-1), (2-2). We will show in this study that the traditional kinetics of electronically excited products of O₃ and O₂ photolysis should be supplemented with the processes of energy transfer between electronically-vibrationally excited levels O₂(a¹Δ_g, *v*) and O₂(b¹Σ_g⁺, *v*), excited atomic oxygen O(¹D) and the O₂ molecules in the ground electronic state O₂(X³Σ_g⁻, *v*). In contrast to the previous models of kinetics of O₂(a¹Δ_g) and O₂(b¹Σ_g⁺), our model takes into consideration the following basic facts: first, photolysis of O₃ and O₂ and the processes of energy exchange between the metastable products of photolysis involve generation of oxygen molecules on highly excited vibrational levels in all considered electronic states – b¹Σ_g⁺, a¹Δ_g and X³Σ_g⁻; second, the absorption of solar radiation not only leads to populating the electronic states on vibrational levels with vibrational quantum number *v* equal to 0 – O₂(b¹Σ_g⁺, *v*=0) (at 762 nm) and O₂(a¹Δ_g, *v*=0) (at 1.27 μm), but also leads to populating the excited electronic-vibrational states O₂(b¹Σ_g⁺, *v*=1) and O₂(b¹Σ_g⁺, *v*=2) (at the 689 nm and 629 nm). In the framework of this study we will compare the models of pure electronic and electronic-vibrational kinetics and show the difference between the two models for the direct problem of calculations of the volume emission rates of the 762-nm and 1.27-μm bands and for the inverse problem of ozone retrieval from both emissions. As it will be shown below, considering the electronic-vibrational kinetics significantly changes the calculated concentrations of the metastable oxygen molecules above 60 km and reduces the discrepancy between the altitude profiles of ozone concentrations retrieved from the 762-nm and 1.27-μm emissions measured simultaneously.

2 Kinetics of electronically-vibrationally excited products of O₃ and O₂ photodissociation in the middle atmosphere

In Fig. 1, the scheme of electronic-vibrational kinetics of the products of O₃ and O₂ photolysis is presented. The excited electronic states are shown by bold lines, and the vibrational levels of these electronic states are shown by thin lines. The vibrational number is denoted by the letter *v*. The circles with italic letters in Fig. 1 denote all types of processes that were taken into account. References to the values of the rates of photodissociation of O₂ and O₃ and of photoexcitation of O₂ used in this study are presented in Table 1, and references to the values of the rate constants of the considered processes are presented in Tables 2–5. Let's describe the processes under consideration.

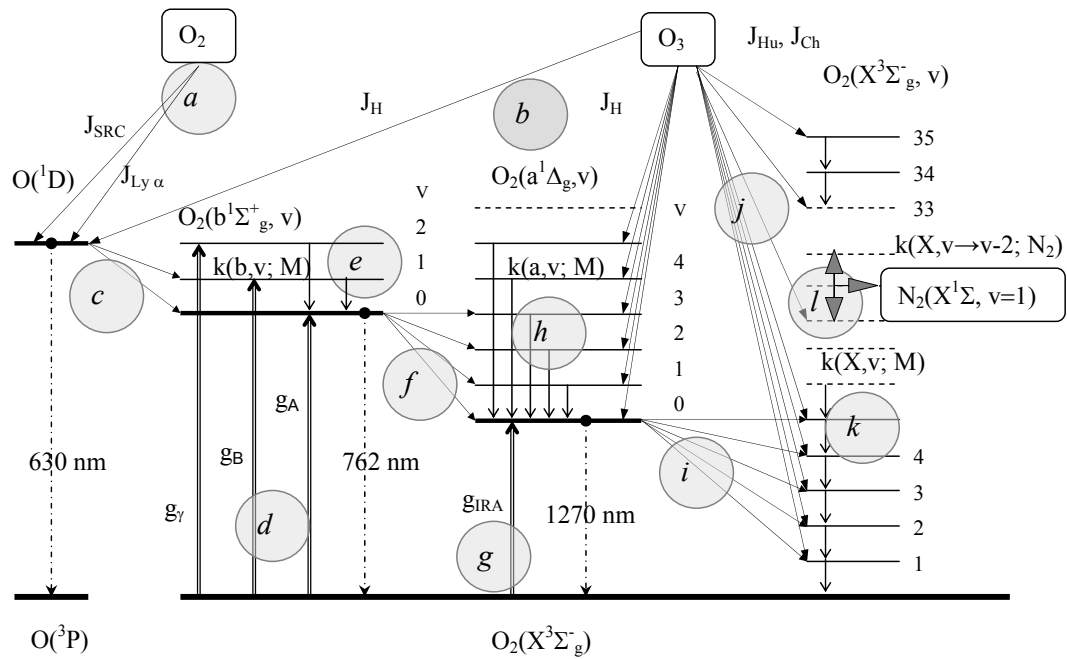


Fig. 1. The scheme of electronic-vibrational kinetics of the products of O₃ and O₂ photolysis in the middle atmosphere.

Table 1. Processes of O₂ and O₃ photodissociation and photoexcitation. Short notations for electronically excited states of oxygen molecule in Tables 1–5: O₂(b¹Σ_g⁺, v)=O₂(b, v), O₂(a¹Δ_g, v)=O₂(a, v), O₂(X³Σ_g⁻, v)=O₂(X, v). J – rate of photodissociation and photoexcitation at the top of the atmosphere, F – quantum yield of the products.

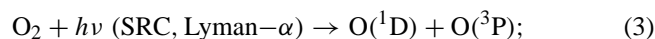
Reaction	J (s ⁻¹)	F	Ref.
O ₂ +hν(SRC)→O(³ P)+O(¹ D)	2.60×10 ⁻⁶	1.0	Rodrigo et al. (1986), DeMore et al. (1997)
O ₂ +hν(Lyman-α)→O(³ P)+O(¹ D)	3.40×10 ⁻⁹	0.48–0.58	Rodrigo et al. (1986), Reddmann and Uhl (2003)
O ₃ +hν→O ₂ (X, v=0–35)+O(³ P)	8.00×10 ⁻³	0.10*	Svanberg et al. (1995)
O ₃ +hν→O ₂ (a, 5)+O(¹ D)		0.045*	Michelson et al. (1994),
O ₃ +hν→O ₂ (a, 4)+O(¹ D)		0.072*	Sparks et al. (1980),
O ₃ +hν→O ₂ (a, 3)+O(¹ D)		0.072*	Thelen et al. (1995),
O ₃ +hν→O ₂ (a, 2)+O(¹ D)		0.135*	Valentini et al. (1987),
O ₃ +hν→O ₂ (a, 1)+O(¹ D)		0.135*	Ball et al. (1995),
O ₃ +hν→O ₂ (a, 0)+O(¹ D)		0.441*	Klais et al. (1980), DeMore et al. (1997), Dylewski et al. (2001)
O ₂ +hν(762 nm band)→O ₂ (b, 0)	5.35×10 ⁻⁹		Bucholtz et al. (1986), Mlynarczyk et al. (1996)
O ₂ +hν (689 nm band)→O ₂ (b, 1)	2.94×10 ⁻¹⁰		
O ₂ +hν (629 nm band)→O ₂ (b, 2)	7.94×10 ⁻¹²		
O ₂ +hν (1.27 μm)→O ₂ (a, 0)	1.54×10 ⁻¹⁰		

* – Presented values are quantum yields for λ=254 nm, however, all calculations of the rate of O₃ photodissociation in the Hartley band are carried out for the values of quantum yields depending on wave length (Yankovsky and Kuleshova, 2006).

Table 2. Processes of O(¹D) deactivation. A – Einstein coefficient, K – rate constant of reaction, other symbols as in Table 1.

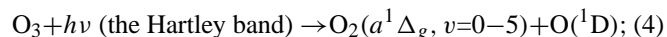
Reaction	A (s ⁻¹), K (cm ³ s ⁻¹)	F	Ref.
O(¹ D)→O+hν (630 nm)	9.0×10 ⁻³		DeMore et al. (1997)
O(¹ D) + O → 2O	4.0×10 ⁻¹²		Yee et al. (1990)
O(¹ D)+O ₂ →O ₂ (b, 1)+O	3.2×10 ⁻¹¹ e ^{67/T}	0.40	Streit et al. (1976), Lee and Slanger (1978), Green et al. (2000)
O(¹ D)+O ₂ →O ₂ (b, 0)+O		0.55	
O(¹ D)+O ₂ →O ₂ (a, 0 or X, 0)+O		≤0.05	
O(¹ D)+O ₃ →2O ₂	2.4×10 ⁻¹⁰		Atkinson et al. (1997)
O(¹ D)+N ₂ →O+N ₂	2.0×10 ⁻¹¹ e ^{107/T}	0.67	DeMore et al. (1997), Tully (1974)
O(¹ D)+N ₂ →O+N ₂ (v≤7)		0.33	

a – photolysis of O₂ in the Schumann-Runge continuum (SRC) in the 120–174-nm region and in the Lyman-α line (Table 1):

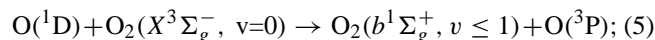


these processes are the main sources of O(¹D) atoms above 80 km (e.g. Rodrigo et al., 1986);

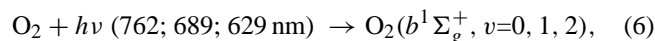
b – photolysis of O₃ in the singlet channel (the Hartley band at 200–310 nm) (Table 1):



c – EE' transfer of electronic excitation energy from the O(¹D) atom to the oxygen molecule. The process of energy transfer from O(¹D) excites not only vibrational level 0, but also vibrational level 1 of the electronic state O₂(b¹Σ_g⁺) (Table 2):

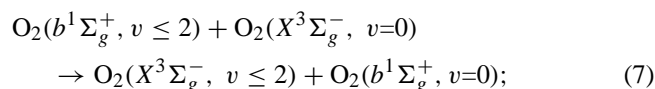


d – excitation of all three considered vibrational levels of the electronic state O₂(b¹Σ_g⁺) due to direct absorption of solar radiation. The rates of absorption at 762, 689 and 629 nm were taken from Bucholtz et al. (1986); Mlynczak and Marshall (1996) (Table 1):



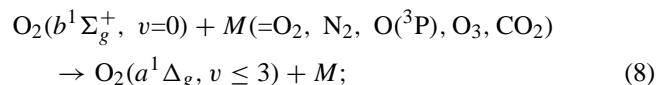
respectively;

e – quenching of vibrational excitation of O₂(b¹Σ_g⁺, v≥1) due to intramolecular near resonance electronic-electronic (EE) exchange (Table 3):

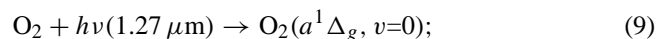


a specific feature of this type of reaction is that the electronic level changes in the initially excited oxygen molecule, while the vibrational quantum number v remains unchanged, and electronic excitation transfers to the collisional partner. Such reactions are from 2 to 3 orders of magnitude faster than the reactions of intermolecular energy transfer between electronic levels (reactions of the type **f** in Fig. 1);

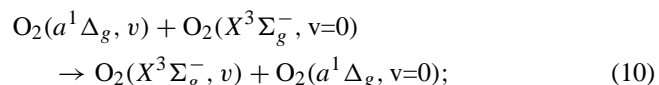
f – formation of O₂(a¹Δ_g, v=0–3) at collisional quenching of O₂(b¹Σ_g⁺, v=0) by the electronic-vibrational (EV) type of the energy exchange (Table 2):



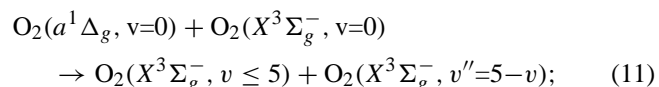
g – the process of excitation of O₂(a¹Δ_g, v=0) due to direct absorption of solar radiation (Table 1):



h – the process of EE quenching of O₂(a¹Δ_g, v), similar to the channel **e** (Table 4):



i – quenching of O₂(a¹Δ_g, v=0) of the type similar to EV-exchange (Table 4):



j – excitation of the vibrational levels of the ground electronic state O₂(X³Σ_g⁻, v) at ozone photolysis in the triplet channel (the Hartley, Huggins, and Chappius bands in the region from 200 to 600 nm); these levels are excited up to v=35 (Table 1):

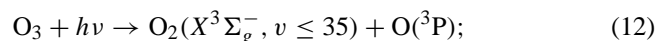
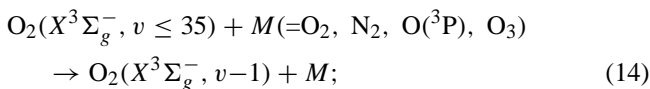
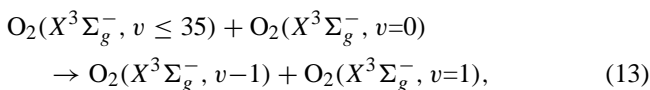


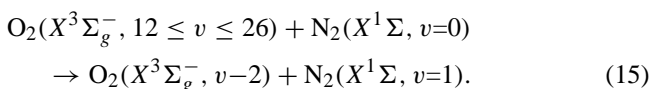
Table 3. Processes of deactivation of O₂(b¹Σ_g⁺, v). Symbols as in Tables 1 and 2.

Reaction	A (s ⁻¹), K (cm ³ s ⁻¹)	F	Ref.
O ₂ (b, 2) → O ₂ (X, 2)+hν (780 nm)	5.4 × 10 ⁻²		Yankovsky (1991)
O ₂ (b, 2)+O → O ₂ (b, 1)+O	1.1 × 10 ⁻¹¹		
O ₂ (b, 2)+O ₂ → O ₂ (X, 2)+O ₂ (b, 0)	1.2 × 10 ⁻¹¹ e ^{-596/T} 3.15 × 10 ⁻¹²		Kalogerakis et al. (2002), Yankovsky (1991)
O ₂ (b, 2)+N ₂ → O ₂ (b, 1)+N ₂	<2 × 10 ⁻¹⁴		Hwang et al. (1999)
O ₂ (b, 2)+O ₃ → 2O ₂ +O	2.9 × 10 ⁻¹⁰		Yankovsky (1991)
O ₂ (b, 1) → O ₂ (X, 1)+hν (771 nm)	7.0 × 10 ⁻²		Krupenie (1972)
O ₂ (b, 1)+O → O ₂ (b, 0)+O	4.5 × 10 ⁻¹²		Pejakovic et al. (2005)
O ₂ (b, 1)+O ₂ → O ₂ (X, 1)+O ₂ (b, 0)	4.2 × 10 ⁻¹¹ e ^{-312/T}		Kalogerakis et al. (2002)
O ₂ (b, 1)+N ₂ → O ₂ (b, 0)+N ₂	<5 × 10 ⁻¹³		Hwang et al. (1999)
O ₂ (b, 1)+O ₃ → 2O ₂ +O	<3 × 10 ⁻¹⁰		Yankovsky (1991)
O ₂ (b, 0) → O ₂ (X, 0)+hν (762 nm)	7.58 × 10 ⁻²		Mlynczak et al. (1993)
O ₂ (b, 0)+O → O ₂ (a, 0)+O	8.0 × 10 ⁻¹⁴	0.75	Atkinson et al. (1997), Hady-Ziane et al. (1992)
O ₂ (b, 0)+O → O ₂ (X, 0)+O		0.25	
O ₂ (b, 0)+O ₂ → O ₂ (a, 0)+O ₂ (X, 3)		0.230	
O ₂ (b, 0)+O ₂ → O ₂ (a, 1)+O ₂ (X, 2)	3.9 × 10 ⁻¹⁷	0.525	Klingshirn and Maier (1985)
O ₂ (b, 0)+O ₂ → O ₂ (a, 2)+O ₂ (X, 1)		0.226	
O ₂ (b, 0)+O ₂ → O ₂ (a, 3)+O ₂ (X, 0)		0.019	
O ₂ (b, 0)+N ₂ → products	2.1 × 10 ⁻¹⁵		Atkinson et al. (1997), see text
O ₂ (b, 0)+CO ₂ → O ₂ (a, 0)+CO ₂	4.2 × 10 ⁻¹³		Atkinson et al. (1997)
O ₂ (b, 0)+O ₃ → O ₂ (a, 0)+O ₃	2.2 × 10 ⁻¹¹	0.3	Amimoto et al. (1980), Atkinson et al. (1997)

k – the processes of vibrational-vibrational (V-V) and vibrational-translational (V-T) deexcitation of vibrational levels O₂(X³Σ_g⁻, v) for v=1–35 (Table 5):



l – the process of VV two-quantum transition in collisions of O₂(X³Σ_g⁻, v) with N₂ for v=12–26 (Table 5):



The vibrational levels of the ground electronic state are populated by the processes of electronic-vibrational (EV) energy exchange with the state O₂(a¹Δ_g, v=0) (Eq. 11). As it was noted above, at ozone photolysis in the Hartley, Huggins and Chappius bands, the vibrational levels of the ground electronic level O₂(X³Σ_g⁻, v) are excited up to the value of v=35 (Eq. 12). Other processes which populate vibrational levels are the processes of EE exchange with the corresponding levels of the electronic states O₂(b¹Σ_g⁺, v) for v=0–2 (Eq. 6) and O₂(a¹Δ_g, v) for v=1–5 (Eq. 10).

In Table 1 the rates of photodissociation of O₂ and O₃ and of photoexcitation of O₂(b¹Σ_g⁺, v) and O₂(a¹Δ_g, v=0) used in this study are presented. The quantum yield of O(¹D) formation in the O₂ photolysis in the Schumann-Runge continuum is equal to 1 (DeMore et al., 1997). For O₃ photolysis in

Table 4. Processes of deactivation of O₂(a¹Δ_g, v). Symbols as in Tables 1 and 2.

Reaction	A (s ⁻¹), K (cm ³ s ⁻¹)	F	Ref.
O ₂ (a, 0)→O ₂ (X, 0)+hν (1.27 μm)	2.58×10 ⁻⁴		Krupenie (1972)
O ₂ (a, v≥1)→O ₂ +hν	2.58×10 ⁻⁴		as O ₂ (a, 0)→O ₂ +hν
O ₂ (a, v≥3)+O ₂ →O ₂ (X, v)+O ₂ (a, 0)	3.6×10 ⁻¹¹		see text
O ₂ (a, 2)+O ₂ →O ₂ (X, 2)+O ₂ (a, 0)	3.6×10 ⁻¹¹		Slanger and Copeland (2003)
O ₂ (a, v≥1)+O→O ₂ +O	10 ⁻¹³ –10 ⁻¹⁶		see text
O ₂ (a, 1)+O ₂ →O ₂ (X, 1)+O ₂ (a, 0)	5.6×10 ⁻¹¹		Slanger and Copeland (2003)
O ₂ (a, 1)+O ₃ →2×O ₂ +O	4.7×10 ⁻¹²		Klais et al. (1980)
O ₂ (a, 0)+O→O ₂ +O	6.5×10 ⁻¹⁷		Lopez-Gonzalez et al. (1992)
O ₂ (a, 0)+O ₂ →O ₂ (X, 5)+O ₂ (X, 0)		0.014	Atkinson et al. (1997), Wild et al. (1984)
O ₂ (a, 0)+O ₂ →O ₂ (X, 4)+O ₂ (X, 1)	3.6×10 ⁻¹⁸ e ^{-220/T}	0.214	
O ₂ (a, 0)+O ₂ →O ₂ (X, 3)+O ₂ (X, 2)		0.772	
O ₂ (a, 0)+O ₃ →O ₂ +O ₃	5.2×10 ⁻¹¹ e ^{-2840/T}		Atkinson et al. (1997)
O ₂ (a, 0)+N ₂ →O ₂ +N ₂	1.0×10 ⁻²⁰		DeMore et al. (1997)

Table 5. Processes of energy transfer and deactivation of O₂(X³Σ_g⁻, v). Symbols as in Tables 1 and 2.

Reaction	K (cm ³ s ⁻¹)	F	Ref.
O ₃ +O→O ₂ (X, v=0–30)+O ₂	5.6×10 ⁻¹² e ^{-1959/T}	F(v)	Balakrishnan and Billing (1996)
O ₂ (X, v≥5)+O→O ₂ +O	K _{VT} =5×10 ⁻¹¹ ×(T/300) ^{0.5}		Breig (1969), Webster and Bair (1972)
O ₂ (X, v=2–4)+O→O ₂ +O	K _{VT} (v)*=1.1×10 ⁻¹² ×(T/300) e ^{1.0·v}		
O ₂ (X, v=1)+O→O ₂ +O	K _{VT} =3×10 ⁻¹²		Slanger and Copeland (2003)
O ₂ (X, v)+O ₂ →O ₂ (X, v-1)+O ₂ (X, v=1)	K _{VV} (v=2)=2.0×10 ⁻¹³ K _{VV} (v=3)=2.6×10 ⁻¹³		Kalogerakis et al. (2005)
O ₂ (X, v=4–20)+O ₂ →O ₂ (X, v-1)+O ₂ (X, 1)	K _{VV} (v)*=1.3×10 ⁻¹² e ^{-0.31·v}		Slanger (1997), Coletti and Billing (2002)
O ₂ (X, v>20)+O ₂ →O ₂ (X, v-1)+O ₂	K _{VT} (v)*=6×10 ⁻¹⁷ ×(T/300) e ^{0.2·v}		
O ₂ (X, v=12–17)+N ₂ →O ₂ (X, v-2)+N ₂ (X, v=1)	K _{VV'} (v)*=3.6×10 ⁻¹⁹ e ^{0.66·v}		Slanger (1997)
O ₂ (X, v=18–26)+N ₂ →O ₂ (X, v-2)+N ₂ (X, v=1)	K _{VV'} (v)*=4.5×10 ⁻¹³ e ^{-0.173·v}		
O ₂ (X, v=1)+O ₂ →2O ₂	K _{VT} =4.2×10 ⁻¹⁹ ×(T/300) ^{0.5}		Lopez-Puertas et al. (1995)
O ₂ (X, v=1)+N ₂ →O ₂ +N ₂ (X, v=1)	K _{VV'} (v)=4.2×10 ⁻¹⁹ ×(T/300) ^{0.5}		

K_{VV}(v)*, K_{VT}(v)* – approximations of the experimental data made by the authors and used in this study.

the Hartley bands, the spectral dependence of quantum yield of O(¹D) and, correspondingly, of O₂(a¹Δ_g), is known in detail (Michelsen et al., 1994). For O₂(a¹Δ_g, v), the quantum yields significantly depend on wave length (Sparks et al., 1980; Valentini et al., 1987; Thelen et al., 1995). The quantum yields of O₂(a¹Δ_g, v) were measured for 6 wavelengths for v=0–7 from 235 to 285 nm (Dylewski et al., 2001). These data show that the part of the electronically-vibrationally excited molecules produced at O₃ photolysis changes from 30% at 285 nm to 70% at 235 nm. At the Hartley band maximum in the region of 254 nm this part is about 60%. This is why for O₂(a¹Δ_g, v) the quantum yields should be known at all wavelengths. With the purpose of presenting the quantum yield as a function of wavelength, we constructed interpolated formulas for quantum yield dependence on the wave numbers in the whole interval of the Hartley band 200–320 nm, for all vibrational quantum numbers from 0 to 5 (Yankovsky and Kuleshova, 2006), using all published experimental data. In particular, it enables us to calculate the total production rate of O₂(a¹Δ_g, v) in O₃ photodissociation in the Hartley band by integration of these functions, the rates of photodissociation and the cross sections of solar radiation absorption over the wavelength. The vibrational levels with v equal to 6 and 7 are excited by radiation, with the wavelength shorter than 240 nm, for which the cross section of O₂ absorption is small and the processes of excitation of the levels with v=6, 7 can be neglected.

The triplet channel of O₃ photodissociation in the Hartley band gives the formation of O₂(X³Σ_g[−], v=0–35). The quantum yields of O₂(X³Σ_g[−], v) also depend significantly on the wavelength. We used the calculations of the quantum yields of O₂(X³Σ_g[−], v) in the Hartley band from Svanberg et al. (1995). At O₃ photodissociation in the Chappius and Huggins bands the levels O₂(X³Σ_g[−], v) are formed at v=0–15. The cross section of the absorption of solar radiation in the Chappius and Huggins bands is small, so the O₃ photodissociation in the Chappius and Huggins bands does not influence the production of O₂(X³Σ_g[−], v) significantly.

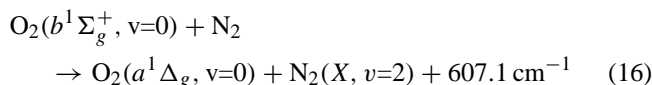
In Table 2, the Einstein coefficient for emission of O(¹D) at 630 nm and the rate constants of O(¹D) deexcitation at collisional processes, as well as the quantum yields of electronically-vibrationally excited products of these processes, are presented. In Green et al. (2000) the total quantum yield of O₂(b¹Σ_g⁺, v≥0) in the reaction O(¹D)+O₂→O₂(b¹Σ_g⁺, v≥0)+O was estimated to be equal to 0.95. In correspondence with the value of the total quantum yield we calculated the quantum yields of O₂(b¹Σ_g⁺, v=1) and O₂(b¹Σ_g⁺, v=0), based on the results of Lee and Slanger (1978).

In Table 3, the Einstein coefficients for emissions of O₂(b¹Σ_g⁺, v) at 780, 771, and 762 nm and the rate constants of deexcitation of O₂(b¹Σ_g⁺, v) at collisional processes, as well as the quantum yields of O₂(a¹Δ_g, v) and O₂(X³Σ_g[−], v) for v from 0 to 3 formed in these processes, are presented.

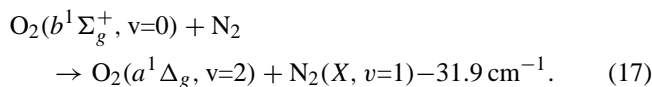
The rate constant of the reaction O₂(b¹Σ_g⁺, v=2)+O₂(X³Σ_g[−], v=0)→O₂(X³Σ_g[−], v=2)+O₂(b¹Σ_g⁺, v=0) was measured in the experiment of Kalogerakis et al. (2002) in the temperature range 110–298 K and in the experiment of Yankovsky (1991) in the range 340–445 K. Both sets of the data correspond to each other. In our calculations we used our approximation of the data of Kalogerakis et al. (2002).

For processes of deexcitation of the states O₂(b¹Σ_g⁺, v=1, 2) by N₂ only the upper limit of the values of the rate constants are known. Our estimations show that these reactions don't influence the populations of the states O₂(b¹Σ_g⁺, v=1, 2). In Tables 3 and 4 the processes of quenching the states O₂(b¹Σ_g⁺, v) and O₂(a¹Δ_g, v) at collisions with O₃ are shown in connection with high values of the rate constants of these processes. However, in the mesosphere the role of such processes is insignificant because of low abundance of ozone.

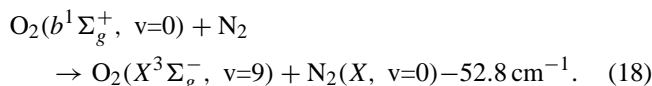
We should discuss the influence of the possible values of quantum yields of the products of the reaction of quenching of O₂(b¹Σ_g⁺, v=0) by N₂. In the model of Mlynarczyk et al. (1993) it is supposed that the quantum yield F(a, 0) of the process



is equal to 1. However, the rate constant of the reaction of quenching of O₂(b¹Σ_g⁺, v=0) by N₂ is almost 100 times greater than the rate constant of the reaction of quenching O₂(b¹Σ_g⁺, v=0) by O₂. In the framework of electronic-vibrational kinetics, possible pathways of the process of quenching of O₂(b¹Σ_g⁺, v=0) by N₂ should be considered. The relatively high value of the rate constant for quenching by N₂, led Braithwaite et al. (1976) to the suggestion that the following quasi-resonance process might exist:



However, another quasi-resonance process is also possible:



There is no information about possible values of the quantum yields of the products of this reaction; however, the ratio between the two pathways of the reaction influence distinctly the ozone concentration retrieval at the region of the second ozone maximum. This is why we consider the suggestion that both quasi-resonance processes (Eqs. 17, 18) exist and are assumed to have the same values of the quantum yields O₂(a¹Δ_g, v=2), F(a, 2), and O₂(X³Σ_g[−], v=9), F(X, 9). For our calculations we used F(a, 2) and F(X, 9) equal to 0.5.

In Table 4, the Einstein coefficients for emission of O₂(a¹Δ_g, v) and the rate constants of deexcitation of O₂(a¹Δ_g, v) at collisional processes are presented. The Einstein coefficient for emission of O₂(a¹Δ_g, v=0) at 1.27 μm

was taken from Krupenie (1972). For the Einstein coefficients for emissions of O₂(a¹Δ_g, v=1–5) the same value was used, because the experimental data are absent. However, radiative deexcitation of O₂(a¹Δ_g, v≥1) can be neglected in the calculations of O₂(a¹Δ_g, v) concentration, due to the fact that the rate of radiative deexcitation is much smaller than the rates of deexcitation at collisions with O₂ (Slanger and Copeland, 2003).

The rate constants of deexcitation of O₂(a¹Δ_g, v≥3) in collisions with O₂ have not been measured and for these processes we used the value of the rate constant of the process O₂(a¹Δ_g, v=2)+O₂ that was measured by Slanger and Copeland (2003). For the processes of collisions of O₂(a¹Δ_g, v≥1) with atomic oxygen the rate constants have not been measured either. So we varied the values of the rate constants of these processes from 10^{−13} to 10^{−16} cm³ s^{−1}. Even for such a broad range of the values of the rate constants these processes do not affect the results of the calculations of O₂(a¹Δ_g, v=0) concentration. In Table 4 the quantum yields of O₂(X³Σ_g[−], v=0–5) in the reaction of collisions of O₂(a¹Δ_g, v=0) with O₂ (Wild et al., 1984) are presented.

The values of the rate constants of the reactions of deexcitation of electronically-vibrationally excited O₂ molecules O₂(a¹Δ_g, v≥1) at collisions with N₂ are so small that such processes do not affect the populations of electronic-vibrational levels under consideration in comparison with the processes of deexcitation at collisions with molecular oxygen. For estimations we used the maximum value for these rate constants 8.4×10^{−14} cm³ s^{−1} from Klais et al. (1980), which is two orders of magnitude smaller than the rate constants of the processes of deexcitation at collisions with molecular oxygen.

The role of quenching electronically excited molecules O₂(a¹Δ_g, v=0) by N₂ is significant, and the corresponding process was taken into account (see Table 4).

In Table 5 the rate constants of V-V and V-T processes of O₂(X³Σ_g[−], v) collisional excitation and deexcitation are presented. In order to calculate the populations of vibrational levels for v=1–35, approximations of the dependencies of rate constants on vibrational quantum numbers on the basis of the known experimental data must be carried out. The presented approximations (see Table 5) give a convenient form for the calculations of the values of the rate constants used in our model within the limits of experimental data errors. With the purpose of constructing kinetic equations for v≤35, the rate constants of V-T deexcitation of O₂(X³Σ_g[−], v) in collisions with O₂ calculated for v≤30 (Coletti and Billing, 2002) were extrapolated for v≤35.

The ozone and oxygen photodissociation is a non-equilibrium stationary process. For a description of such kind of processes, using the principle of detailed equilibrium is inapplicable for the calculation of the rate constant of the inverse process of the upper state excitation by the transition from the lower state. This is why we don't use the princi-

ple of detailed equilibrium for calculations of populations of the considered electronic-vibrational states. For inverse processes of V-V and V-T energy transfer between vibrational states of the ground electronic state O₂(X³Σ_g[−], v), we use the rate constants calculated by Billing et al. (1992); Coletti and Billing (2002) from the measured cross sections of collisional reactions. The inverse processes of populating the electronically-vibrationally excited states O₂(b¹Σ_g⁺, v) and O₂(a¹Δ_g, v) are insignificant in comparison with the processes of populating from the upper states or directly by photodissociation, because the energy difference is greater than 1 eV. The estimations show that in our model we can neglect these processes.

The experimental methods of the measurements of the rate constants of deexcitation processes could be conventionally divided into two groups: measurements for low (200–400 K) and those for high temperatures, for example, experiments in shock tubes, which were carried out at the temperatures of higher than one thousand Kelvins. It should be noted that at high temperatures the measured rate constant might be a superposition of the rate constants for several states (Polack, 1979). In accordance with the atmospheric conditions, we use the values of the rate constants measured in the temperature interval 150–350 K.

At conditions when the local thermodynamic equilibrium (LTE) for electronic-vibrational states does not exist, the populations of the states are calculated by solving the system of kinetic equations for all 45 electronic-vibrational states under consideration: the first excited state of atomic oxygen, O(¹D), three states of O₂(b¹Σ_g⁺, v), six states of O₂(a¹Δ_g, v) and 35 states of O₂(X³Σ_g[−], v).

The populations of the states of these excited species are described by the system of differential equations:

$$\frac{\partial n_i}{\partial t} = \sum_{k \neq i} (n_k \cdot p_{i,k}) - n_i \cdot q_i + F_i, \quad (19)$$

where i – the state number ($i=1-45$), n_i – the population of the i -th state, $p_{i,k}$ – the production rate of species i from species k ($k=1-45$, $k \neq i$) in collisional processes of energy transfer, q_i – the total loss rate of species i in the processes of collisional and radiative deactivation, F_i – the volume production rate of the i -th species in the processes of photolysis of O₂ and O₃ molecules and in chemical reactions (for example, in the reaction of collision of O with O₃).

Then the system of differential Eqs. (19) can be presented as a matrix equation for the vector of the state populations \mathbf{n}

$$\frac{\partial \mathbf{n}}{\partial t} = \mathbf{A} \cdot \mathbf{n} + \mathbf{F}. \quad (20)$$

We are solving a stationary problem. In this case the system of equations is written as a linear algebraic system

$$\mathbf{n} = \mathbf{A}^{-1} \cdot \mathbf{F}. \quad (21)$$

The matrix \mathbf{A} is a quasi-diagonal square sparse matrix. The method of solving the system of equations is described in

Olemskoy (2006). In order to derive the ozone concentration from the measured intensities of emissions, the system of implicit algebraic equations is solved by the method of parameter fitting.

The computer code for calculating the rate of photodissociation of ozone and molecular oxygen, taking into account the spectral dependence of quantum yields of the products of O₂ and O₃ photolysis in the interval of wavelengths from 120 to 850 nm, was developed. The computer code enables us to calculate the rates of: 1) the formation of O(¹D) atoms in the O₂ photolysis in the Schumann-Runge continuum and in the Lyman- α line (3) and O₃ photolysis in the Hartley band (4); 2) the formation of O₂(a¹ Δ_g , v) in O₃ photolysis in the Hartley band (4); 3) the formation of O₂(X³ Σ_g^- , v) in O₃ photolysis in the Hartley, Chappius and Huggins bands (12) for different solar zenith angles (from -80° to 80° SZA). In our calculations of the photodissociation rate, the model of photodissociation in the Schumann-Runge continuum, suggested by DeMajistre et al. (2001), and the model of photodissociation in the Schumann-Runge bands, suggested by Koppers and Murtagh (1996), were used. In the code model MSIS 90 was used for the main atmospheric constituents, the O₃ model was taken from Keating et al. (1989), the atomic oxygen model was taken from Llewellyn and McDade (1996), the CO₂ model was taken from Kauffmann et al. (2002). The solar spectrum was taken from Allen and Frederick (1982). The photodissociation cross sections of the solar radiation for the Hartley bands were taken from DeMore et al. (1997).

In this way, the developed method enables us to calculate the altitude profiles of the concentration of O₂ molecules in any considered electronic-vibrational state in the middle atmosphere. However, at present, only the information about the populations of O₂(a¹ Δ_g , v=0) and O₂(b¹ Σ_g^+ , v=0) can be obtained from the atmospheric experiments. In principle, the formulation and solution of the inverse problem for any state under consideration is possible, but the accuracy of the solution for upper states decreases because the values of the rate constants are less known and the populations of these states are much smaller than for the lower states.

3 Concentrations of electronically-vibrationally excited oxygen in the middle atmosphere

The proposed model was used to calculate the altitude profiles of the number densities of O₂ molecules in electronic-vibrational states. The calculations were made for the conditions of the experiment METEORS (Mlynchak et al., 2001), in which both emissions at 762 nm and 1.27 μ m were measured simultaneously. It was carried out for 32° N and for the Solar zenith angle 38°.

In Fig. 2 the altitude profiles of the number densities of the molecules in the states O₂(b¹ Σ_g^+ , v) for v=0, 1 and 2 and the measured number densities of O₂(b¹ Σ_g^+ , v=0) (Mlynchak et

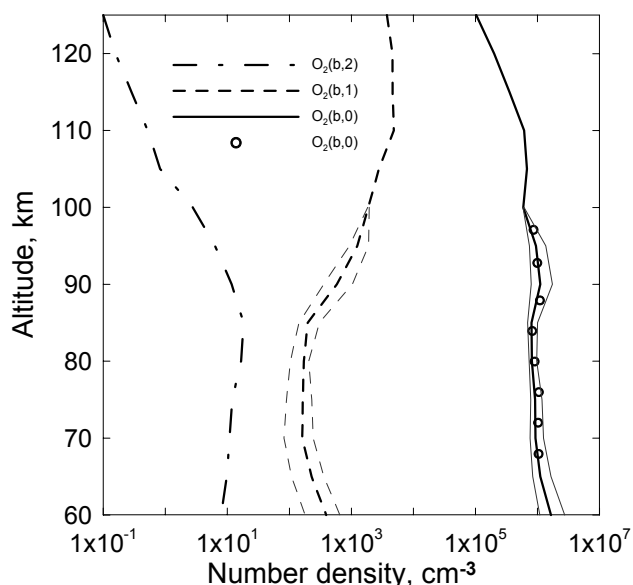


Fig. 2. Altitude profiles of the number densities of the molecules in the state O₂(b¹ Σ_g^+ , v) for v=0, 1 and 2. Circles – experimental data of METEORS for O₂(b¹ Σ_g^+ , v=0) (Mlynchak et al., 2001). The bold curves – calculations for the conditions of experiment METEORS in accordance with our model. The altitude profiles of the number densities of molecules in the states O₂(b¹ Σ_g^+ , v) for v=0 and 1, calculated for two ozone altitude profiles [O₃]' equal to 0.5 and 2.0, are shown by thin grey lines.

al., 2001) are shown. With the purpose of showing how the choice of the [O₃] profile other than the one from Keating et al. (1989) changes the results, the altitude profiles of the number densities of molecules in the states O₂(b¹ Σ_g^+ , v) for v=0 and 1 were also calculated for two other ozone altitude profiles [O₃]', for variations of [O₃]/[O₃] equal to 0.5 and 2.0.

In Fig. 3 the relative contributions of different processes to the total rate of production of O₂(b¹ Σ_g^+ , v=0) are shown. In correspondence with the fact that above 85 km the main process of the O₂(b¹ Σ_g^+ , v=0, 1) population is the Reaction (5) (channels 3 and 4 in Fig. 3), the ratio between the populations of vibrational levels v=0 and 1 correlates with the quantum yields of the O₂(b¹ Σ_g^+ , v=0) and O₂(b¹ Σ_g^+ , v=1) formation in this reaction (see Fig. 2). At 125 km, where the process of radiative deactivation dominates among the processes of deexcitation, the results of our calculations show that the ratio [O₂(b¹ Σ_g^+ , v=1)]/[O₂(b¹ Σ_g^+ , v=0)] becomes the same as the ratio of the quantum yields: 0.40/0.55. Below 100 km the contribution of the processes of the O₂(b¹ Σ_g^+ , v=0, 1) population due to the absorption of solar radiation at 762 nm and 689 nm becomes important (channels 5 and 2 in the Fig. 3). The drastic reduction in the O₂(b¹ Σ_g^+ , v=1) concentration in comparison with the concentration of the O₂(b¹ Σ_g^+ , v=0) at the altitudes below 90 km (see Fig. 2) is governed by the fast reaction of the EE exchange O₂(b¹ Σ_g^+ , v=1)+O₂(X³ Σ_g^- ,

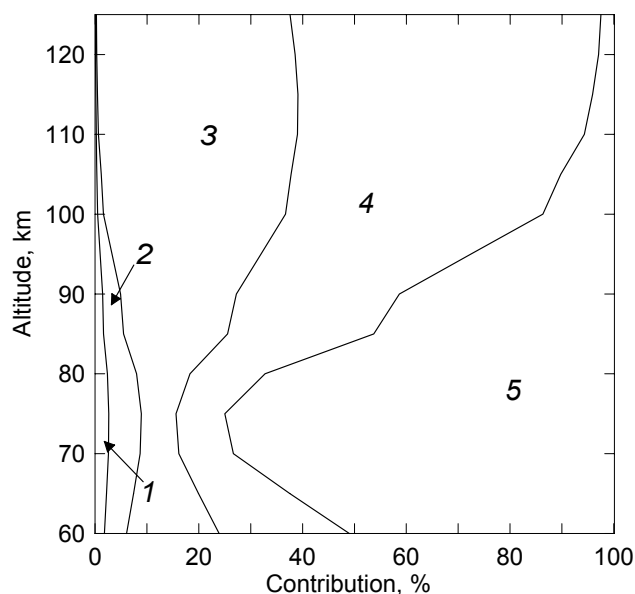


Fig. 3. Areas of diagram indicate the relative contributions of direct and indirect processes to the total rate of O₂(b¹Σ_g⁺, v=0) production, in percent. Indirect processes: 1 – absorption of solar radiation O₂+hν (629 nm)→O₂(b¹Σ_g⁺, v=2) (magnified by 10); 2 – absorption of solar radiation O₂+hν (689 nm)→O₂(b¹Σ_g⁺, v=1); 3 – energy transfer O(¹D)→O₂(b¹Σ_g⁺, v=1). Direct processes: 4 – energy transfer O(¹D)→O₂(b¹Σ_g⁺, v=0); 5 – absorption of solar radiation O₂+hν (762 nm)→O₂(b¹Σ_g⁺, v=0).

v=0)→O₂(X³Σ_g⁻, v=1)+O₂(b¹Σ_g⁺, v=0). The minimum of the contributions of channels 3 and 4 in Fig. 3 at 70–80 km is connected to the fact that below 80 km the channel of the O(¹D) formation in the O₂ photolysis in the Schumann-Runge continuum (Eq. 3), dominating at higher altitudes, gives way to the formation of O(¹D) in ozone photolysis in the Hartley band (4).

In Fig. 4 the altitude profiles of the number densities of the molecules in the states O₂(a¹Δ_g, v) for v=0, 1, 2 and 4 and the measured number densities of O₂(a¹Δ_g, v=0) (Mlynchak et al., 2001) are shown, although the calculations were also made for v=3 and 5. With the purpose of showing how the choice of the [O₃] profile other than the one from Keating et al. (1989) changes the results, the altitude profiles of the number densities of the molecules in the states O₂(a¹Δ_g, v) for v=0 and 1 were also calculated for two variations of [O₃]/[O₃], equal to 0.5 and 2.0.

In Fig. 5 the relative contributions of the different processes to the total rate of production of O₂(a¹Δ_g, v=0) are shown. The O₂(a¹Δ_g, v=0) population is governed by ozone photolysis in the Hartley band (channels 2 and 3 in Fig. 5) and the energy transfer in the processes O(¹D)→O₂(b¹Σ_g⁺, v)→O₂(a¹Δ_g, v) (channel 4 in Fig. 5). The local maximum of contributions of the channels 2 and 3 at the region of 90 km in Fig. 5 is connected with the local ozone max-

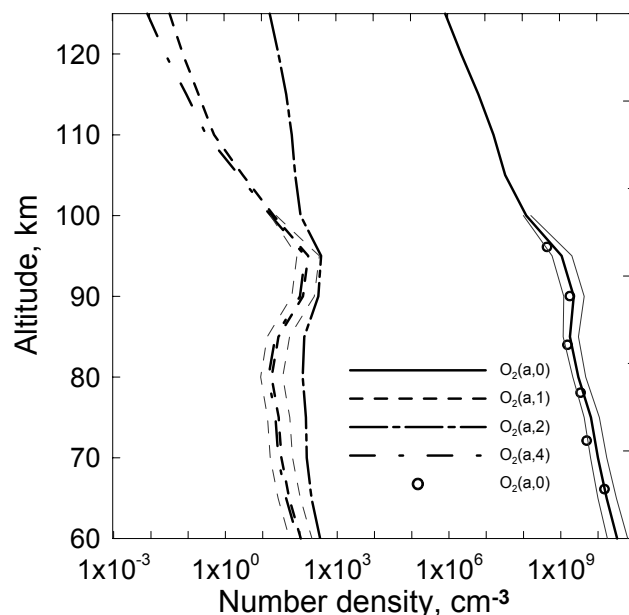


Fig. 4. Altitude profiles of the number densities of the molecules in the states O₂(a¹Δ_g, v) for v=0, 1, 2 and 4. The bold curves – calculations for the conditions of experiment METEORS (Mlynchak et al., 2001) in accordance with our model. Circles – experimental data of METEORS for O₂(a¹Δ_g, v=0) (Mlynchak et al., 2001). The altitude profiles of number densities of molecules in the states O₂(a¹Δ_g, v) for v=0 and 1, calculated for two ozone altitude profiles [O₃]' at variations of [O₃]/[O₃] equal to 0.5 and 2.0, are shown by thin grey lines.

imum at this altitude. The ratio between the direct and indirect processes of the O₂(a¹Δ_g, v=0) population strongly depends on altitude (see Fig. 5). The indirect process occurs by means of fast reactions: first, an EE energy exchange O₂(a¹Δ_g, v>1)+O₂(X³Σ_g⁻, v=0)→O₂(X³Σ_g⁻, v)+O₂(a¹Δ_g, v=0); second, VT-quenching at collisions with atomic oxygen O₂(a¹Δ_g, v)+O(³P)→O₂(a¹Δ_g, v=0)+O(³P) (see Table 4).

Figure 4 shows that the vertical profiles of the O₂(a¹Δ_g, v≥1) concentrations significantly differ by shape from the [O₂(a¹Δ_g, v=0)] profile. The concentrations of O₂(a¹Δ_g, v≥1) are much smaller than the O₂(a¹Δ_g, v=0) concentration, because the O₂(a¹Δ_g, v≥1) states are rapidly deactivated in the process of the EE energy exchange (see Table 4). The radiative deexcitation is not significant for the entire altitude interval. Thus, as EE energy exchange is a much faster process than the processes of V-V exchange between the vibrational sublevels of the electronic state O₂(a¹Δ_g), the relative populations of O₂(a¹Δ_g, v≥1), except for O₂(a¹Δ_g, v=2), reflect the initial populations of the vibrational sublevels O₂(a¹Δ_g, v) formed in O₃ photolysis (see Table 1). This is why the concentrations of O₂(a¹Δ_g, v≥1) below 100 km are close to each other and the vertical profiles of the O₂(a¹Δ_g, v≥1) concentrations, with the exception of

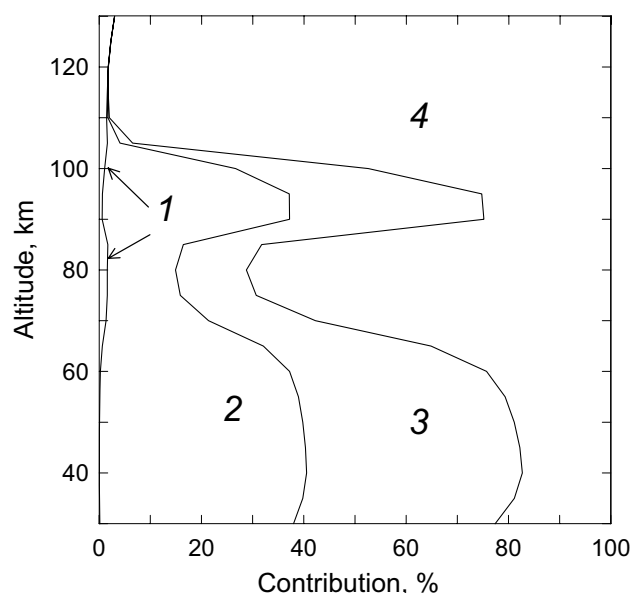


Fig. 5. Areas of diagram indicate the relative contributions of direct and indirect processes to the total rate of O₂(a¹Δ_g, v=0) production, in percent. Direct processes: 1 – absorption of solar radiation O₂+hν (1.27 μm)→O₂(a¹Δ_g, v=0); 2 – ozone photolysis in the Hartley band O₃+hν→O₂(a¹Δ_g, v=0). Indirect processes: 3 – ozone photolysis in the Hartley band O₃+hν→O₂(a¹Δ_g, v≥1); 4 – energy transfer O(¹D)→O₂(b¹Σ_g⁺, v)→O₂(a¹Δ_g, v).

[O₂ (a¹Δ_g, v=2)], are similar by shape and correlate with the profile of the ozone concentration. As can be seen from Fig. 4, the [O₂ (a¹Δ_g, v=2)] are higher than the [O₂ (a¹Δ_g, v=1, 4)] for the entire altitude interval, because O₂ (a¹Δ_g, v=2) is populated additionally by the quasi-resonance process of quenching of O₂(b¹Σ_g⁺, v=0) at collisions with N₂ (see the discussion of Table 3 in Sect. 2).

The model also enables us to calculate the number densities of O₂ in the ground electronic state with the vibrational quantum number from 1 to 35. As can be seen from Fig. 1 and Table 5, high vibrational levels of the O₂(X³Σ_g⁻) and also energy transfer from O₂(b¹Σ_g⁺, v) and O₂ (a¹Δ_g, v) should be considered for correct calculations of the concentration of the O₂(X³Σ_g⁻, v=1).

In Fig. 6 the altitude profile of the O₂(X³Σ_g⁻, v=1) concentration and the contributions of different channels of the O₂(X³Σ_g⁻, v=1) population are shown. As can be seen from Fig. 6, ozone photolysis in the Hartley, Huggins and Chapuis bands is the main channel of the O₂(X³Σ_g⁻, v=1) population up to 95 km, however, in the range 70–85 km the absorption of solar radiation by oxygen at 689 and 762 nm gives almost the same contribution. Above 95 km ozone photolysis gives way to oxygen photolysis in the Shumann-Runge continuum and in the Lyman-α. As can be concluded from our calculations, vibrational excitation of O₂ in the reaction of ozone with atomic oxygen (Table 5) is insignificant during daytime (curve 4 in Fig. 6).

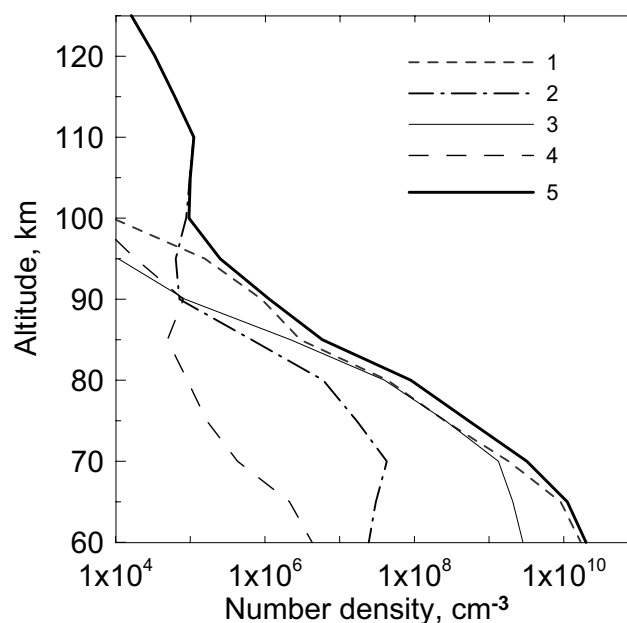


Fig. 6. Altitude profile of the number densities of the molecules in the state O₂(X³Σ_g⁻, v=1) calculated selectively for four main non-LTE channels if only one channel has been taken into account for the conditions of experiment METEORS (Mlynczak et al., 2001) in accordance with our model: 1 – ozone photolysis in the Hartley, Huggins and Chapuis bands; 2 – photolysis of O₂ in the Shumann-Runge continuum and Lyman-α; 3 – absorption by O₂ of solar radiation at 689 and 762 nm bands; 4 – reaction O₃+O→O₂(X³Σ_g⁻, v)+O₂ (see Table 5); 5 – total density (all channels are taken into account).

The altitude profiles of the concentration of O₂(X³Σ_g⁻, v=1) were calculated with the purpose of solving the problem of non-equilibrium radiation of H₂O in the 6.3-μm band in the middle atmosphere. The process of quasi-resonance V-V energy exchange between the first excited vibrational levels of the H₂O and O₂ molecules is very fast; this is why it is important to take into account this source of vibrational excitation of H₂O(010) (Manuilova et al., 2001).

4 762-nm and 1.27-μm emissions in the middle atmosphere

We used our new model to calculate the concentrations of O₂(a¹Δ_g, v=0) and O₂(b¹Σ_g⁺, v=0) and, correspondingly, the intensities of the 1.27-μm and 762-nm emissions in the middle atmosphere.

It should be stressed that the model of pure electronic kinetics is a particular case of the model of electronic-vibrational kinetics. The electronic kinetics model can be obtained from the electronic-vibrational kinetics model by the following assumptions: 1) – only electronically excited products are formed in O₃ photolysis; 2) – the processes of energy

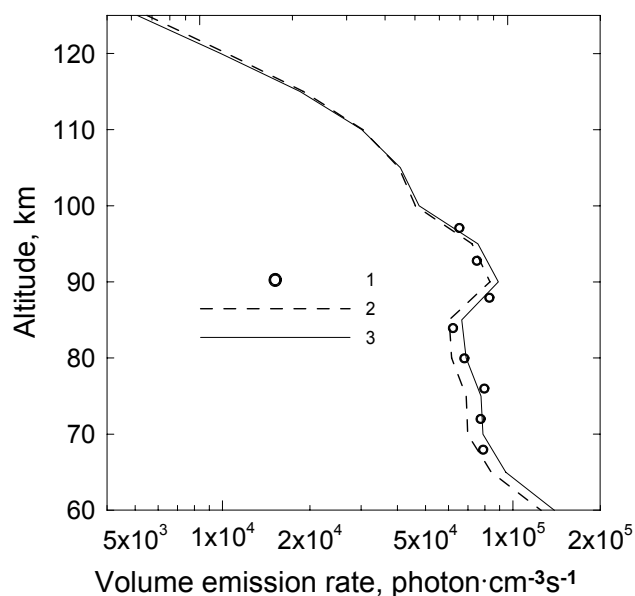


Fig. 7. Volume emission rate at 762 nm. Circles (1) – experimental data of METEORS (Mlynczak et al., 2001). Curves – calculations for the conditions of experiment METEORS: 2 – in accordance with the model of Mlynczak et al. (1993); 3 – in accordance with our model.

transfer between electronic states at collisions occur without vibrational excitation. Accordingly, only 17 processes remain from more than 100 listed in Tables 1–5. This model totally corresponds to the model of Mlynczak et al. (1993). All calculations presented below have been made for both models; the pure electronic model is called by us as the model of Mlynczak et al. (1993).

Figure 7 presents the comparison of the experimental data on the vertical profile of the volume emission rate at the wavelength of 762 nm (Mlynczak et al., 2001) and the calculations for the experimental conditions provided by our model and the model of only electronic kinetics.

In the same experiment (Mlynczak et al., 2001), the intensity of the 1.27- μm emission was measured simultaneously with the 762-nm emission. In Fig. 8 the experimental data on the vertical profile of the volume emission rate at the wavelength of 1.27- μm are compared with the calculations for the experimental conditions provided by our model and the model of Mlynczak et al. (1993). For the entire altitude interval, the values of the volume emission rate at the wavelength of 1.27 μm , calculated in accordance with our model, are lower than the results calculated in accordance with the model of Mlynczak et al. (1993). The discrepancy between the volume emission rates at 1.27 μm , calculated in accordance with the electronic-vibrational kinetics model, and the pure electronic model is 15–60% at the region of 60–125 km.

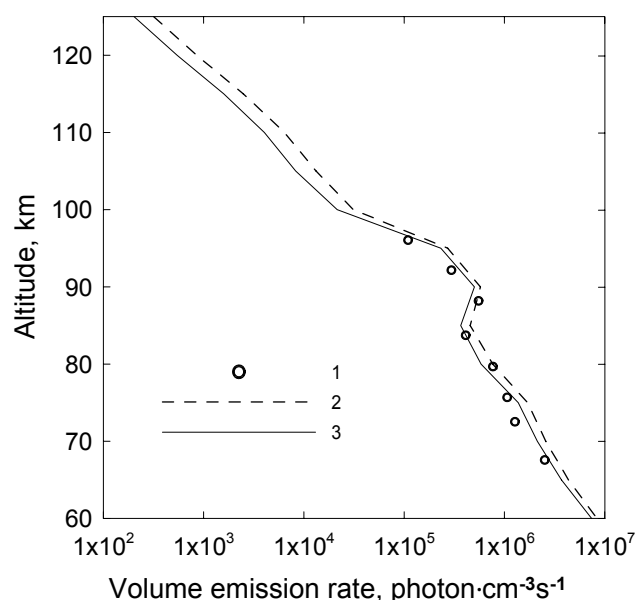


Fig. 8. Volume emission rate at 1.27 μm . Circles (1) – experimental data of METEORS (Mlynczak et al., 2001). Curves – calculations for the conditions of experiment METEORS: 2 – in accordance with the model of Mlynczak et al. (1993); 3 – in accordance with our model.

5 Retrieval of the vertical ozone profile from the measured intensity profiles of the 762-nm and 1.27- μm emissions

We will show that consideration of electronic-vibrational kinetics is very important for the problem of ozone retrieval from the measurements of the intensity in the Atmospheric and IR Atmospheric bands of the O_2 molecule. For the purpose of revealing which errors evolve due to the use of the pure electronic kinetics, we carried out the following numerical experiments.

For the first numerical experiment, the test ozone mixing ratio vertical profiles were taken from Marsh et al. (2002), where HRDI instrument observations of ozone in the mesosphere and lower thermosphere are presented. The “measured” volume emission rates in the 762-nm and 1.27- μm bands were calculated for the test ozone mixing ratio in accordance with the electronic-vibrational kinetics model for the atmospheric conditions of this experiment. In the second stage, the inverse problem of ozone vertical profile retrieval from the “measured” volume emission rates in the 762-nm and 1.27- μm bands was solved in accordance with the pure electronic model of Mlynczak (1993). Figure 9 shows that there is a considerable discrepancy between the retrieved ozone vertical profiles and the test ones (for March and December HRDI data) in the whole altitude range of 65–97 km. The maximum discrepancy between the retrieved ozone mixing ratio and the test one occurs at about 75 km. For March, this discrepancy reaches 25% for the ozone

mixing ratio retrieved from the 762-nm emission, and for the 1.27- μm emission the retrieved ozone mixing ratio is two times smaller than the test one. For December, at 75 km the discrepancy reaches 14% for the ozone mixing ratio retrieved from 762-nm emission and 33% for the ozone mixing ratio retrieved from 1.27- μm emission. From the numerical experiment which was described above, it can be concluded, that in the framework of pure electronic kinetics the retrieval of the ozone mixing ratio from the 762-nm emission is preferable to the retrieval from the 1.27- μm emission.

The second numerical experiment is the interpretation of the atmospheric experiment on the retrieval of the vertical ozone profile from simultaneous measurements of the intensity in the Atmospheric and IR Atmospheric bands of the O₂ molecule carried out in the experiment METEORS (Mlynczak et al., 2001). Using our model and the model of Mlynczak et al. (1993), we have solved the inverse problem of the [O₃] determination from the METEORS volume emission rates at 762 nm and 1.27 μm presented in Mlynczak et al. (2001). Figure 10 presents the results of the retrieval of the ozone concentration.

Above 65 km, according to our model, the vibrational-electronic kinetics of the products of O₃ and O₂ photolysis play an important role in the mechanism of the formation of these emissions. As a result, above 65 km the retrievals of [O₃] by our model and the model of Mlynczak et al. (1993) differ significantly.

In accordance with the calculations for the model of Mlynczak et al. (1993), in the region near 85–90 km, the O₃ concentration retrieved from the intensity of the O₂ band at 762 nm is 45–30% greater than the O₃ concentration retrieved from the intensity of the O₂ band at 1.27 μm (see dashed lines in Fig. 10).

For our model the vertical [O₃] profiles retrieved from both emissions are closer to each other, and in the altitude range of 80–90 km the discrepancy is 20–17% (solid lines in Fig. 10). The [O₃] value retrieved from the intensity of the 1.27- μm band, in accordance with our model in the range of the local ozone peak at 80–90 km, is 40–15% as large as that obtained for the model of Mlynczak et al. (1993) (lines 3 and 4 in Fig. 10).

As can be seen from both numerical experiments (Figs. 9, 10), up to 90 km the differences between the ozone abundances retrieved in accordance with our model and the model of pure electronic kinetics of O₃ and O₂ photolysis from the emission at 762 nm are much smaller than the corresponding difference between the ozone abundances retrieved in accordance with both models from the 1.27- μm emission. Mlynczak et al. (1993) considered only populating O₂(b¹ Σ_g^+ , v=0), using the total rate constant of collisions of O(¹D) with O₂. We considered the process of populating the electronic-vibrational levels O₂(b¹ Σ_g^+ , v=0, 1), using the same total rate constant, but taking into account the quantum yields of the O₂(b¹ Σ_g^+ , v=0) and the O₂(b¹ Σ_g^+ , v=1) for-

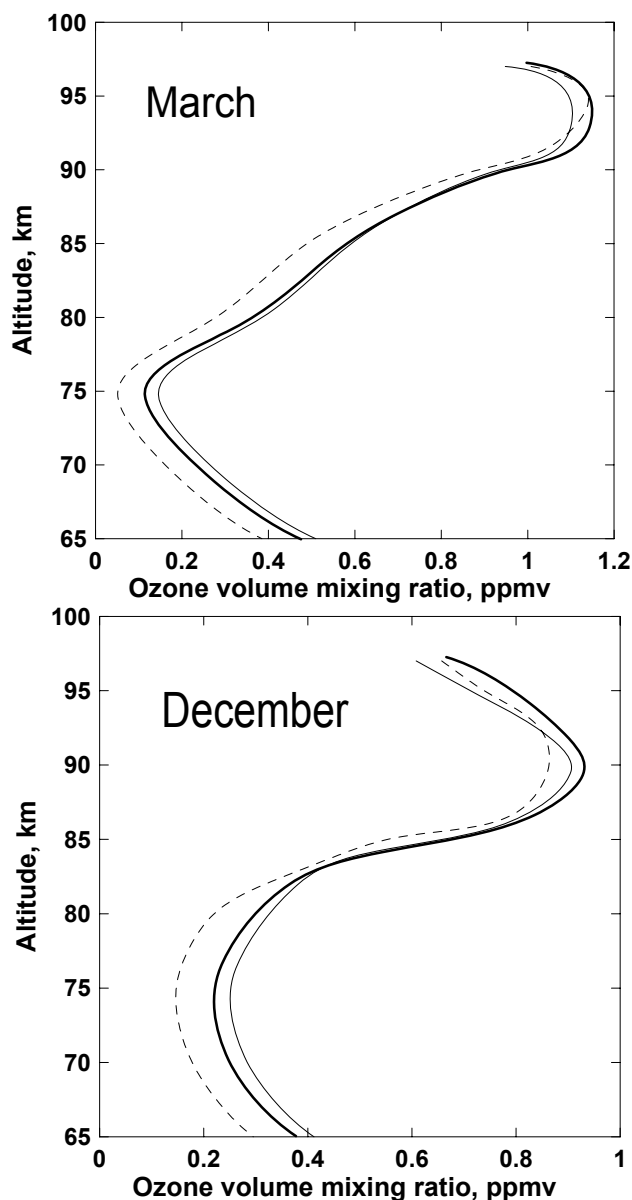


Fig. 9. Altitude profiles of ozone concentration retrieved from “measured” O₂ emissions at 762 nm (thin solid line) and 1.27 μm (dashed line) in accordance with pure electronic kinetics model. “Measured” volume emission rates at 762 nm and 1.27 μm were calculated in accordance with electronic-vibrational kinetics model at using HRDI ozone profiles for March and December (thick solid line) (Marsh et al., 2002).

mation in this reaction. However, the state O₂(b¹ Σ_g^+ , v=1) is deactivated by the mechanism of EE deexcitation to the level v=0 (Table 3). This is why the ozone concentrations retrieved from the 762-nm emission, in accordance with our model, and with the pure electronic model are closer to each other than those retrieved from the 1.27- μm emission.

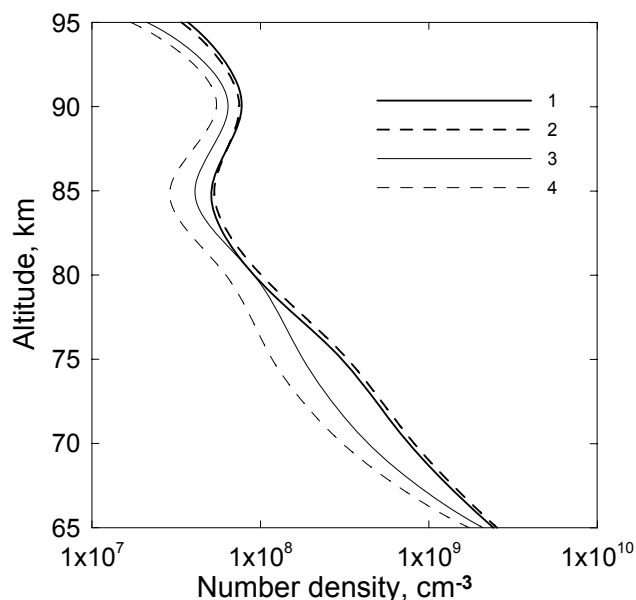


Fig. 10. Altitude profiles of ozone concentration retrieved from simultaneous observations of O₂ emissions at 762 nm and 1.27 μm in METEORS (Mlynczak et al., 2001). Retrievals in accordance with: our model – solid lines, model of Mlynczak et al. (1993) – dashed lines. Curves 1 and 2 – retrievals from measurement of emission at 762 nm O₂(b¹Σ_g⁺, v=0 → X³Σ_g⁻, v=0). Curves 3 and 4 – retrievals from measurement of emission at 1.27 μm O₂(a¹Δ_g, v=0 → X³Σ_g⁻, v=0).

Based on the results of ozone retrievals from emissions at 762 nm and 1.27 μm, presented in Figs. 9 and 10, one can conclude that ozone abundance retrieval carried out in accordance with the model of only electronic kinetics of O₃ and O₂ photolysis (Mlynczak et al., 1993) from the emission at 762 nm, which is formed by the transition from the state O₂(b¹Σ_g⁺), is preferable to retrieving the profiles of ozone abundance from the Infrared Atmospheric band of O₂ emission at 1.27 μm, which is formed by the transition from the state O₂(a¹Δ_g). This conclusion is the opposite to the traditional point of view but is not surprising, because in our model it was shown that the mechanism of populating the O₂(a¹Δ_g, v) states is much more complicated than that of populating the O₂(b¹Σ_g⁺, v) states (see Fig. 1 and Tables 1–4).

It should be noted that we came to this assertion on the basis of the analysis of only two numerical experiments. The final conclusion about the errors introduced in the retrieved values of ozone concentrations when using the model of only electronic kinetics of O₃ and O₂ photolysis for retrieval of the profiles of ozone concentration from the measurements in the bands at 762 nm and 1.27 μm can only be made after analyzing a great deal of data (e.g. in the satellite experiment ODIN-OSIRIS both emissions are measured simultaneously during a long period of time; Murtagh et al., 2002).

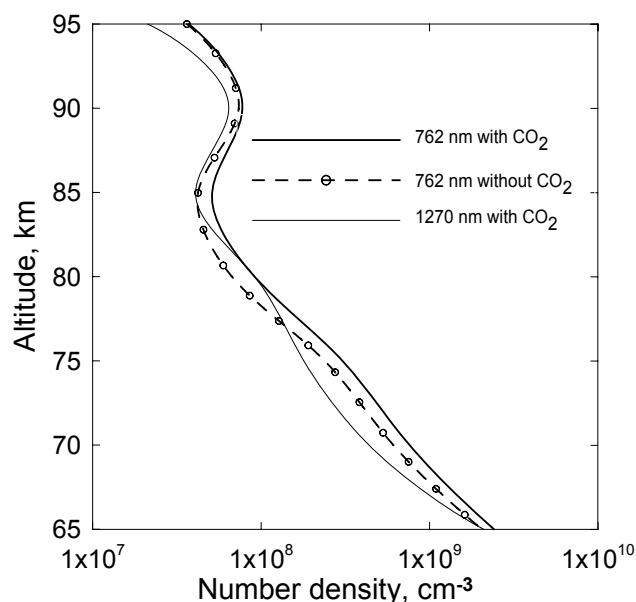


Fig. 11. Altitude profiles of ozone concentration retrieved from simultaneous observations of O₂ emissions at 762 nm and 1.27 μm in METEORS (Mlynczak et al., 2001). Retrievals in accordance with our model: taking into account CO₂ altitude profile – solid lines, with CO₂ mixing ratio equal to 0 – dashed lines.

It is interesting to point to the influence of CO₂ abundance on the retrieval of ozone concentrations from the measurements in the band at 762 nm which is connected with the high value of the rate constant of reaction of deexcitation of O₂(b¹Σ_g⁺, v=0) by CO₂, whereas the CO₂ concentration does not influence the retrieval of ozone concentration from the measurements in the band at 1.27 μm (Fig. 11). For the calculations presented in Fig. 11 we used the CO₂ altitude profile from Kauffmann et al. (2002), which gives a significant decrease in the CO₂ volume mixing ratio above 75 km.

Comparison of the ozone concentrations retrieved from the measurements in the band at 762 nm, taking into account the [CO₂] altitude profile and with CO₂ mixing ratio equal to 0 in the whole altitude region shows, in the framework of our model, a sensitivity of ozone concentrations retrieval to the [CO₂] altitude profile below 90 km (Fig. 11).

6 Conclusions

1. We have developed the model of kinetics of the excited products of ozone and oxygen photolysis, taking into account the processes of energy transfer between electronically-vibrationally excited states of the oxygen molecule of O₂(a¹Δ_g, v) and O₂(b¹Σ_g⁺, v), excited oxygen atoms O(¹D), and oxygen molecules in the ground state O₂(X³Σ_g⁻, v).

2. Above 65 km the previous model of electronic kinetics of the excited products of the ozone and oxygen photolysis should be replaced by the model of electronic-vibrational kinetics.
3. The proposed model allows for calculation not only of vertical profiles of the O₂(a¹Δ_g, v=0) and O₂(b¹Σ_g⁺, v=0) concentrations, but also of the profiles of [O₂(a¹Δ_g, v≤5)] and [O₂(b¹Σ_g⁺, v=0, 1, 2)]. Correspondingly, in accordance with our model, not only the intensity of the 1.27-μm and 762-nm emissions, but also the intensity of emissions formed by transitions from electronically-vibrationally excited levels, such as O₂(b¹Σ_g⁺, v=1)→O₂(X³Σ_g⁻, v=0) at 689 nm and O₂(b¹Σ_g⁺, v=2)→O₂(X³Σ_g⁻, v=0) at 629 nm, can be calculated in the middle atmosphere. The model also enables us to calculate the number densities of O₂ molecules in the ground electronic state with the vibrational quantum numbers from 1 to 35.
4. With the consideration of the electronic-vibrational kinetics of the excited products of the ozone and oxygen photolysis, the discrepancy between the altitude profiles retrieved from the simultaneously measured intensities of the 762-nm and 1.27-μm emissions in the experiment METEORS (Mlynczak et al., 2001) becomes significantly smaller than it was for only the electronic kinetics model. The developed model, in principle, gives an opportunity to retrieve the ozone density profiles from different emissions formed by transitions from electronically-vibrationally excited levels of singlet O₂ molecules in the middle atmosphere.
5. Based on the results of the numerical experiments on ozone retrievals (using the experimental ozone mixing ratio profiles from HRDI experiment (Marsh et al., 2002) and simultaneously measured emissions at 762 nm and 1.27 μm in the experiment METEORS (Mlynczak et al., 2001)), one can conclude that in the case of the pure electronic kinetics model the ozone abundance retrieval from the emission at 762 nm is preferable to retrieving the profiles of ozone abundance from the infrared Atmospheric band of O₂ emission at 1.27 μm. Using the 1.27-μm emission measurements for ozone concentration retrieval above 65 km is incorrect if the interpretation of experiments is carried out in accordance with models of pure electronic kinetics of O₃ and O₂ photolysis.

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