

## Non-equilibrium emission of the middle atmosphere in the IR rovibrational water vapor bands

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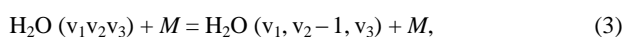
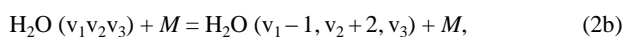
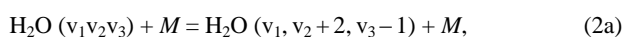
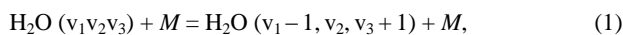
A new kinetic model of 13 excited vibrational levels of the H<sub>2</sub>O molecule has been developed. This model takes into account all vibrational-translational (V-T) and vibrational-vibrational (V-V) processes of the energy exchange at collisions of H<sub>2</sub>O with N<sub>2</sub>, O<sub>2</sub>, and O, which are important under conditions of the middle atmosphere. Different possible values of the rate constants of inelastic collisional processes are analyzed with the allowance made for new experimental data. Thirty-three rovibrational transitions that form the water vapor bands at 1.4, 1.9, 2.7, 3.2, 4.7, and 6.3 μm are considered. Populations are calculated for 13 excited vibrational states of the H<sub>2</sub>O molecule for daytime in midlatitudes.

The intense development of space-based measurements of infrared (IR) radiation of the middle atmosphere in the molecular bands has aroused considerable interest in the models of the radiation fields in the IR molecular rovibrational bands of atmospheric gases under conditions of disturbed local thermodynamic equilibrium (LTE). The study of the vibrational kinetics of the H<sub>2</sub>O molecule in the middle atmosphere and development of the models of non-equilibrium radiation of water vapor in the spectral region of 1.4–6.3 μm are needed to construct the algorithm for solving inverse problems, like, for instance, reconstructing water vapor concentration in the atmospheric regions with disturbed LTE. The importance of obtaining information on the H<sub>2</sub>O molecule in the upper stratosphere and mesosphere is connected with the fact that, because of the dissociation, the concentration of water vapor at these altitudes is closely related to the content of hydrogen- and oxygen-containing components (H, OH, O, O<sub>3</sub>, etc.). Above 40-km height, the catalytic cycles including free hydrogen radicals destruct odd oxygen very quickly. The need in monitoring H<sub>2</sub>O in the mesosphere became more urgent in connection with revealing of long-period trends in temperature (up to 30 K at 87 km for 40 years), composition, and emissions of the middle atmosphere. In particular, the drastic decrease of ozone in the mesosphere during the last 40 years that was predicted based on the revealed trends calls for explanation.

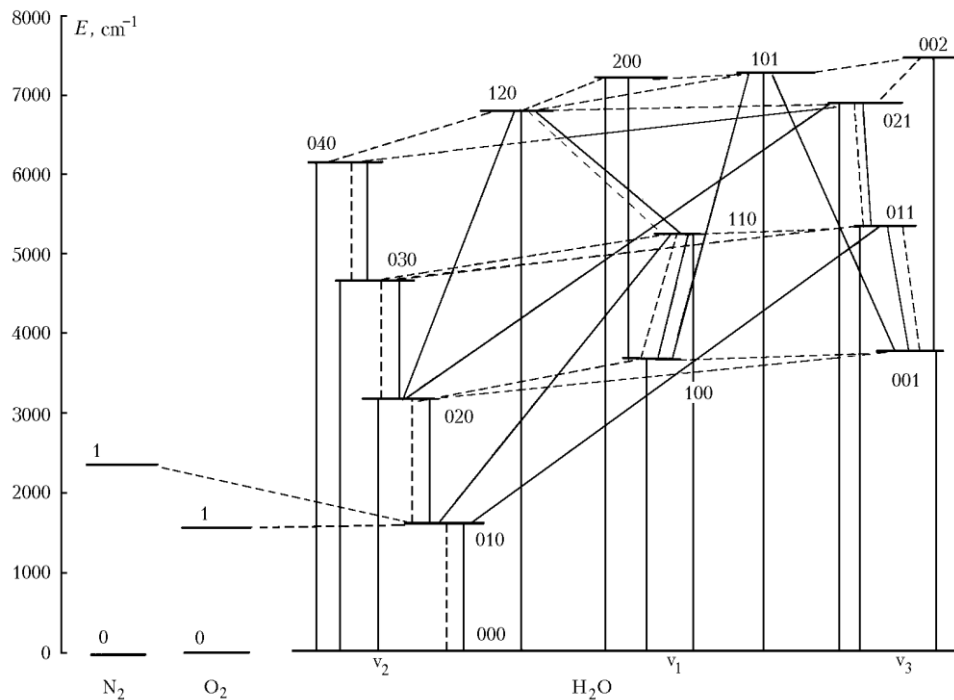
The newly proposed model of vibrational kinetics accounts for 13 excited vibrational states of

the H<sub>2</sub>O molecule (Fig. 1). Thirty-three rovibrational transitions that form the water vapor bands at 1.4, 1.9, 2.7, 3.2, 4.7, and 6.3 μm are considered. To compile a full spectroscopic database for 33 RV bands, intensities and wave numbers of spectral lines of nine water vapor hot bands in the region from 1500 to 3700 cm<sup>-1</sup> have been calculated<sup>1</sup> in addition to those from HITRAN-92 database. The dipole moment function of the water vapor molecule was determined based on precision quality experimental data on the line intensities in the RV bands. The obtained function allows estimating the intensities of lines corresponding to hot transitions.<sup>1</sup> The use of efficient λ-iteration technique<sup>2</sup> for solution of the equation of radiative transfer, enabled the radiative transfer and absorption of the solar radiation to be correctly taken into account for all spectral lines of 33 RV bands considered.

Under atmospheric conditions, the following processes of vibrational-translational (V-T) and intramolecular vibrational-vibrational (V-V) energy exchange should be included in the consideration of inelastic collisions (see Fig. 1):

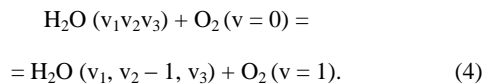


where  $M = \text{N}_2, \text{O}_2, \text{and O}$ .



**Fig. 1.** The scheme of considered vibrational states and transitions. Solid lines are for radiative transitions, and dashed lines correspond to vibrational-vibrational (V-V) and vibrational-translational (V-T) transitions at collisions.

The most important processes of the intermolecular vibrational-vibrational (V-V) energy exchange at inelastic collisions are the following:



The rate constants of the inelastic collisional processes were chosen based on new experimental data recently published in the literature. The quickest processes are the processes (1) of the exchange between the energetically close levels: 100 and 001, 110 and 011, 120 and 021, 200, 101, and 002; the rate of these processes is close to the gas-kinetic rate. The rate constants of deactivation of the states 001 and 100,  $k_{32}$ , [process (2)] at collisions with  $\text{N}_2$  and  $\text{O}_2$  were measured by laser fluorescence method.<sup>3</sup> The rate constants of deactivation of the state 010 [process (3)] at collisions with  $\text{N}_2$  and  $\text{O}_2$  were measured by acoustic method.<sup>4</sup> Unfortunately,  $k_{32}$  and  $k_{10}$  at collisions with  $\text{N}_2$  and  $\text{O}_2$  were not measured by the same method. The ratio between the rate constants  $k_{32}$  and  $k_{10}$  at collisions with  $\text{N}_2$  and  $\text{O}_2$  measured by different methods is about 10. At the same time, the ratio between the rate constants  $k_{32}$  and  $k_{10}$  at collisions with  $\text{H}_2\text{O}$  and  $\text{H}_2$  measured by the method of stimulated laser fluorescence is close to unity. That is why we present our calculations using two values of the rate constant  $k_{10}$  at collisions with  $\text{N}_2$  and  $\text{O}_2$ : version 1 with  $k_{10} = 4.8 \cdot 10^{-14} \text{ cm}^3 \cdot \text{s}^{-1}$  corresponding to the measurements from Ref. 4 and version 2 with  $k_{10}$  ten times larger.

Since the process of exchange of the vibrational energy between the water vapor and oxygen molecules (4) is rather fast, it is important to take into account all sources of vibrational excitation of  $\text{O}_2$ . Vibrationally excited oxygen is mostly generated in the process of photolysis of  $\text{O}_3$  in the UV

Hartley bands. We took into account generation of vibrationally excited  $\text{O}_2$  in the process of photolysis of both  $\text{O}_3$  and  $\text{O}_2$ . Our model of this source of  $\text{O}_2(v=1)$  is based on analysis of the process of direct generation of vibrationally excited oxygen in the ground electronic state, as well as the process of relaxation of other products of photolysis of  $\text{O}_2$  and  $\text{O}_3$ , namely,  $\text{O}(^1\text{D})$ ,  $\text{O}_2(a^1\Delta_g, v)$ , and  $\text{O}_2(b^1\Sigma_g^+, v)$ . Figure 2 depicts the contributions of  $\text{O}_2$  and  $\text{O}_3$  photolysis and the reaction  $\text{O}_3 + \text{O} \rightarrow \text{O}_2(X, v) + \text{O}_2$  to the generation of  $\text{O}_2(v=1)$ . As is seen from Fig. 2, the contribution of the latter reaction can be neglected, whereas the effect of  $\text{O}_2$  photolysis on generation of the vibrationally excited oxygen becomes significant only at heights above 85 km. In Refs. 5 and 6, it is assumed that the number of  $\text{O}_2(v=1)$  molecules generated at a single event of photodissociation of the  $\text{O}_3$  molecule is equal to four for the entire altitude range. Figure 3 depicts the altitude dependence of the number of  $\text{O}_2(v=1)$  molecules generated for one event of photodissociation of the  $\text{O}_3$  molecule and the effect of different channels of the vibrational-electronic relaxation of the products of ozone photolysis on generation of  $\text{O}_2(v=1)$ . It follows from Figs. 2 and 3 that generation of  $\text{O}_2(v=1)$ , due to photolysis of  $\text{O}_3$  and  $\text{O}_2$ , strongly depends on the altitude and that the conversion of the electronic energy into the vibrational one at collisions of  $\text{O}_2(a^1\Delta_g, v)$  generated in the  $\text{O}_3$  photolysis with  $\text{O}_2$  is the main channel of  $\text{O}_2(v=1)$  generation.

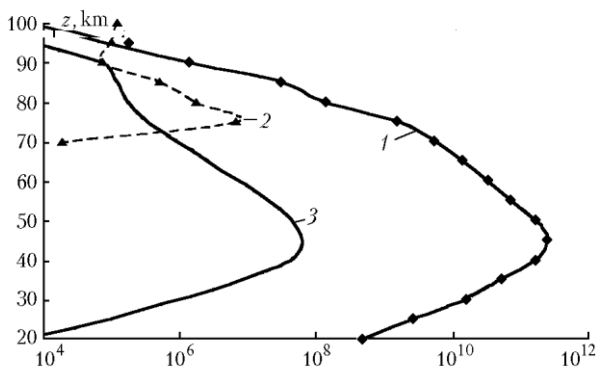


Fig. 2. Altitude dependence of  $O_2(v=1)$  concentration: photolysis of  $O_3$  (curve 1), photolysis of  $O_2$  (2), and  $O_3 + O \rightarrow O_2(X, v) + O_2$  (3), rhombs are for the total contribution.

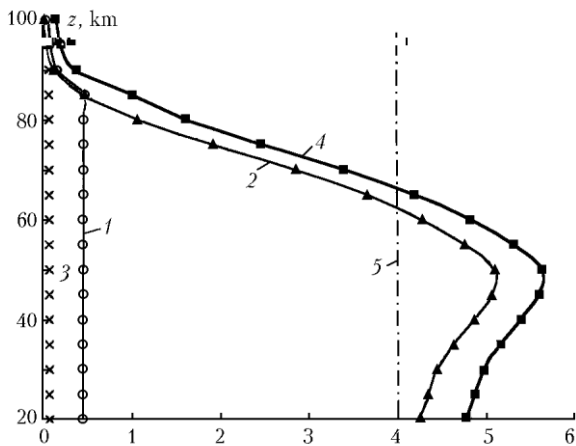


Fig. 3. Altitude dependence of the number of  $O_2(v=1)$  molecules and the contribution of different channels of the vibrational-electronic relaxation of the products of ozone photolysis to generation of  $O_2(v=1)$ :  $O_2(X, v)$  (curve 1),  $O_2(a, v)$  (2),  $O_2(b, v)$  (3), total contribution (4), and Ref. 5 (5).

Figures 4 and 5 depict the populations of vibrational states in the form of vibrational temperatures  $T_{\text{vib}}$ . Figure 4 demonstrates the role of  $O_3$  photolysis in generation of the vibrationally excited oxygen: if generation of  $O_2(v=1)$  in photolysis of  $O_3$  is ignored, then LTE for the vibrational state 010 of the  $H_2O$  molecule is disturbed in daytime at the altitude of 65 km, and if the effect of photolysis is taken into consideration, then the level of LTE disturbance for the state 010 in daytime goes down to 40 km because of the fast intermolecular V-V exchange between  $O_2(v=1)$  and  $H_2O(010)$  (4). The allowance for the effect of  $O_3$  photolysis yields an increase in  $T_{\text{vib},010}$  by 4 K at the altitude about 50 km. Our calculations confirm the conclusion from Refs. 5 and 6 that the growth of difference between the intensities of daytime and nighttime radiation in the 6.3- $\mu\text{m}$   $H_2O$  band at the altitudes of 40–60 km is mostly explained by generation of vibrationally excited  $O_2$  in the process of  $O_3$  photolysis.

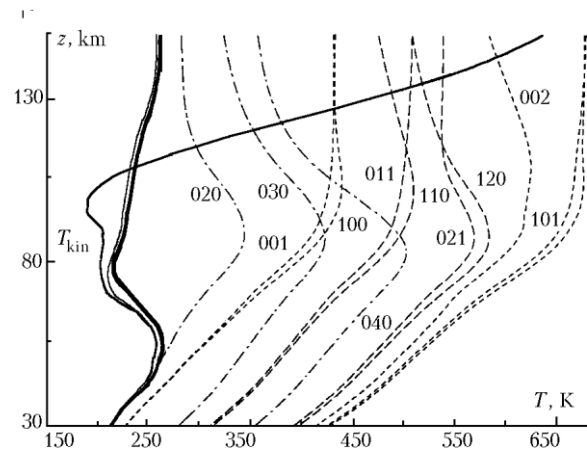


Fig. 4. Vibrational temperature of states of the  $H_2O$  molecule in daytime (dashed and dot-and-dash lines). Thin curve corresponds to the vibrational temperature of the state 010 calculated ignoring the effect of photolysis of  $O_3$  and  $O_2$ ; the bold curve shows the temperature calculated with the allowance for these processes.

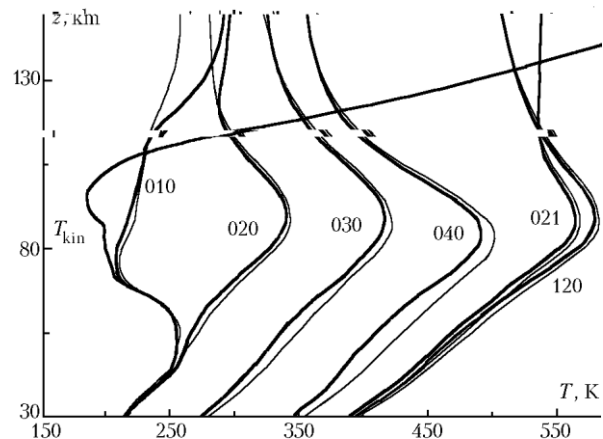


Fig. 5. Vibrational temperatures of the states of the  $H_2O$  molecule with nonzero quantum number  $v_2$ : calculation for the version 1 (thin curves) and calculation for the version 2 with the rate constant  $k_{10}$  of the process (3) ten times higher than  $k_{10}$  for the version 1 (bold curves).

Figure 5 depicts the calculated populations of the vibrational states of the  $H_2O$  molecule for the two values of the rate constants of collisional processes (3). In version 2, the use of the rate constant  $k_{10}$  of deactivation of the state 010 ten times larger than  $k_{10}$  for version 1 gives a decrease in the vibrational temperatures for the states with  $v_2 \neq 0$ : at the altitudes of 80–90 km the differences between  $T_{\text{vib}}$  calculated in the two versions of the rate constants vary from 10 K for the state 040 to several Ks for the state 010. Thus, in the region of maximum deviation from the LTE, the effect of the rate constants of the processes (3) on the population of vibrational states with  $v_2 \neq 0$  and, consequently, on the intensity of the spectral and integral radiation of the 6.3- $\mu\text{m}$  band may be significant. That is why, for more accurate interpretation of spectra of limb radiation of the middle atmosphere in the IR water vapor bands it is necessary to measure the three main rate constants of deactivation of the vibrational states of  $H_2O$  molecule [processes (1)–(3)] using the same method.

### Acknowledgments

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### References

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