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The new model of non-equilibrium middle atmosphere radiation in the infrared ro-vibrational water vapor bands.

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The new kinetic model of excited vibrational levels of the H_2O molecule was developed. In the model 54 vibrational-translational (V-T) and vibrational-vibrational (V-V) processes of energy exchange at collisions of H_2O with N_2, O_2 and O, which are important at the atmospheric conditions, were taken into account. Different variants of possible values of the rate constants of non-elastic collisional processes were analyzed considering the new experimental data. The 32 ro-vibrational transitions forming 1.4, 1.9, 2.7, 3.2, 4.7 and 6,3 μm water vapor bands were taken into account. In addition to the spectroscopic information contained in HITRAN-96 the frequencies and intensities of 9 ro-vibrational bands were calculated with the purpose of creation of the entire spectroscopic database for all 32 ro-vibrational bands. The calculations of the non-equilibrium populations of the vibrational levels of the H_2O molecule using the effective accelerated lambda-iteration technique gave the opportunity to consider the radiative transfer and absorption of the solar radiation correctly for the all spectral lines of the 32 ro-vibrational bands. The near-resonant vibrational energy exchange between $H_2O(010)$ level and the first vibrationally excited level of O_2, O_2(v=1), is one of the most important processes that affect the $H_2O(010)$ population. Vibrationally excited O_2 is produced mainly in the photolysis of O_3 in the ultraviolet Hartley bands.

We considered production of vibrationally excited O_2 both in the O_3 and O_2 photolysis. Our model of this source of O_2(v=1) is based both on analysis of the process of direct forming of vibrationally excited oxygen in the fundamental electronic state in photolysis and the analysis of relaxation processes of the other products of O_3 and O_2 photolysis ($O(^1D)$, $O_2(a^1\Delta g, v)$, $O_2(b^1\Sigma_g^+, v)$). The calculated populations of the excited vibrational levels of the H_2O molecule and examples of the calculated for the conditions of the CRISTA experiment spectral limb radiation of the middle atmosphere are presented. Dependence of the populations of the excited vibrational levels of the H_2O molecule and limb spectral radiances in 6.3 μm band on the rate constants of collisional transitions is carefully examined. Examples of [H_2O] retrievals from SABER/TIMED measurements of intensity of 6.3 μm emission are discussed.