

Why the oxygen IR emission at 1.27 μm is not the best way for ozone retrieval in the mesosphere?

Rada O. Manuilova and Valentine A. Yankovsky

Saint-Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034 Russia, r.manuylova@spbu.ru

In the framework of model of electronic vibrational kinetics of excited products of O_3 and O_2 photolysis in the MLT of the Earth, YM2011, we have tried to answer the formulated above question. In our study we propose to retrieve the $[\text{O}_3]$ using as proxies electronic-vibrationally excited levels of oxygen molecule, namely $\text{O}_2(\text{b}1, v=0, 1)$, $\text{O}_2(\text{a}1, v=0)$ and excited atom $\text{O}(1\text{D})$. Concerning the $[\text{O}_3]$ retrieval in the range of 50–100 km, the emissions at 1.27 μm formed by transition from $\text{O}_2(\text{a}1, v=0)$ and at 762 nm formed by transition from $\text{O}_2(\text{b}1, v=0)$ are the most intensive ones among all emissions under consideration. However, considering the complexity of kinetics of the excited components: choosing $\text{O}(1\text{D})$ as a proxy for $[\text{O}_3]$ retrieval, requires taking into account five aeronomical reactions. For other proxies the number of aeronomical reactions is as follows: $\text{O}_2(\text{b}1, v=1) - 13$; $\text{O}_2(\text{b}1, v=0) - 18$; $\text{O}_2(\text{a}1, v=0) - 25$. Increasing the number of reactions that must be considered when using a proxy from $\text{O}(1\text{D})$ to $\text{O}_2(\text{a}1, v=0)$ depends on the fact that, calculating the population of each of the underlying electronic-vibrationally excited state requires considering the mechanisms of the population of the upper levels. Using the $\text{O}_2(\text{a}1, v=0)$ is also associated with the problem of poorly known rate coefficients for some important processes. For example, the rate constant of reaction $\text{O}_2(\text{a}1, v=0) + \text{O}(^3\text{P}) \rightarrow \text{products}$ is known with uncertainty 200%. The next criterion of a “good” proxy is the value of $[\text{O}_3]$ retrieval uncertainty. Above 90 km, $\text{O}_2(\text{a}1, v=0)$ becomes the worst proxy among all under consideration with the uncertainty exceeding 100%. In the interval 50–98 km $\text{O}_2(\text{b}1, v=1)$ is the “good” proxy with the value of uncertainty less than 20% below 90 km and less than 25% up to 98 km. Therefore, $\text{O}_2(\text{b}1, v=1)$ is the preferable proxy at the altitudes of 50–98 km. Commonly used $[\text{O}_3]$ retrieval proxy, $\text{O}_2(\text{a}1, v=0)$, transition from which forms the 1.27 μm O_2 IR Atmospheric band, has more than one hour photochemical lifetime in the MLT. On the other hand, the $\text{O}(1\text{D})$ and $\text{O}_2(\text{b}1, v=0, 1)$ lifetime in the altitude region of 50–200 km is less than 14 sec. So, the proposed $\text{O}_2(\text{b}1, v=0, 1)$ and $\text{O}(1\text{D})$ proxies can be used for tracking fast variations of the O_3 atmospheric concentrations generated by wave processes, electron precipitations, solar flux changes, and so on, when the $\text{O}_2(\text{a}1, v=0)$ proxy becomes useless. Summarizing, in the framework of the YM2011 model we have developed the new methods of $[\text{O}_3]$ retrieval, which utilize electronic-vibrational transitions from the oxygen molecule second singlet level $\text{O}_2(\text{b}1, v=0, 1)$. For $[\text{O}_3]$ retrieval up to 98 km we recommend $\text{O}_2(\text{b}1, v=1)$ as proxy by measuring intensities of emissions at 688, 771 and 874 nm bands.