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

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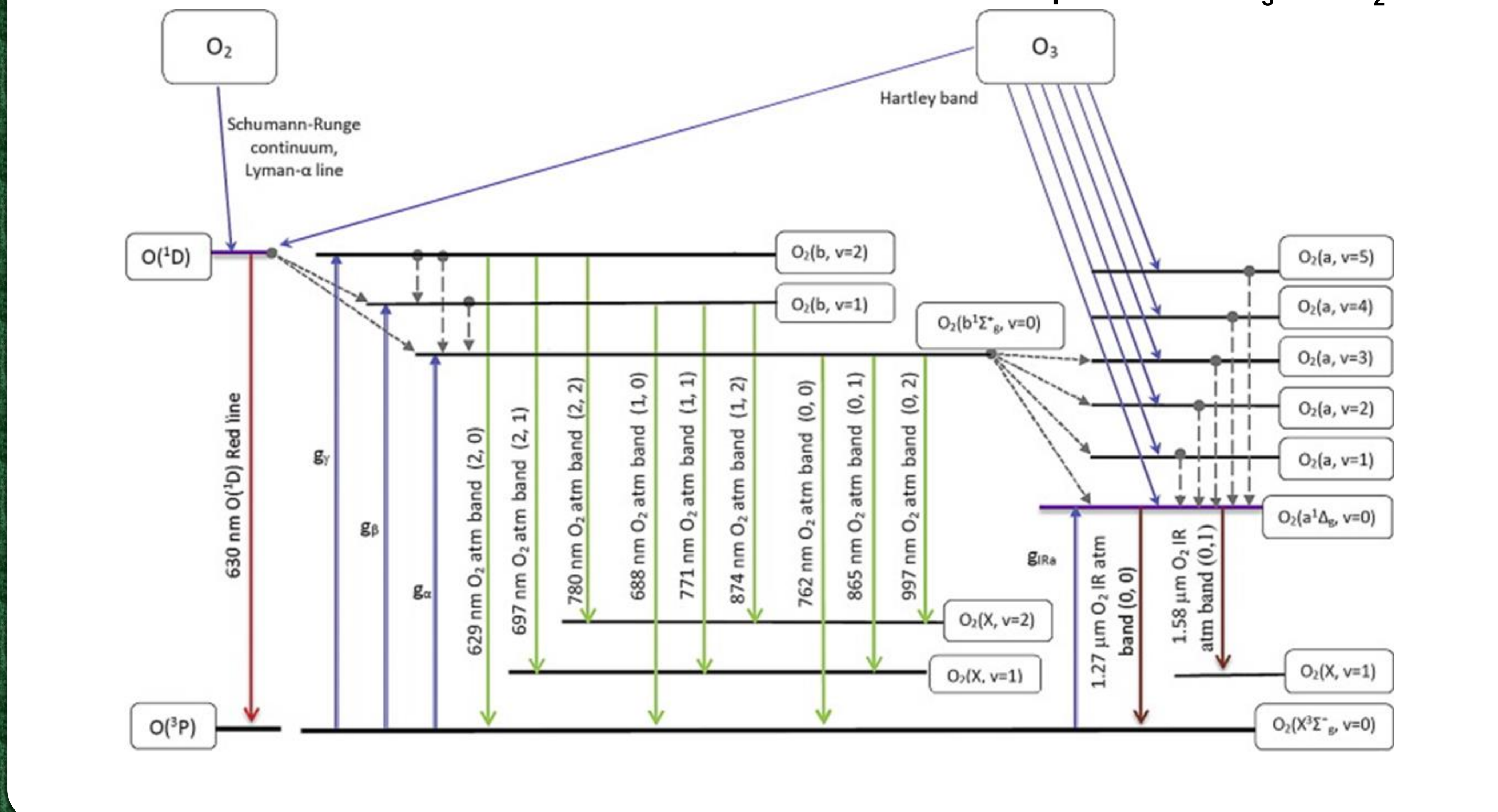

Fig.1. The model takes into account 10 excited states of molecules of oxygen $O_2(b^1\Sigma_g, v=0-2)$, $O_2(a^1\Delta_g, v=0-5)$ and metastable atom $O(^1D)$ and more than 60 aeronomical reactions.

Sloping lines − the processes of O_2 and O_3 photolysis. Double vertical lines − the processes of solar radiation absorption in the 762 nm (g_α), 688 nm (g_β), 629 nm (g_γ) and in the 1.27 μm (g_{IRa}) bands. Slant lines − energy transfer from $O(^1D)$ to the $O_2(b^1\Sigma^+_g$, v=0, 1) and from $O_2(b^1\Sigma^+_g$, v=0) to $O_2(a^1\Delta_g$, v=0−3) and from $O_2(b^1\Sigma^+_g$, v) at collisional quenching. Dashed lines − the processes of V-V and V-T relaxation. Red line − the processes of radiative emissions from $O(^1D)$ (630 nm). Green lines − the processes of radiative emissions from electronic-vibrational levels $O_2(b^1\Sigma^+_g$, v=0 − 2). Brown lines − processes of radiative emissions from $O_2(a^1\Delta_g$, v=0) to $O_2(X^3\Sigma_g$, v=0, 1). All emissions could be used as proxies of $[O_3]$ and $[O(^3P)]$ in MLT.

Problems

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 $[O_3]$ using as proxies electronic-vibrationally excited levels of oxygen molecule, namely $O_2(b^1\Sigma^+_g$, v=0, 1), $O_2(a^1\Delta_g$, v=0) and excited atom $O(^1D)$ (Fig. 1). Population of $O_2(b^1\Sigma_g$, v=2) doesn't depend on $[O_3]$ (Fig. 2). Concerning the $[O_3]$ retrieval in the range of 50–100 km, the emission at 1.27 μm formed by transition from $O_2(a^1\Delta_g$, v=0) and emission at 762 nm formed by transition from $O_2(b^1\Sigma^+_g$, v=0) are the most intensive ones among all emissions under consideration. However, considering the complexity of kinetics of the excited components: choosing $O(^1D)$ as a proxy for $[O_3]$ retrieval, requires taking into account five aeronomical reactions. For other proxies the number of aeronomical reactions is as follows: $O_2(b^1\Sigma^+_g$, v=1) − 13; $O_2(b^1\Sigma^+_g$, v=0) − 18; $O_2(a^1\Delta_g$, v=0) − 25. Increasing the number of reactions that must be considered when using a proxy from $O(^1D)$ to $O_2(a^1\Delta_g$, 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 $O_2(a^1\Delta_g$, v=0) is also associated with the problem of poorly known rate coefficients for some important processes. For example, the rate constant of reaction $O_2(a^1\Delta_g, v=0) + O(^3P) \rightarrow$ *products* is known with uncertainty 200%, $O_2(b^1\Sigma^+_g, v=0) + O(^3P) \rightarrow$ *products* (with uncertainty 25 − 300%), $O_2(a^1\Delta_g, v\geq1) + O_3 \rightarrow$ *products* (with uncertainty 43%) etc.

Results of sensitivity study

The next criterion of a "good" proxy is the value of $[O_3]$ retrieval uncertainty. Above 90 km, $O_2(a^1\Delta_g$, v=0) becomes the worst proxy among all under consideration with the uncertainty exceeding 100% (Fig. 3b). In the interval 50−98 km $O_2(b^1\Sigma^+_g$, 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 (Fig. 3a). Therefore, $O_2(b^1\Sigma^+_g$, v=1) is the preferable proxy at the altitudes of 50−98 km. Commonly used $[O_3]$ retrieval proxy, $O_2(a^1\Delta_g$, 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 $O(^1D)$ and $O_2(b^1\Sigma^+_g$, v=0, 1) lifetime in the altitude region of 50−200 km is less than 14 sec (Fig. 4). So, the proposed $O_2(b^1\Sigma^+_g$, v=0, 1) and $O(^1D)$ 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 $O_2(a^1\Delta_g$, v=0) proxy becomes useless.

The more suitable alternatives exist!

Based on this complex analysis we concluded that the optimal proxy for $[O_3]$ retrieval is $O_2(b^1\Sigma^+_g$, v=1) in the altitude interval 50−98 km and $O_2(b^1\Sigma^+_g$, v=0) in the altitude interval 85−98 km. It should be noted, that lifetimes of $O_2(b^1\Sigma^+_g$, v=0, 1, and 2) are not more than 14 sec in MLT, what gave the opportunity to register the short-period $[O(^3P)]$ and $[O_3]$ variations. It is important to note that above 100 km neither of the proxies under consideration can provide ozone retrieval of sufficient accuracy.

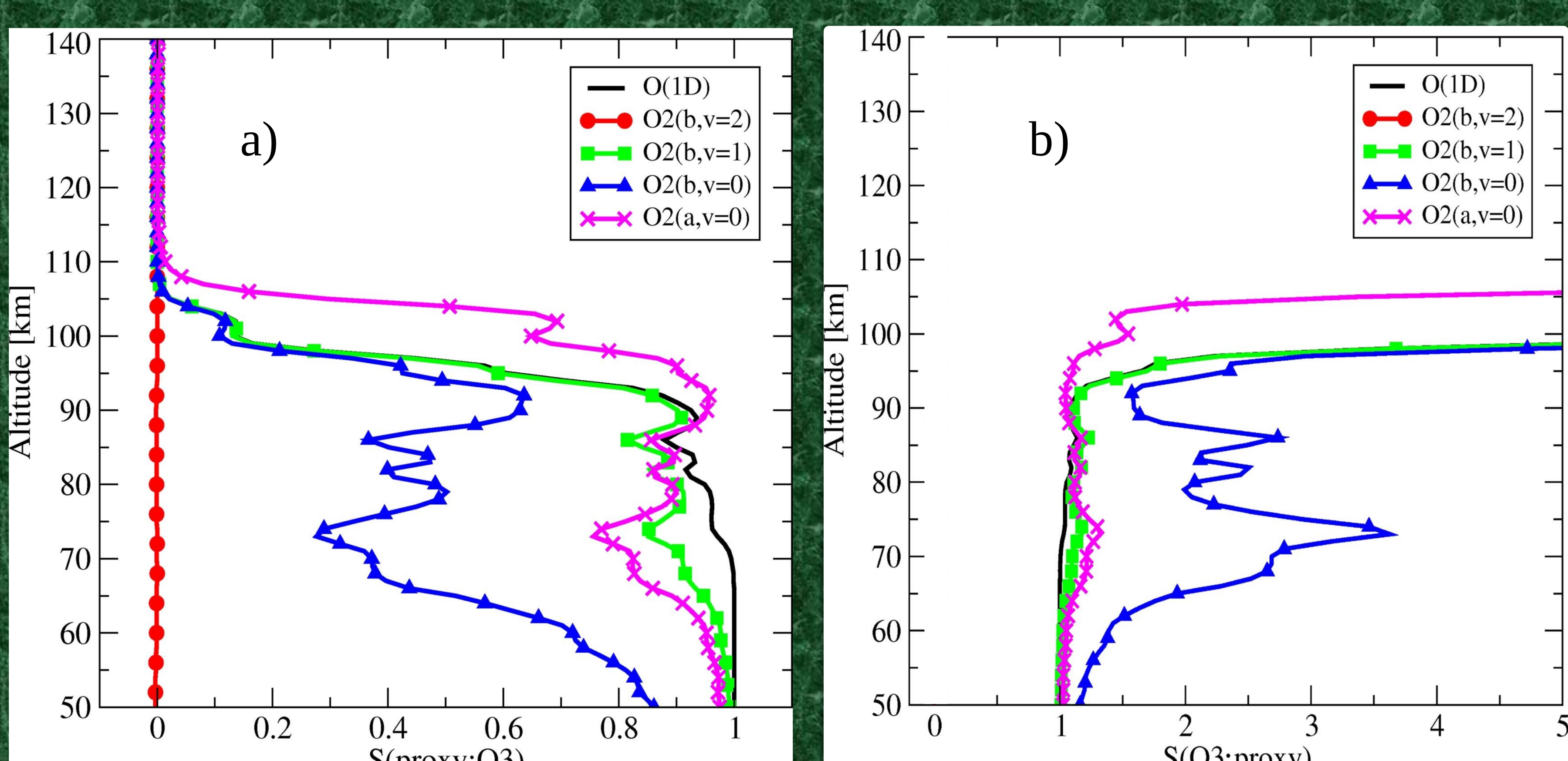

Fig.2. a) Sensitivity coefficient of the proxy concentration to $[O_3]$ for the **forward** problem, *S(proxy; O₃)*. b) Sensitivity coefficient of $[O_3]$ to the proxy concentration to for the **inverse** problem, *S(O₃; proxy)*, Type of proxy: $O(^1D)$ – black line; $O_2(b^1\Sigma^+_g$, v=2) – red line with filled circles; $O_2(b^1\Sigma^+_g$, v=1) – green line with filled squares; $O_2(b^1\Sigma^+_g$, v=0) –blue line with filled triangles; $O_2(a^1\Delta_g$, v=0) – rose line with crosses. **Optimal proxies for $[O_3]$ retrieval are: $O_2(b^1\Sigma^+_g$, v=1), $O_2(a^1\Delta_g$, v=0) and $O(^1D)$.**

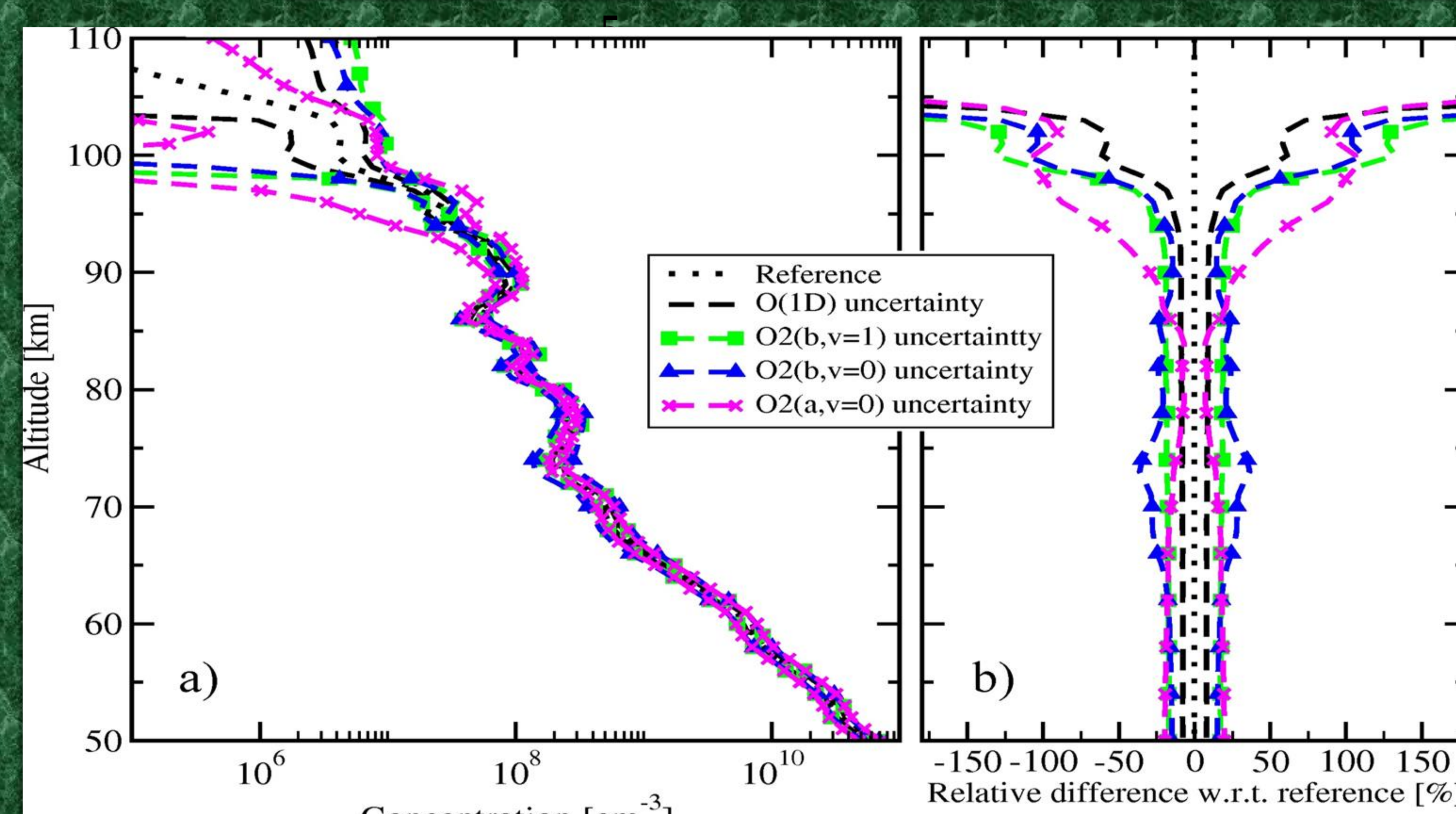

Fig 3. Uncertainties of $[O_3]$ retrieval (the limits ±σ) for different proxies:

a) absolute values, b) relative values.

The predetermined reference altitude profile of $[O_3]$ is presented by the dotted curve, and is taken from SABER L2,2010, day 172, latitude 43.0, SZA=70.5. Type of proxy: $O(^1D)$ – black dashed line; $O_2(b^1\Sigma^+_g$, v=1) – green dashed line with filled squares; $O_2(b^1\Sigma^+_g$, v=0) – blue dashed line with filled triangles; $O_2(a^1\Delta_g$, v=0) – rose dashed line with crosses.

Comments to Figures 2 and 3.

In the range of 50–85 km, $O_2(a^1\Delta_g$, v=0) is available proxy, with an uncertainty value of less than 15 − 20%. Above 90 km, $O_2(a^1\Delta_g$, v=0) becomes the worst proxy, with uncertainty exceeding 100% (rose curve in Fig. 3). In terms of the 'worst' proxy in the mesosphere (up to 90 km), $O_2(b^1\Sigma^+_g$, v=0), the value of retrieval uncertainty exceeds 35% at 65-80 km (blue curve in Fig. 3).

Therefore, $O_2(b^1\Sigma^+_g$, v=1) is the preferable proxy at altitudes of 50−98 km (green curve in Fig. 3). It is important to note that, according to Fig. 2 and Fig. 3, at above 98 km neither of the proxies under consideration can provide ozone retrieval of sufficient accuracy.

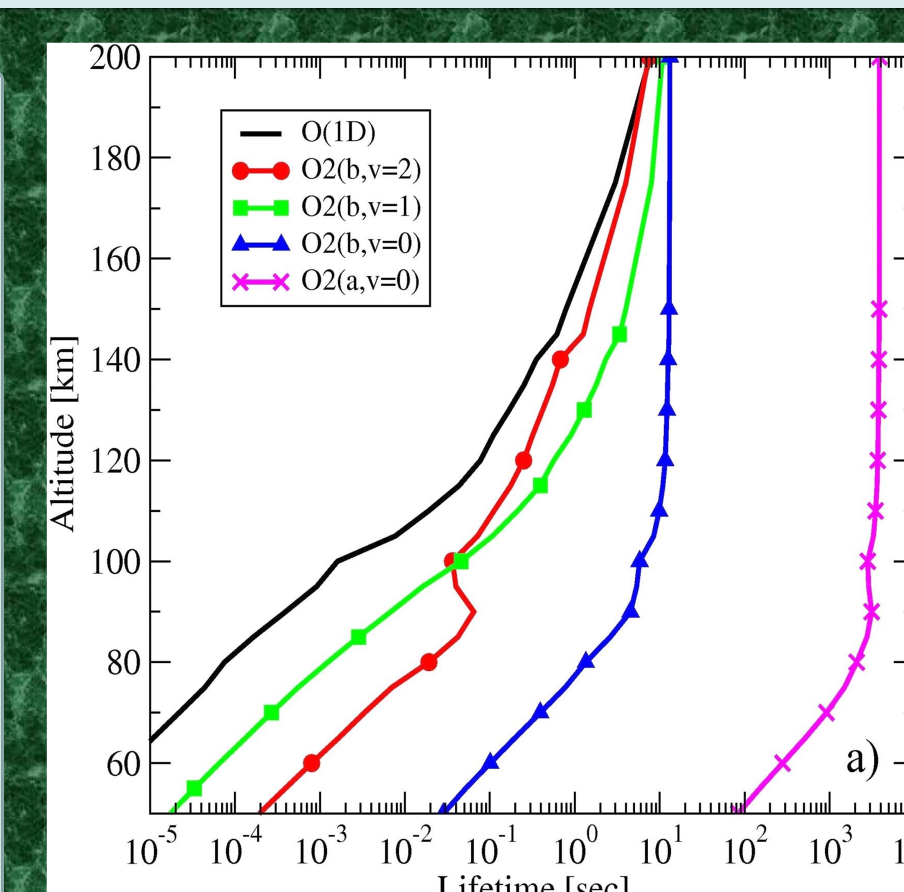

Fig 4. Typical photochemical lifetimes of proxies $O(^1D)$, $[O_2(b^1\Sigma^+_g$, v=0, 1, 2)] and $O_2(a^1\Delta_g$,v=0) in the mesosphere and lower thermosphere. See the type of proxy in the caption to Fig. 2.

Note: $O_2(a^1\Delta_g$,v=0) lifetime is about one hour, the lifetimes of the other proxies are less than 14 sec.