Relaxation of vibrational levels $H_2O(002, 101, 200)$: effect of new rate constants on the H_2O vibrational level populations and ro-vibrational spectra in the mesosphere and lower thermosphere

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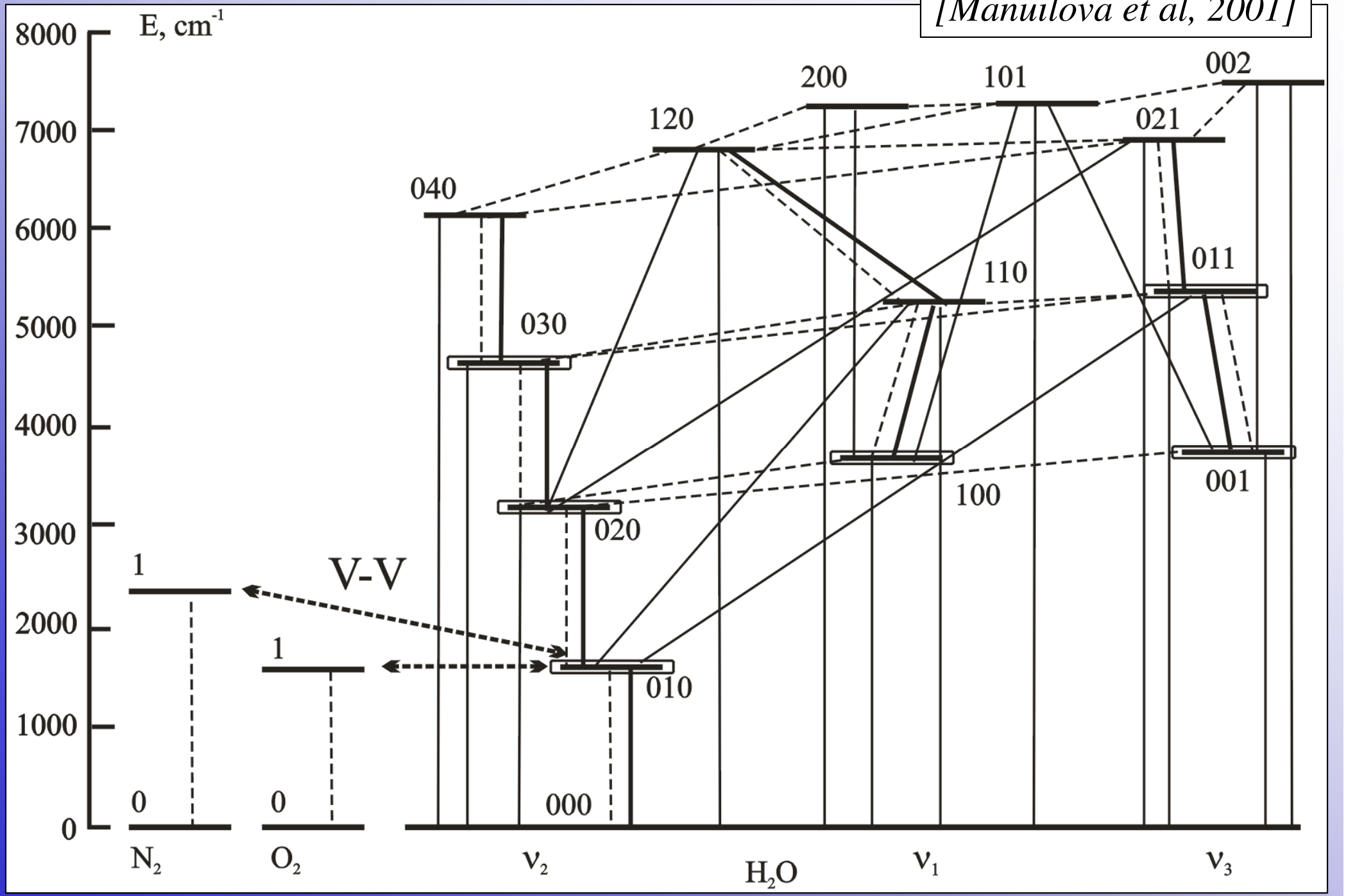
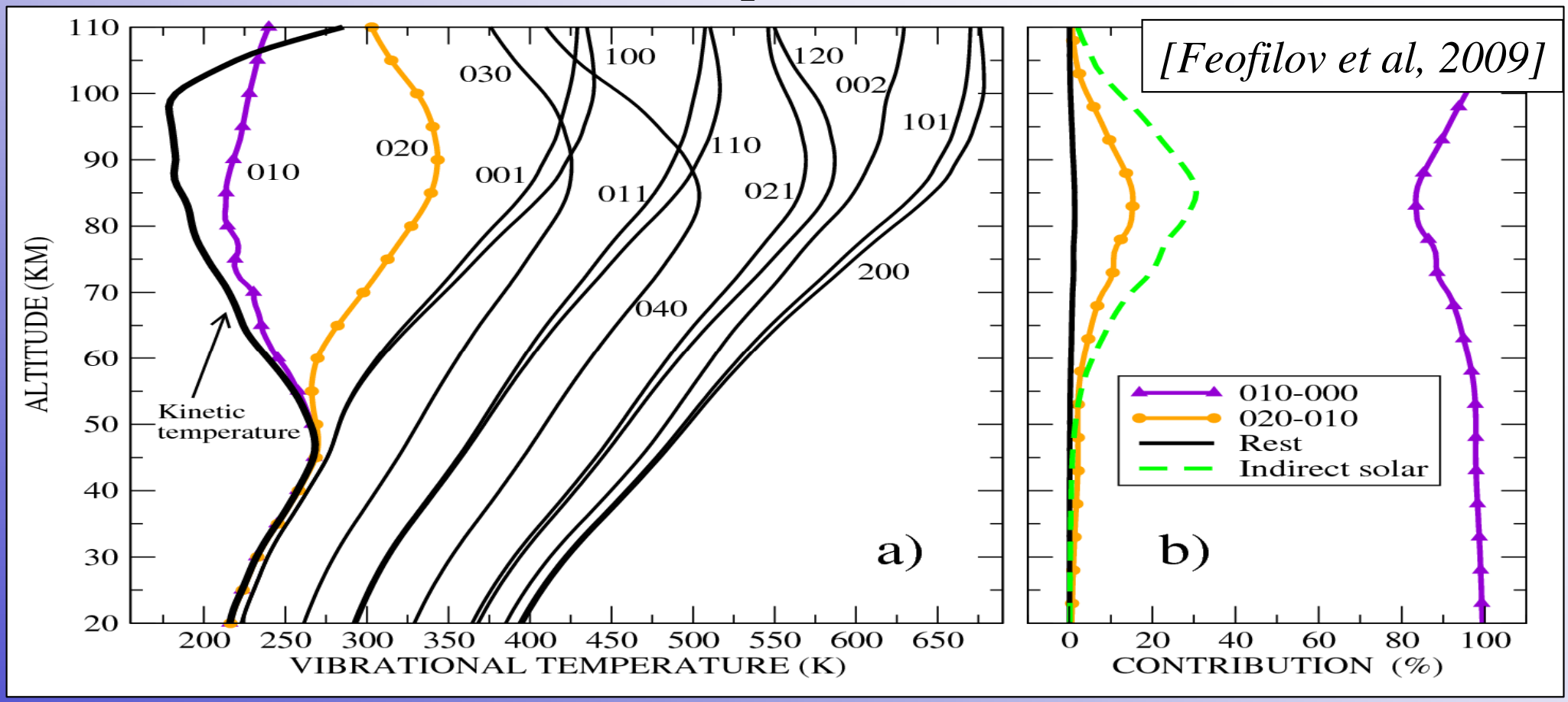
Model of vibrational kinetics of the H_2O molecule

[Manuilova et al, 2001]



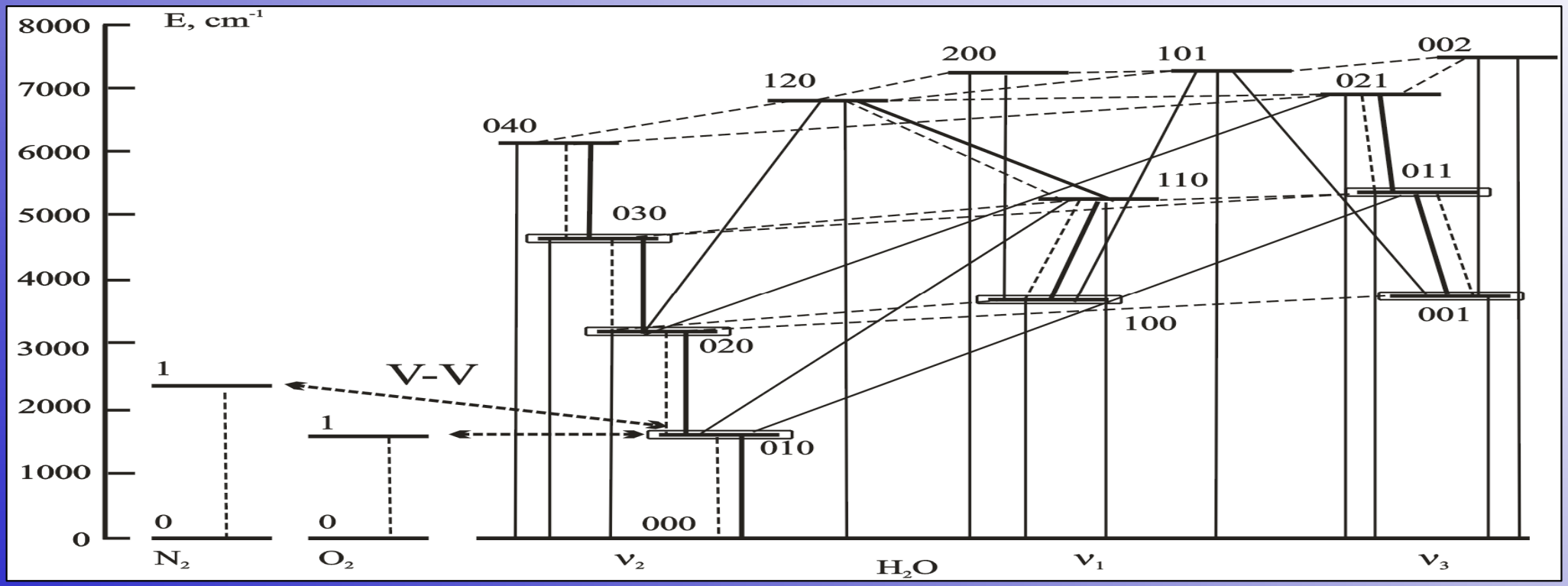
Breakdown of the Local Thermodynamic Equilibrium (non-LTE) for H_2O vibrational levels.



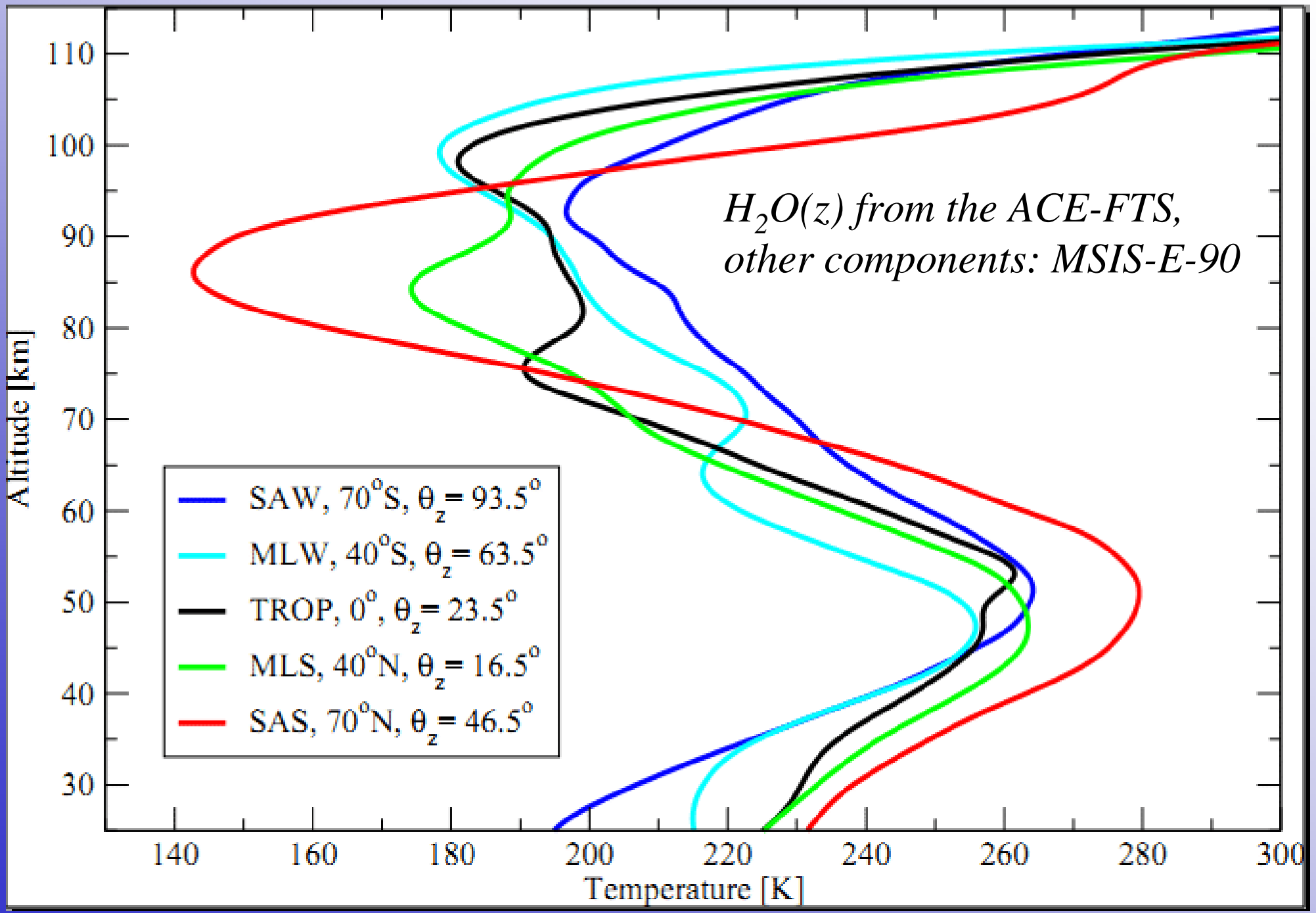
Simulation for mid-latitude conditions (June 23, 2002, lon = 39.6°N, lat = 256.2°): a) vibrational temperatures of H_2O levels; b) contributions of different transitions to 6.3 μm SABER channel. The fundamental band (010–000 transition) dominates the signal at all altitudes with admixture (up to 20%) of the first hot band transition (020–010) at 60–100 km. The dashed line on Fig. b demonstrates the indirect contributions of the upper levels since they pump the 010 and 020 levels through a series of V–V and V–T exchanges as well as through radiative transitions.

Motivation

- Main processes of vibrational energy exchange in atmospheric H_2O:
  1) $H_2O(v_1;v_2;v_3) + O_2(0) \leftrightarrow H_2O(v1;v_2-1;v_3) + O_2(1)$
  2) $H_2O(v_1;v_2;v_3) + M \leftrightarrow H_2O(v_1;v_2-1;v_3) + M$
  3) $H_2O(v_1;v_2;v_3) + M \leftrightarrow H_2O(v_1-1;v_2+2;v_3) + M$
  4) $H_2O(v_1;v_2;v_3) + M \leftrightarrow H_2O(v_1;v_2+2;v_3-1) + M$
- The rate constants for 3) and 4) are known only for (001,100 →020).
- We have estimated ([Barnes et al., 2004]) the rate constants of processes 3) and 4) for the upper vibrational levels: **4 times larger** than currently used (!)
- What is the effect of new rate constants on the $H_2O(v_1;v_2;v_3)$ and atm. spectra?

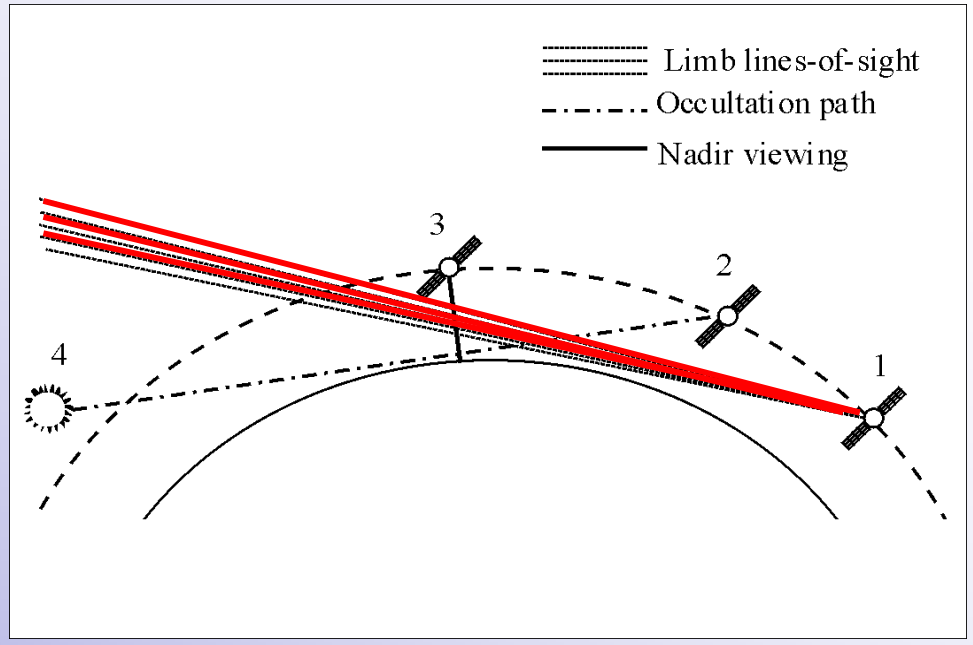


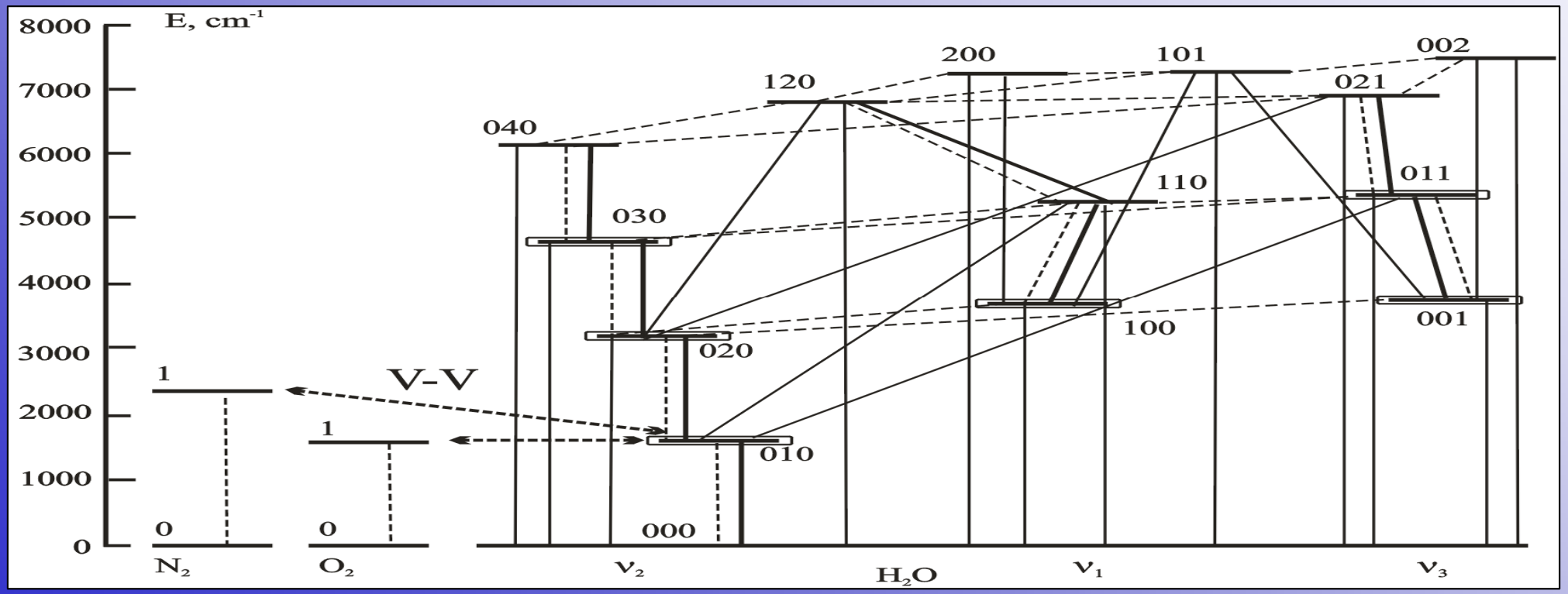
Atmospheric models used in the study



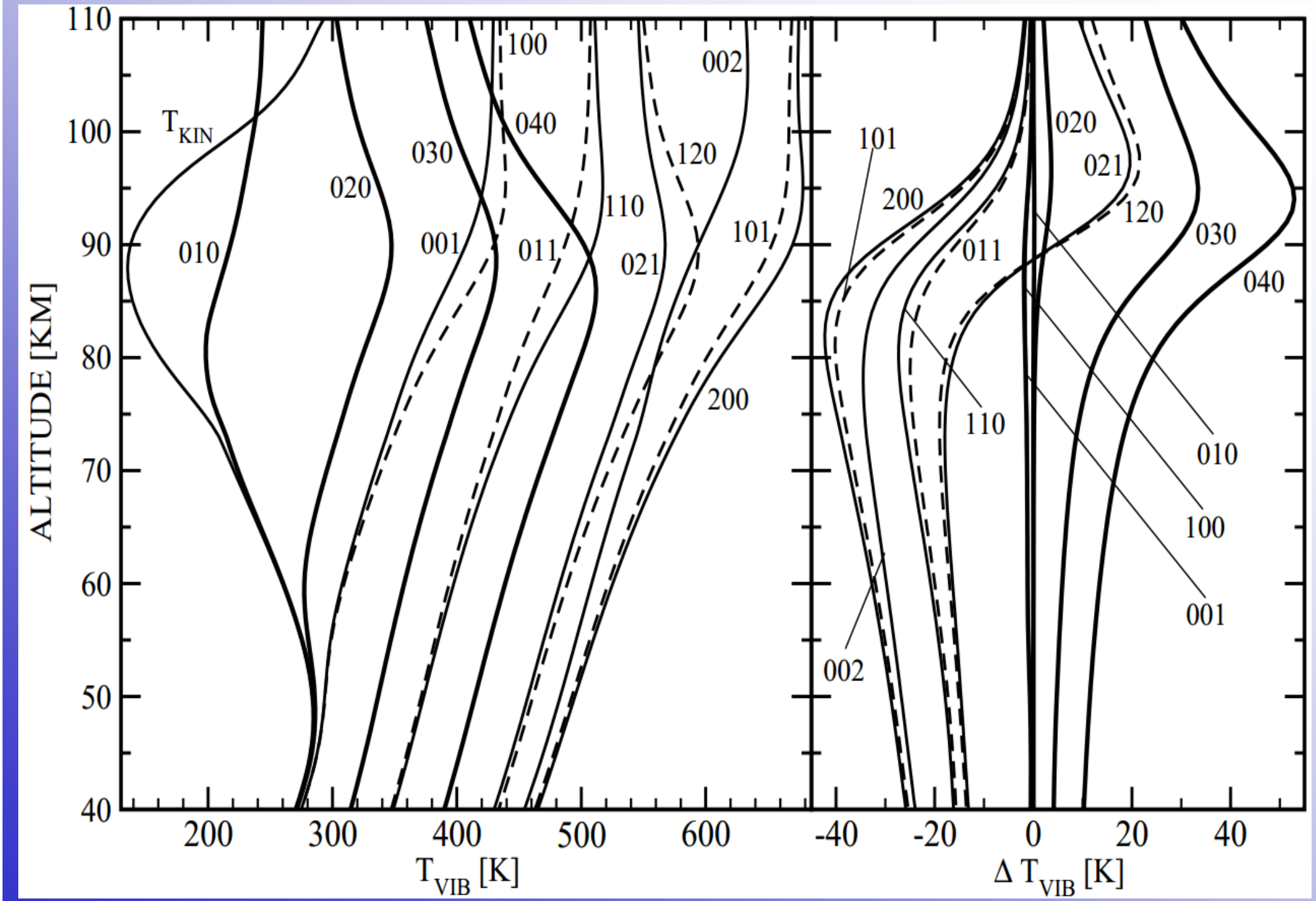
Analysis approach

- ALI-ARMS non-LTE research code [Kutepov et al., 1998; Gusev and Kutepov, 2003; Feofilov and Kutepov, 2012]
- Calculating the $H_2O(v_1,v_2,v_3)$ populations at all height using the "standard" and updated rate coefficients
- Estimating limb radiances in the MLT

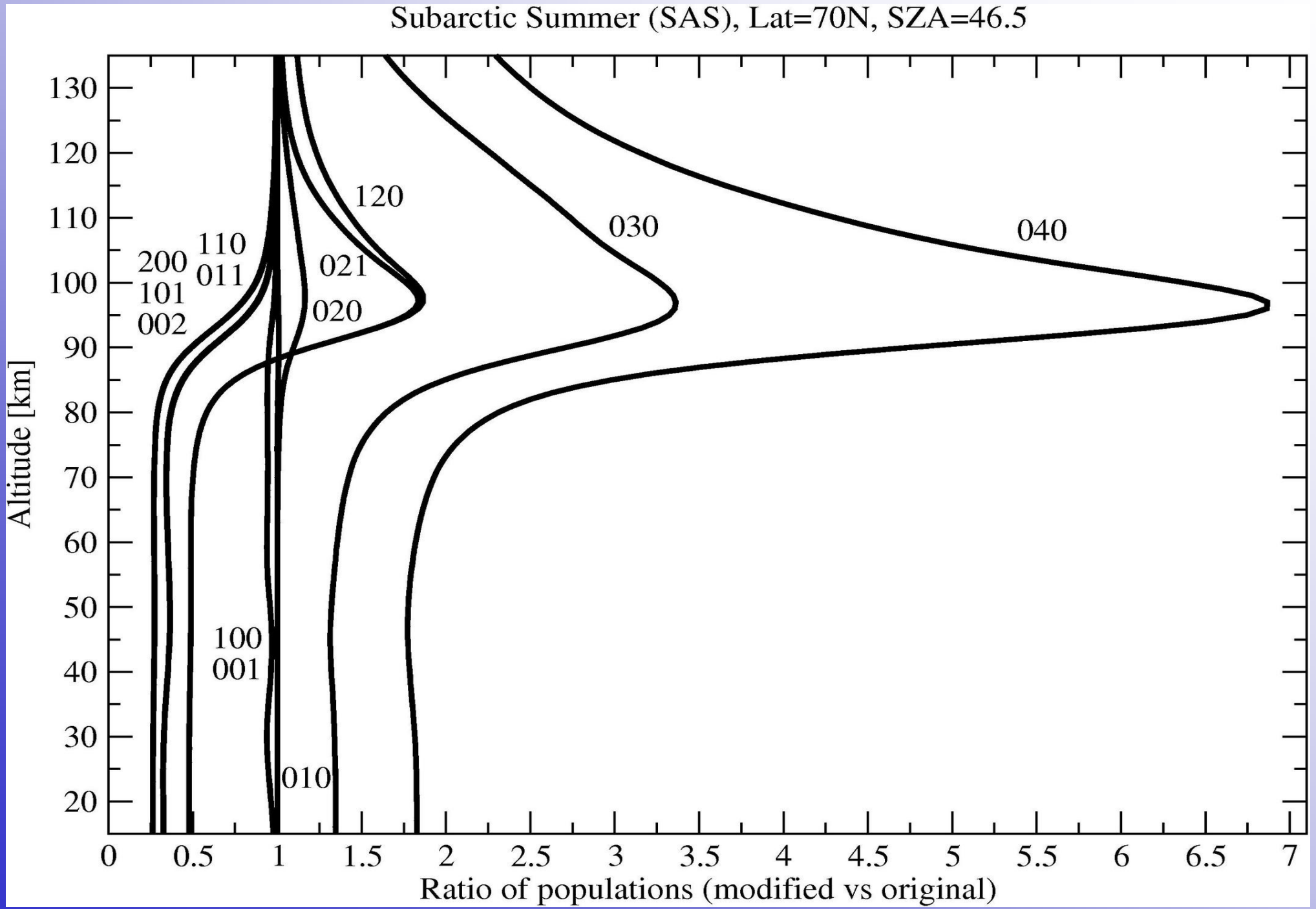




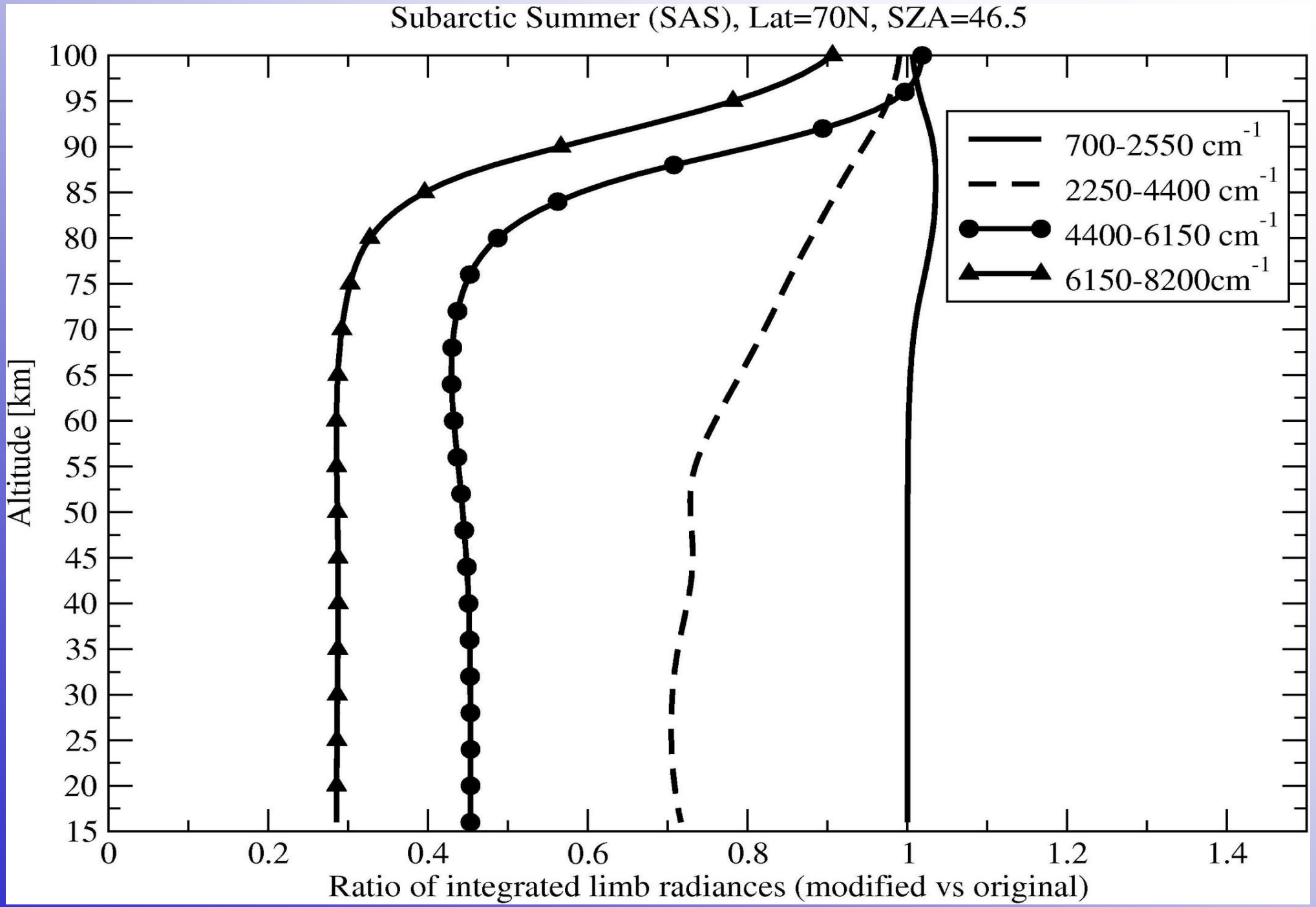
Sensitivity of vibrational level populations: T_{vib}



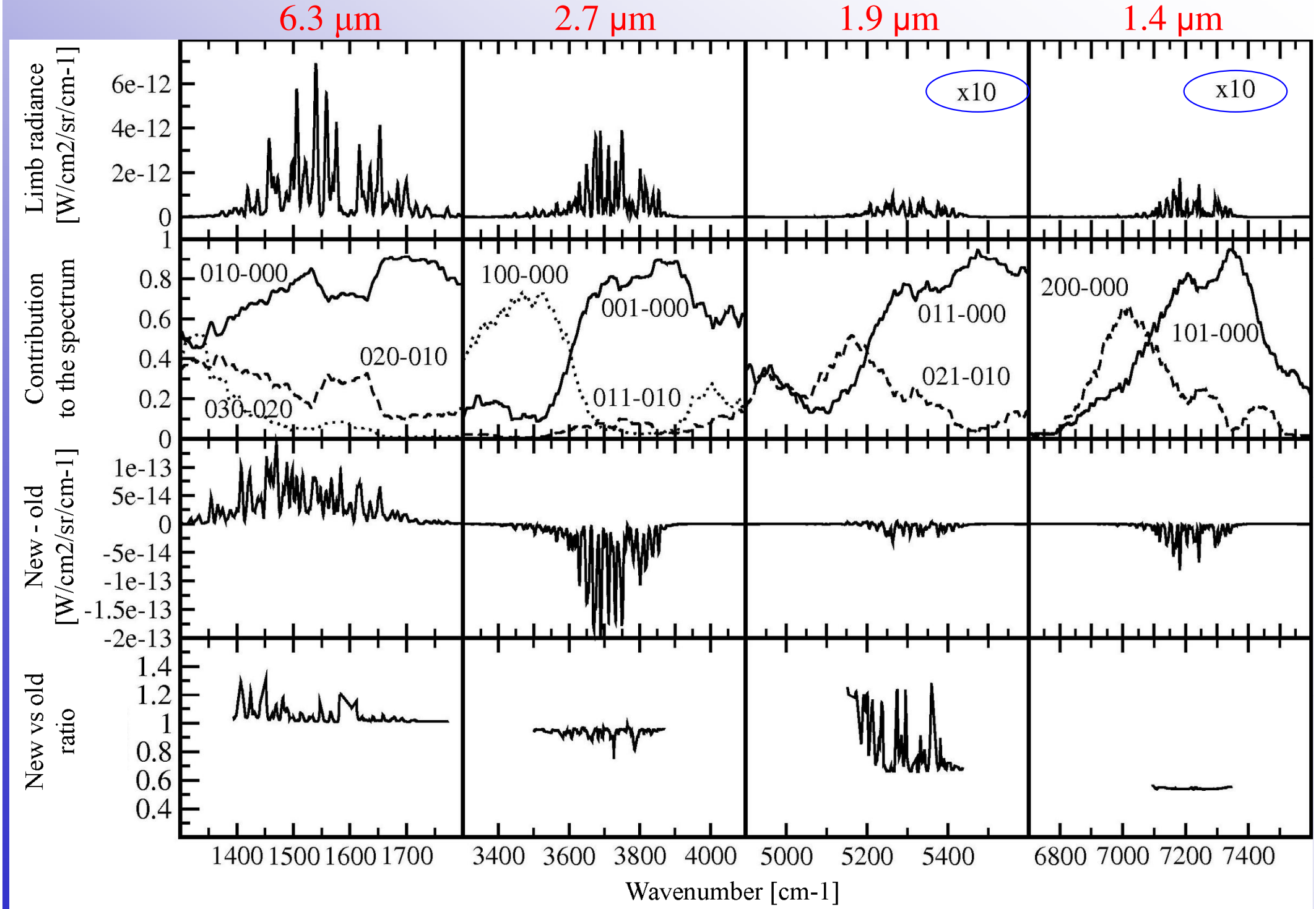
Sensitivity of vibrational level populations: ratios



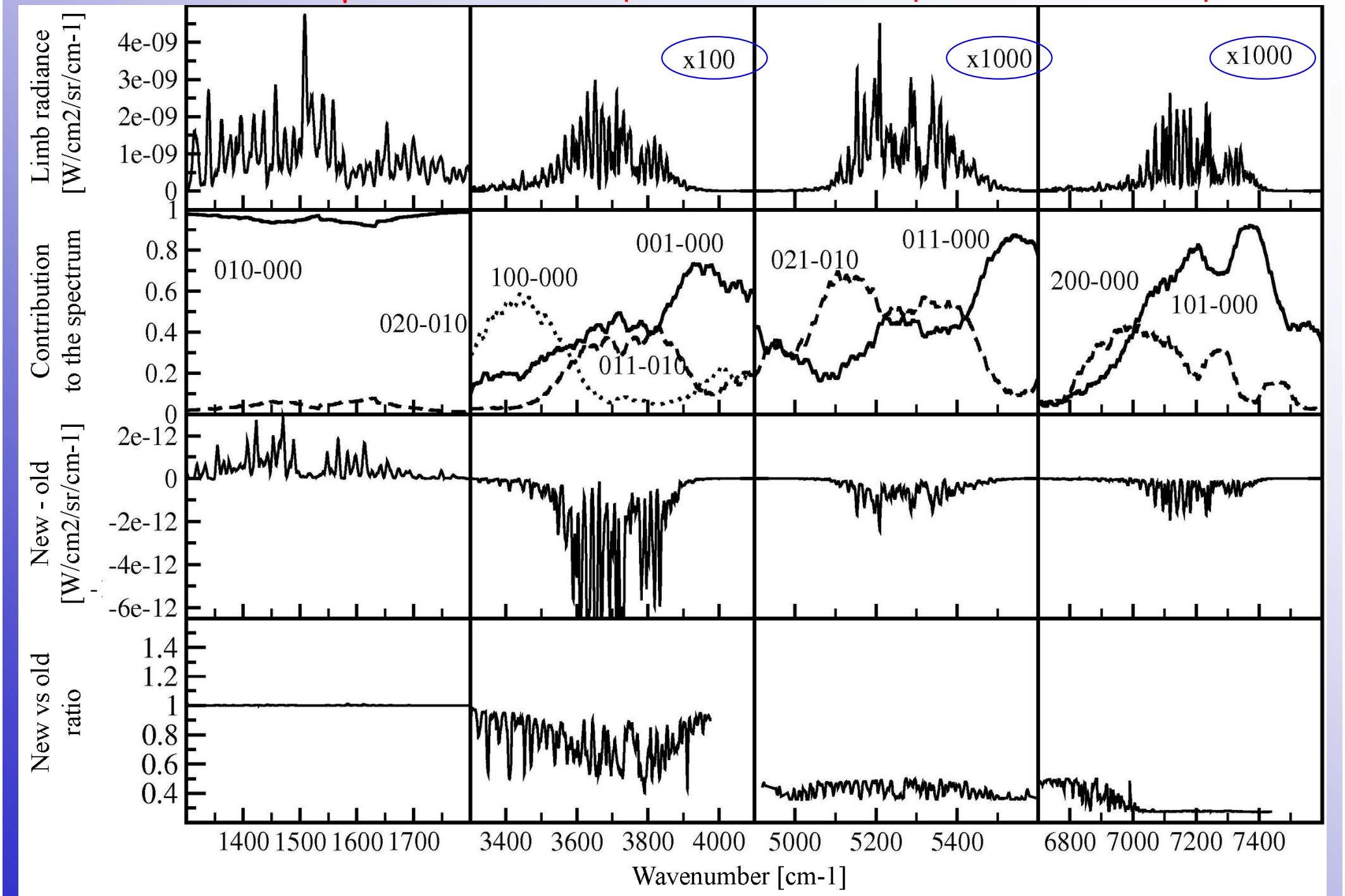
Integrated limb radiances for 6.3, 2.7, 1.9, 1.4 µm bands



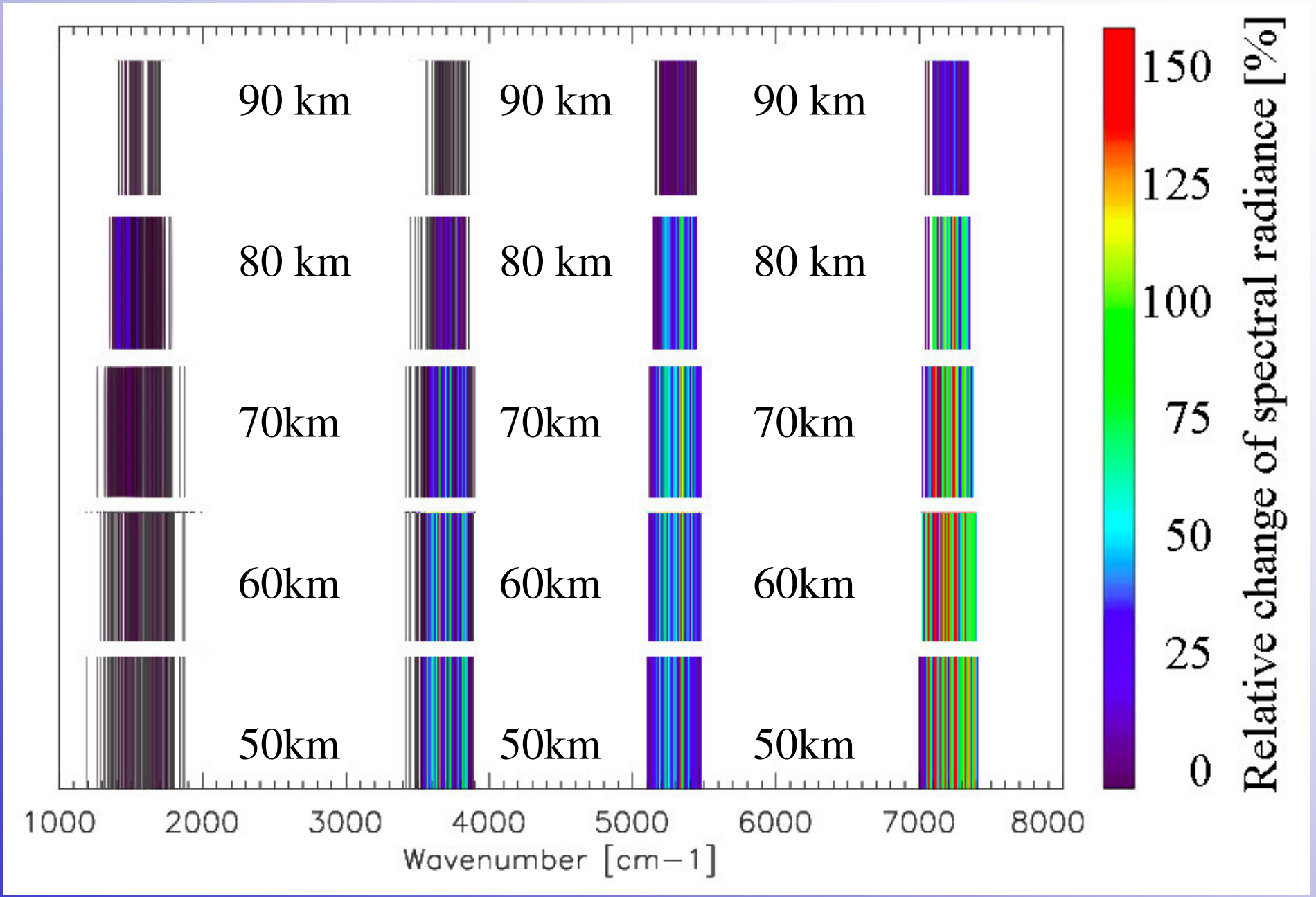
Sensitivity of limb radiance at 90 km



Sensitivity of limb radiance at 50 km



Safe and unsafe microwindows



Conclusions and outlook

- The effect of new rate constants on the H_2O vibrational level populations and on the atmospheric spectra in the MLT is significant, the T_{vib} increase for the v_2=2,3,4 levels reaches 40K at heights > 80km.
- The effect for the 6.3 μm band and, therefore, for the MLT energetics is small, while the 2.7, 1.9, 1.4 μm bands are sensitive to this quenching rate (30–70% change in the limb radiance integrated in a whole band).
- "Safe" and "unsafe" microwindows have been defined for the H_2O retrievals.
- New experimental and theoretical estimations of rate constants for the collisional transitions from the upper vibrational levels of H_2O molecule are necessary to reduce the number of unsafe microwindows.