Infrared radiation of ozone in the mesosphere and lower thermosphere: energetic effects and remote sensing

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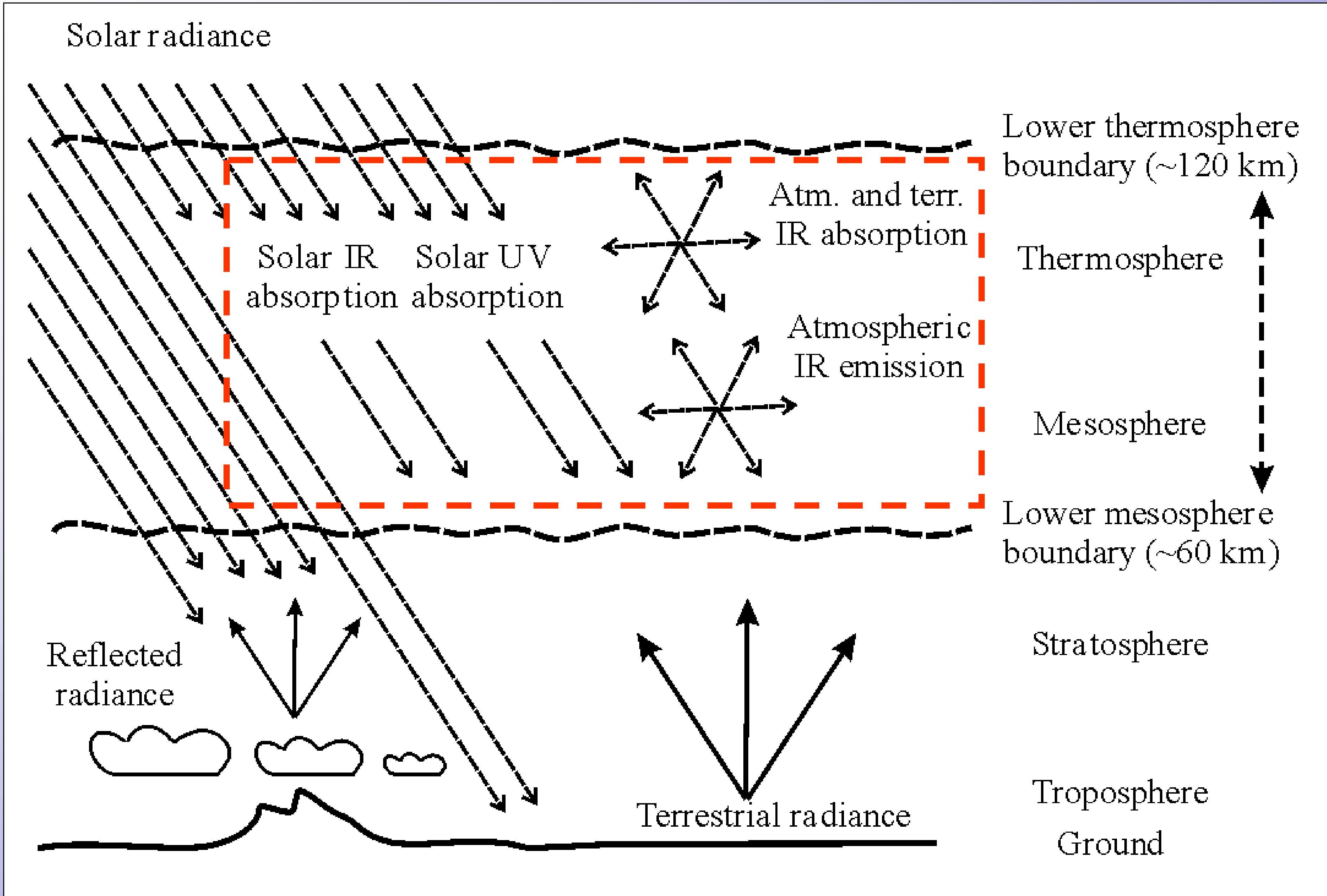
MLT - why bother?

- MLT is a "gateway" between the lower atmosphere and space.
- MLT is sensitive to solar influence and to the inputs from below.
- Anthropogenic changes in greenhouse gases may change this input.
- Noctilucent clouds observed in polar MLT in the summer time are very sensitive to temperature changes and there are debates on their role as a "miner's canary" for global changes.
- MLT area absorption and emission in molecular bands affects the atmospheric observations of other areas.

Object of Study: IR radiance in the MLT



Cooling/heating rates

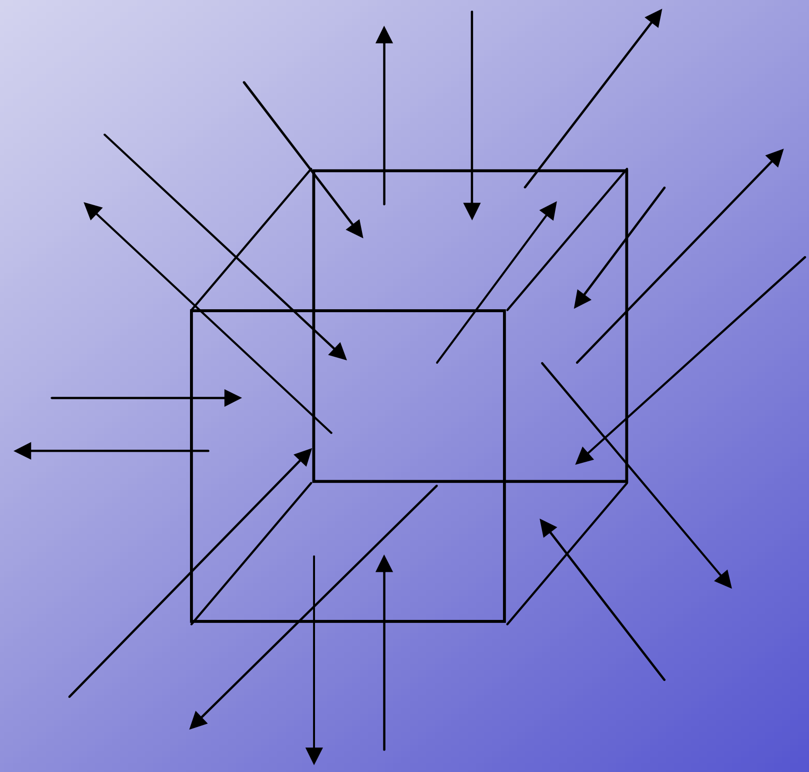
Radiative cooling/heating = radiative flux divergence

in W/m^3:

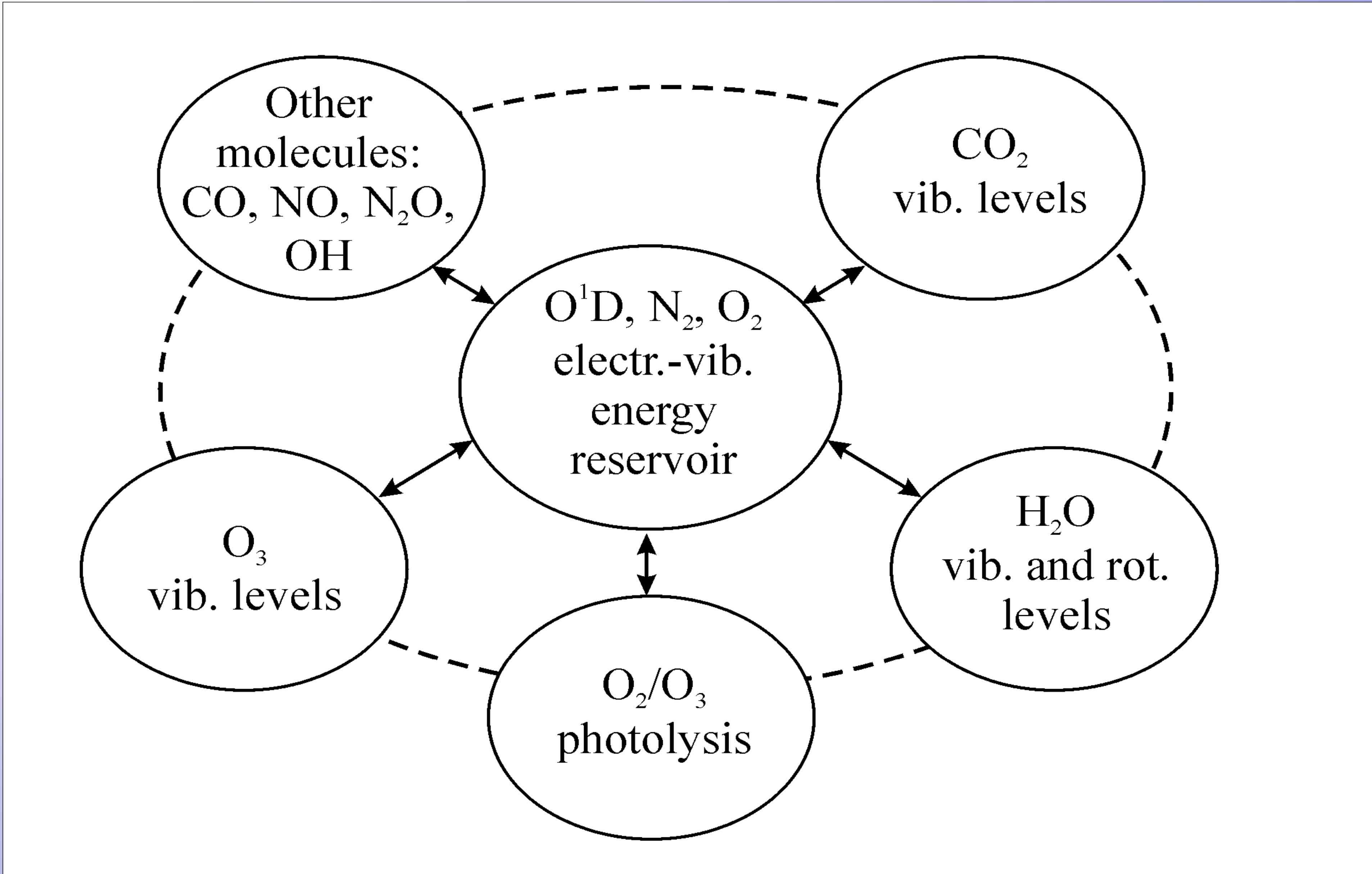
$$H(z) = \frac{1}{4\pi} \int_{\Omega} \int_{-\infty}^{+\infty} \mu \frac{dI_{\mu\nu}(z)}{dz} d\nu$$

in K/day:

$$h(z) = H(z) \cdot \frac{24 \cdot 60 \cdot 60}{C_p(z)\rho(z)}$$



Energy Exchange Between Atmospheric Molecules



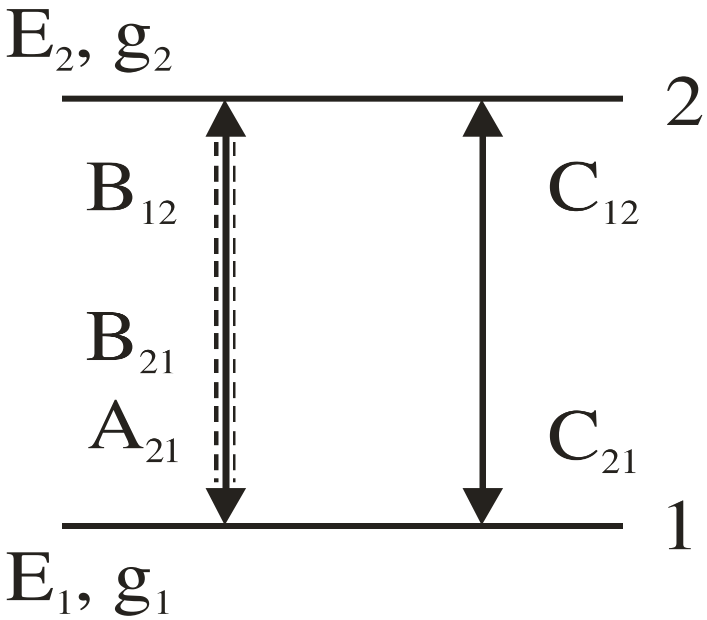
An important peculiarity of the MLT

- Infrared radiance absorption/emission corresponds to vibrational excitation/de-excitation of the molecules.
- To estimate the energetic characteristics of the given area or to interpret the infrared observations in MLT one needs to know the vibrational levels populations.

BUT !!!

- In the upper atmosphere, the collisions between the molecules are **not** frequent and the populations are **not** defined by local temperature.
- Breakdown of Local Thermodynamic Equilibrium (LTE).
- Special methodology is applied (non-LTE modeling).

LTE and non-LTE: two-level atom



$$\begin{cases} (\underbrace{A_{21}+B_{21}\bar{J}}_{R_{21}} + C_{21})\, n_2 = (\underbrace{B_{12}\bar{J}}_{R_{12}} + C_{12})\, n_1 \\ n_1+n_2=n \end{cases}$$

In the lower atmosphere:

$R \ll C$

$R_{21}n_2 \sim R_{12}n_1$

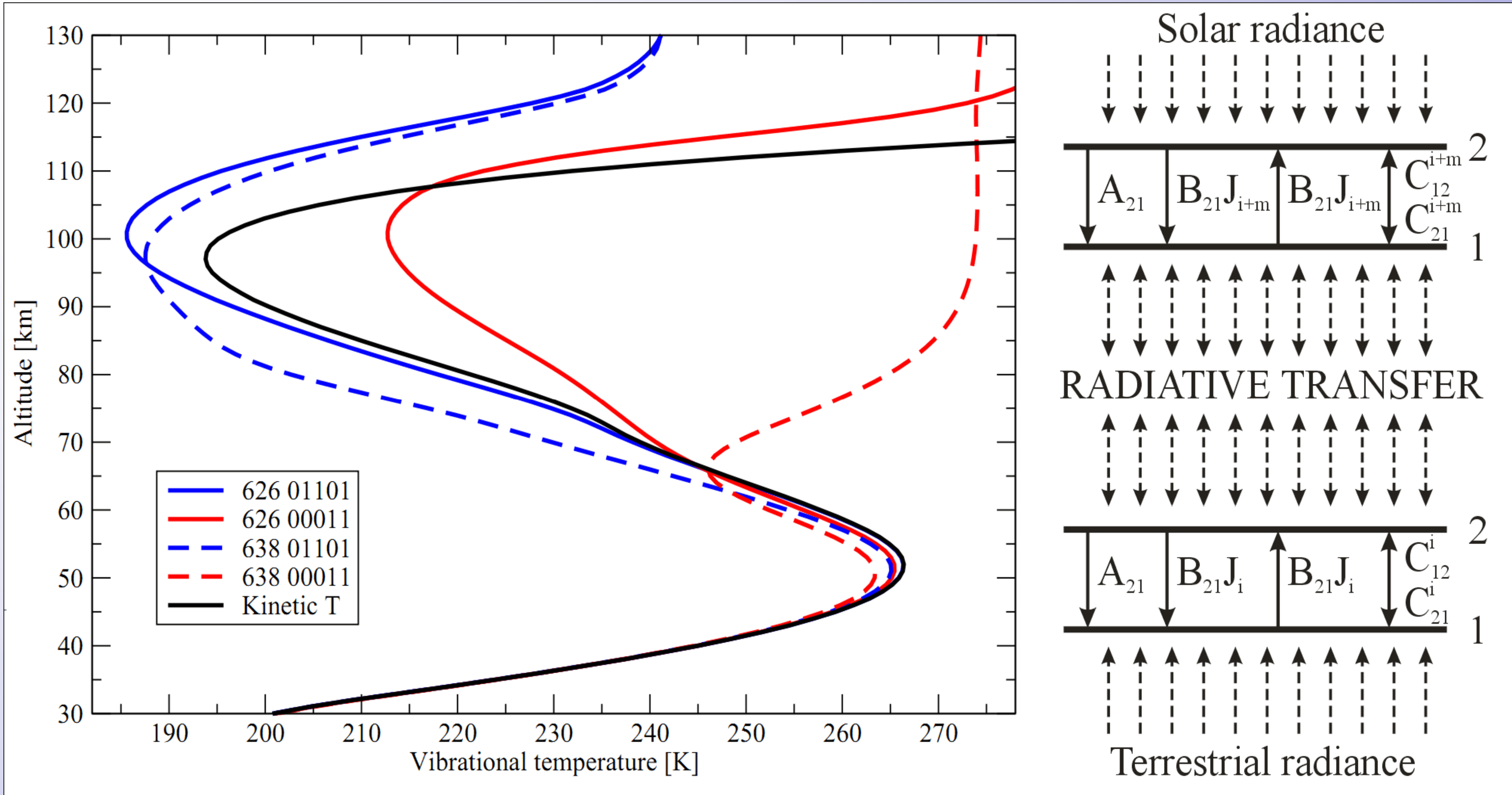
$$n_2C_{21} = n_1C_{12}$$

$$\frac{n_2}{n_1} = \frac{g_2}{g_1}\, e^{-\frac{E_2-E_1}{kT}}$$

In the upper atmosphere:

Collisions are less frequent, and the populations are not defined by local temperature anymore = non-LTE

Non-LTE populations: vibrational temperatures

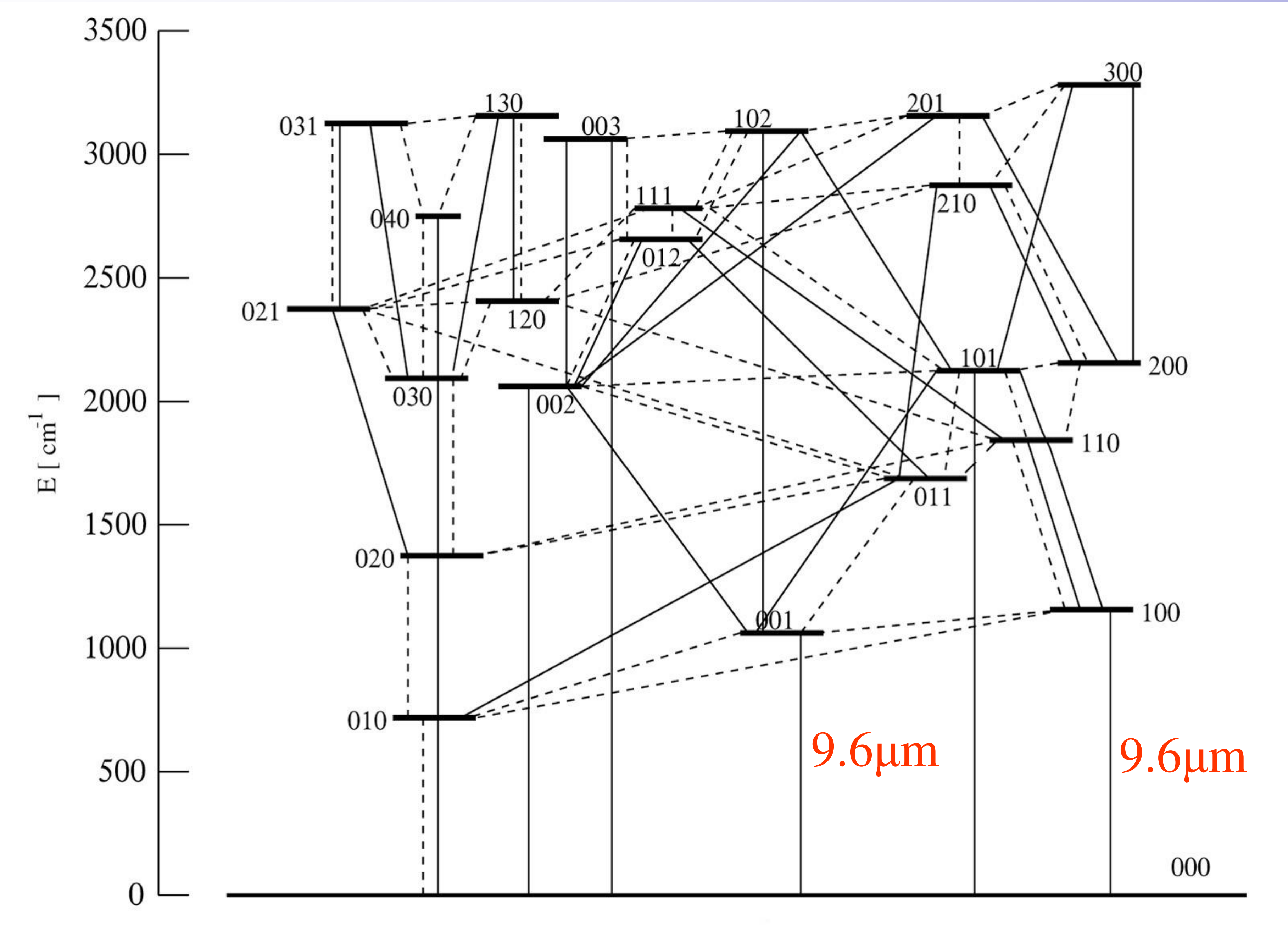


$$\frac{n_l}{n_0} = \frac{g_l}{g_0} \cdot e^{-(E_l - E_0)/kT_{vib}}$$

$T_{vib}=T_{kin}$: LTE

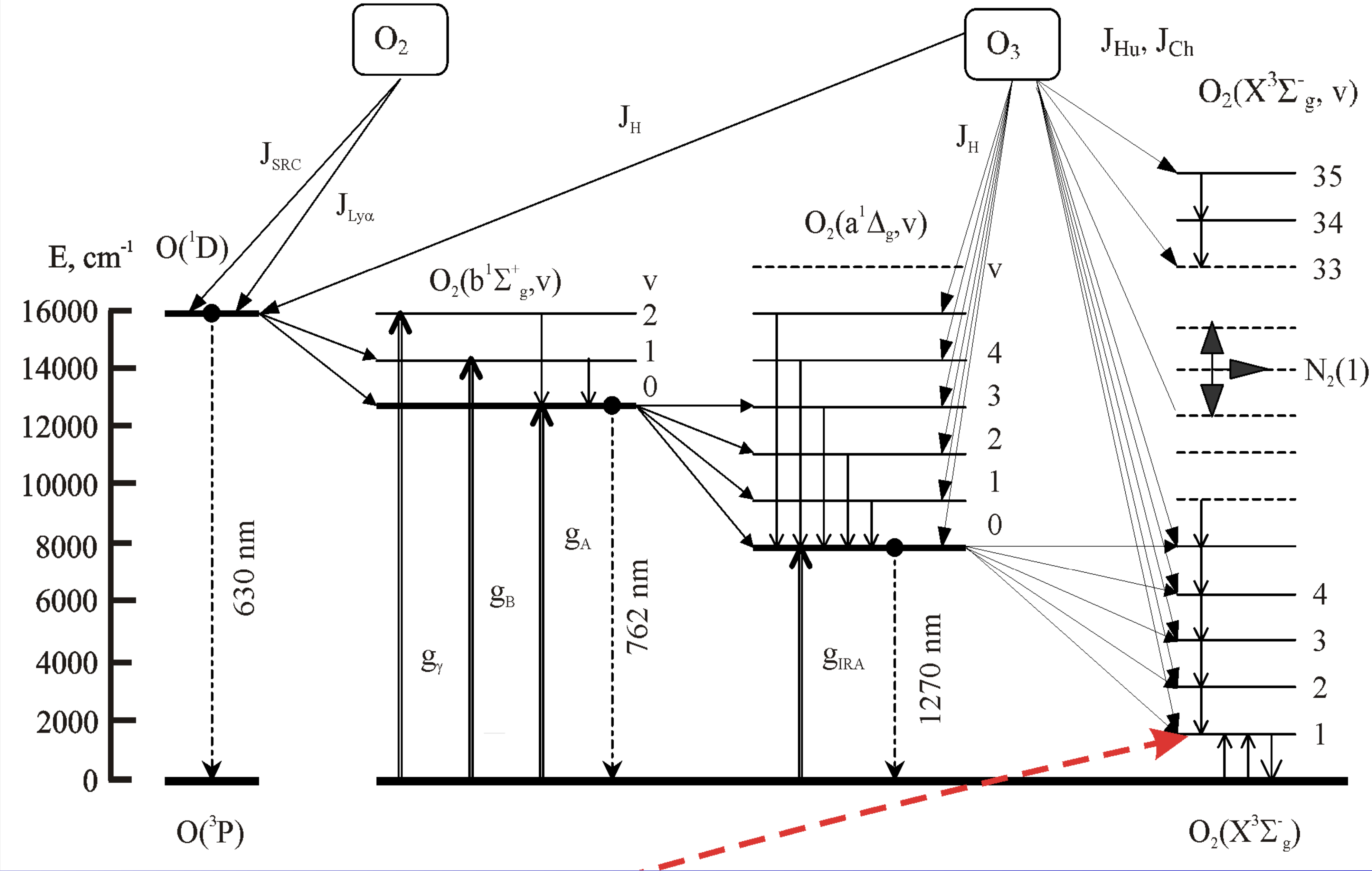
$T_{vib}\neq T_{kin}$: non-LTE

O_3 levels and transitions



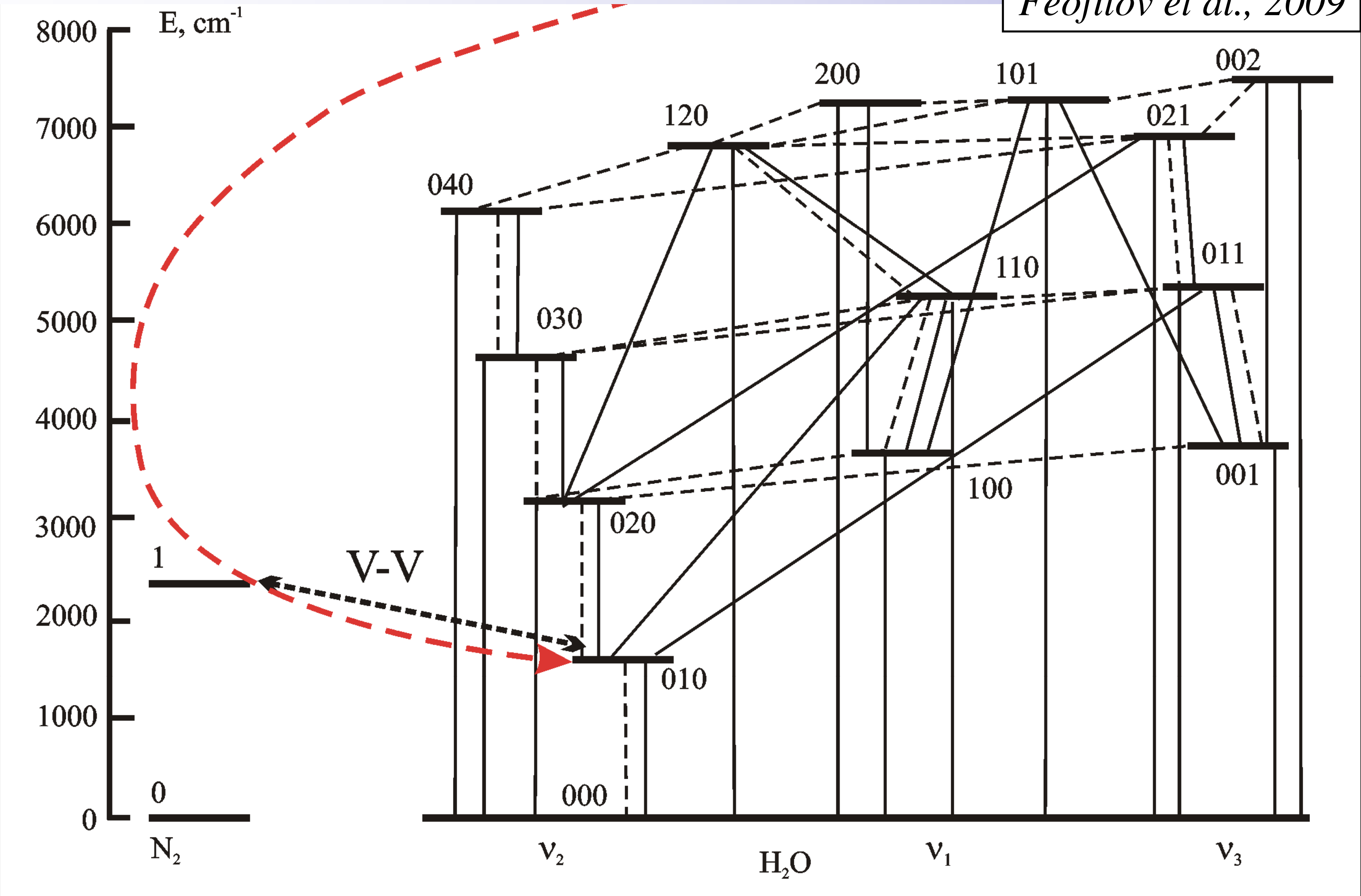
O_2/O_3 photolysis products

Yankovsky and Manuilova, 2006



H_2O levels and transitions

Feofilov et al., 2009



Energy exchange processes for O_3

$$O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \overset{k_{int1}}{\leftrightarrow} O_3(v_1 - 1, v_2, v_3 + 1) + M$$

$$O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \overset{k_{int2}}{\leftrightarrow} O_3(v_1 - 1, v_2 + 1, v_3) + M$$

$$O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \overset{k_{int3}}{\leftrightarrow} O_3(v_1, v_2 + 1, v_3 - 1) + M$$

Intra-molecular energy transfer

$$O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \overset{k_{VT1}}{\leftrightarrow} O_3(v_1, v_2 - 1, v_3) + M$$

$$O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \overset{k_{VT2}}{\leftrightarrow} O_3(v_1 - 1, v_2, v_3) + M$$

$$O_3(v_1, v_2, v_3) + M(N_2, O_2, O) \overset{k_{VT3}}{\leftrightarrow} O_3(v_1, v_2, v_3 - 1) + M$$

Vibrational-translational exchange

$$O_3(000) + N_2(v = 1) \overset{k_{VV1}}{\leftrightarrow} O_3(200) + N_2(v = 0) + 130\ \mathrm{cm}^{-1}$$

$$O_3(000) + O_2(v = 1) \overset{k_{VV2}}{\leftrightarrow} O_3(100) + O_2(v = 0) + 456\ \mathrm{cm}^{-1}$$

$$O_3(000) + O_2(v = 1) \overset{k_{VV3}}{\leftrightarrow} O_3(001) + O_2(v = 0) + 517\ \mathrm{cm}^{-1}$$

$$O_3(102) + O_2(v = 0) \overset{k_{VV4}}{\leftrightarrow} O_3(000) + O_2(v = 2) - 4.9\ \mathrm{cm}^{-1}.$$

Vibrational-vibrational exchange

$$O_2 + O(^3P) + M \rightarrow O_3(v_1, v_2, v_3) + M,$$

Three-body recombination

Plus emission / absorption of radiation

Three-body recombination and nascent population model

A hybrid of models

Manuilova et al (1998) kinetics for lower states, by collisions with N_2, O_2, O^3P

Quasi-continuum Is treated in terms of rate constants

A) Gil-Lopez et al., (2005): Zero surprisal model of nascent population, $E_{D\,I}$ is the dissociation energy

$$P(v)= (1- E(v)/E_D)^{1.5} / \sum_v (1- E(v)/E_D)^{1.5}$$

B) Kaufmann et al. (2006): Zero surprisal model or all excitation goes on 00v3, with v3=3,5 or 8

C) Fernandez et al. (2009, 2010): single level nascent population at O_3 (006), assuming that about 70% of recombination energy goes to vibrations

An inconsistency between O_3 retrieved from 9.6 um and simulated/measured 4.8 um radiance

4.8 microns emission from 200, 101, 002 for known O3 was 2-3 times lower than measured for ~ 75 km

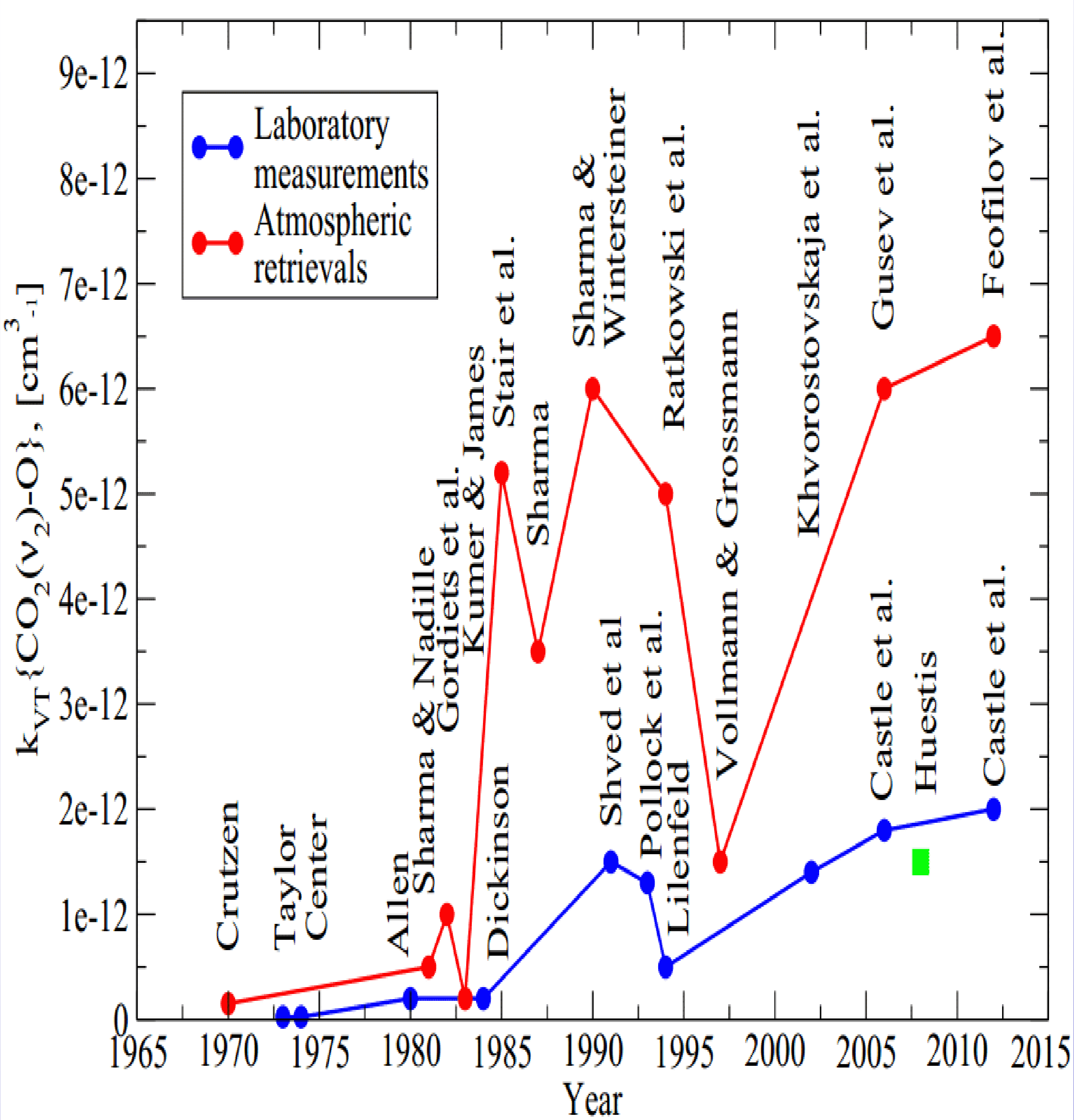
Kaufmann et al, 2006:

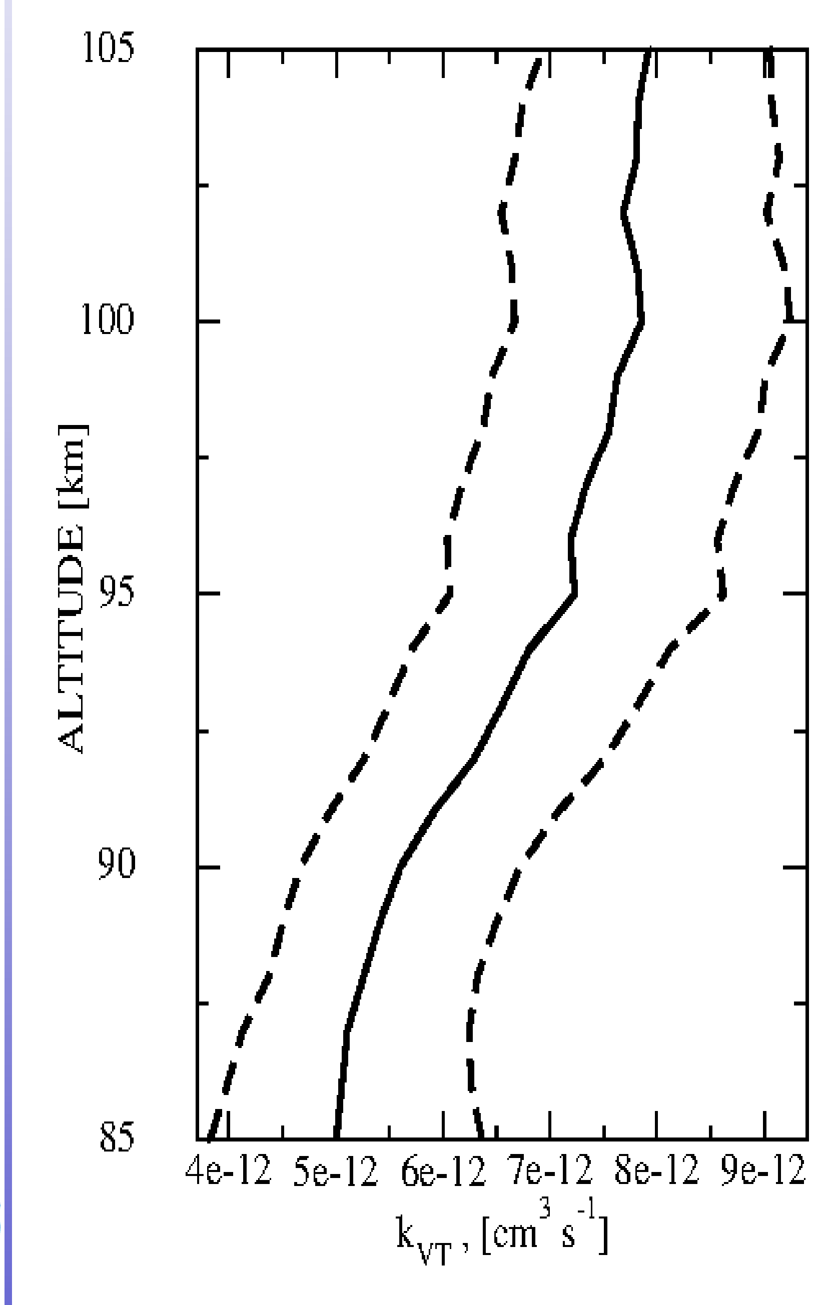
The rate of stretching to bending mode transition 001,100-> 010 K_{D2} must be 3-4 lower than well known measured value

Fernandez et al., 2010:

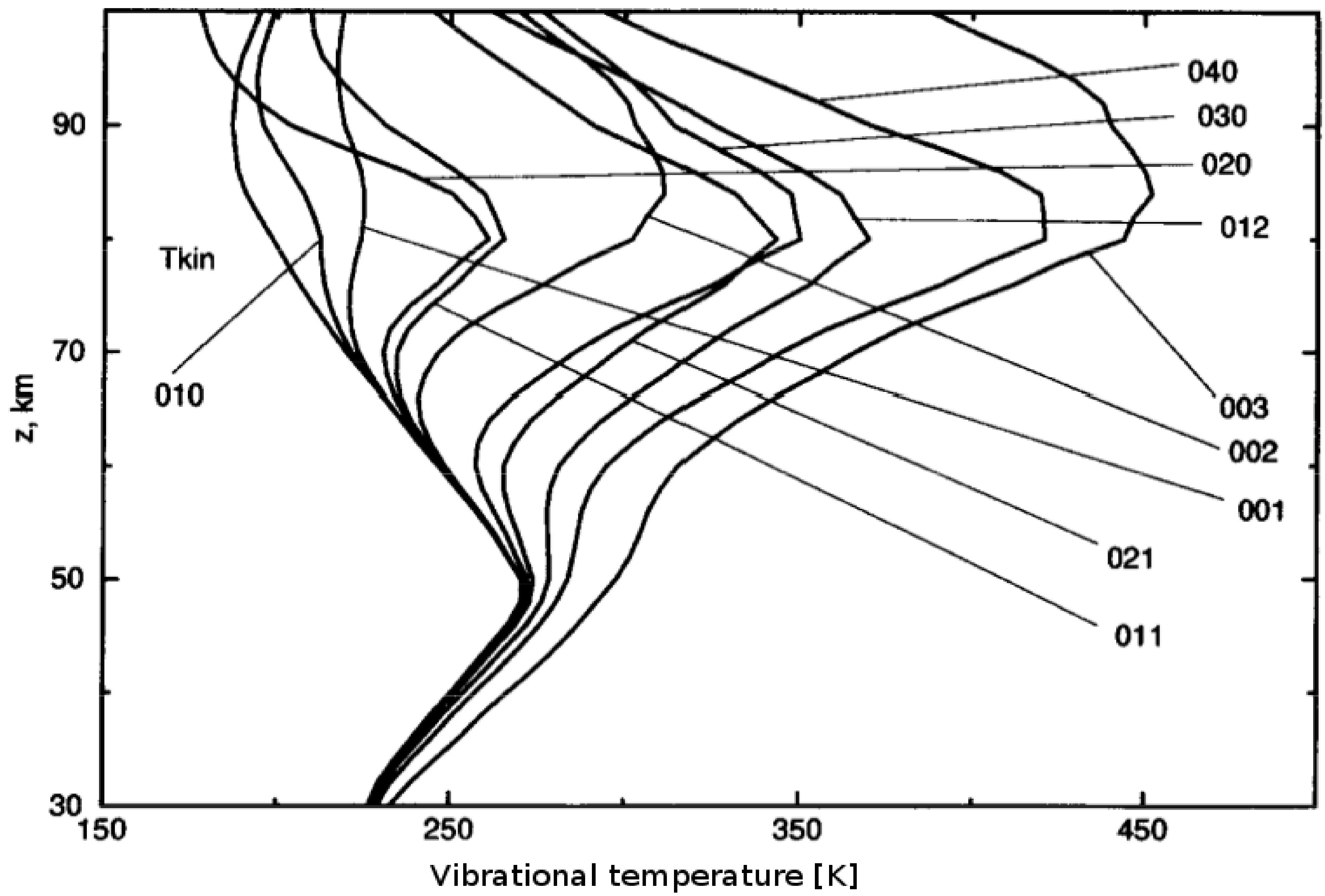
new bending to stretching mode transitions, for lower levels 020->100,001 SSH estimated K_{2D}
For higher levels – harmonic oscillator rule

$k_{VT}\{CO_2\text{-}O\}$ measurements: lab vs atmosphere

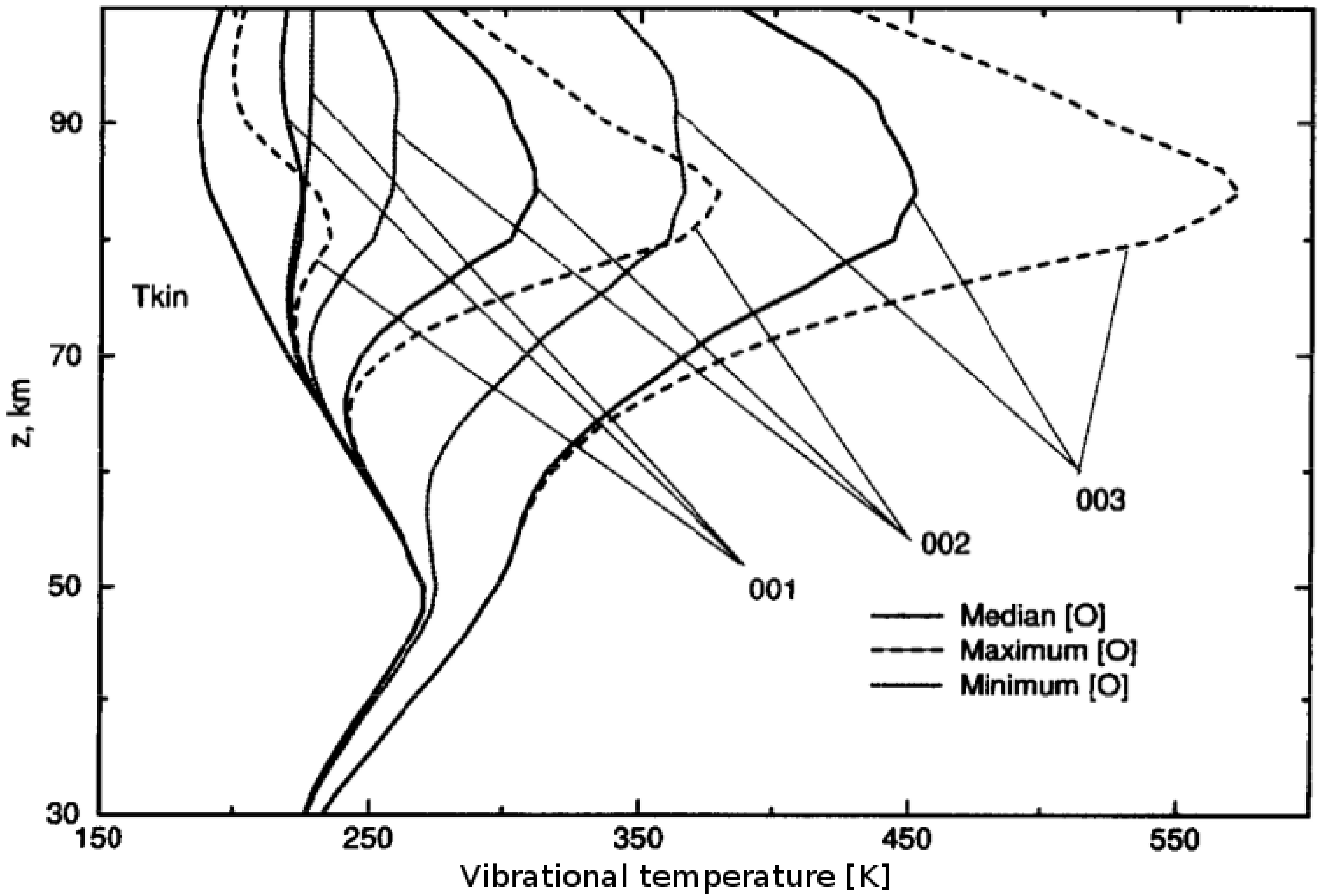




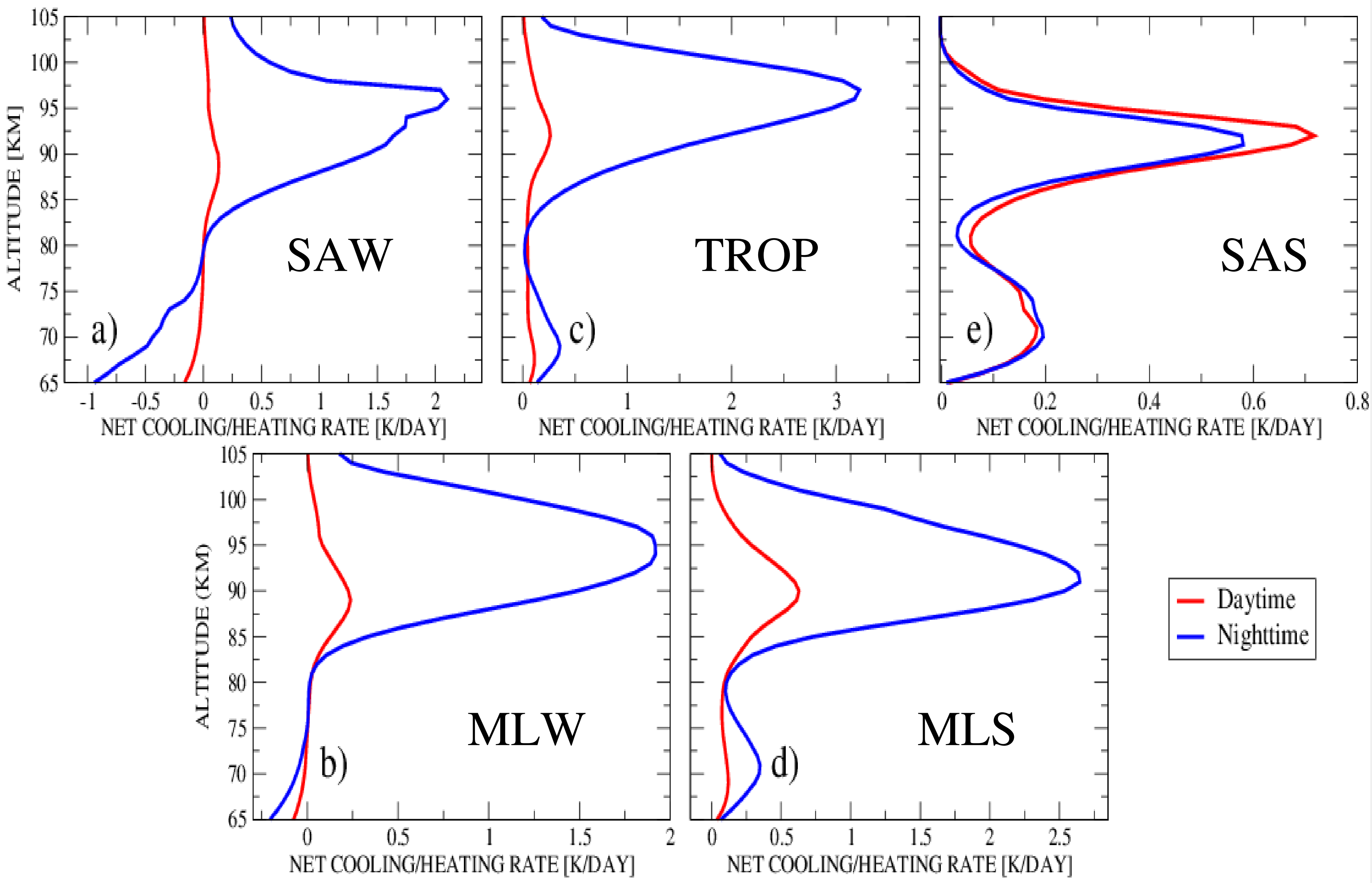
O_3 vibrational level populations – midlatitude day



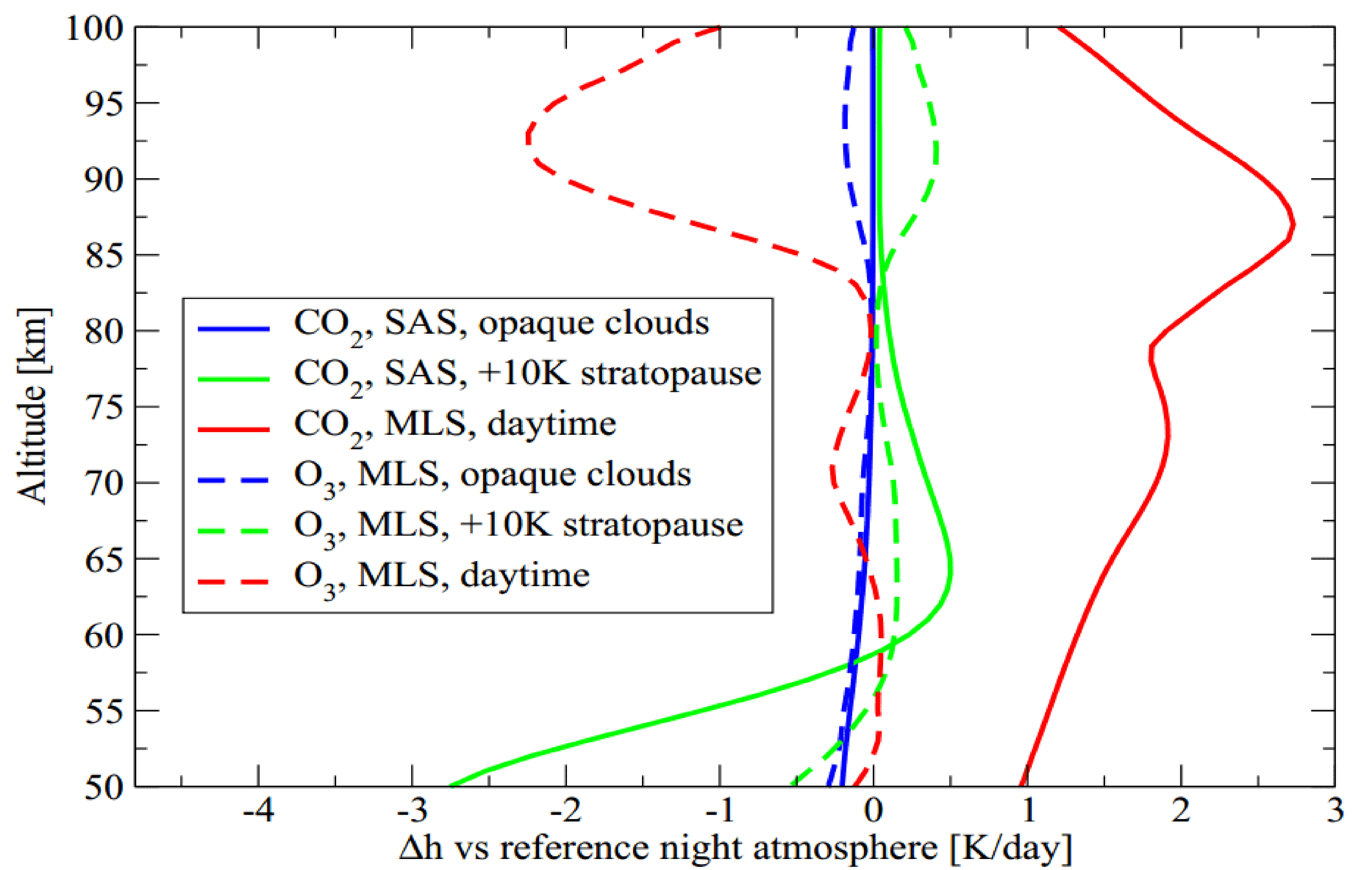
Sensitivity of v_3-levels to atomic O



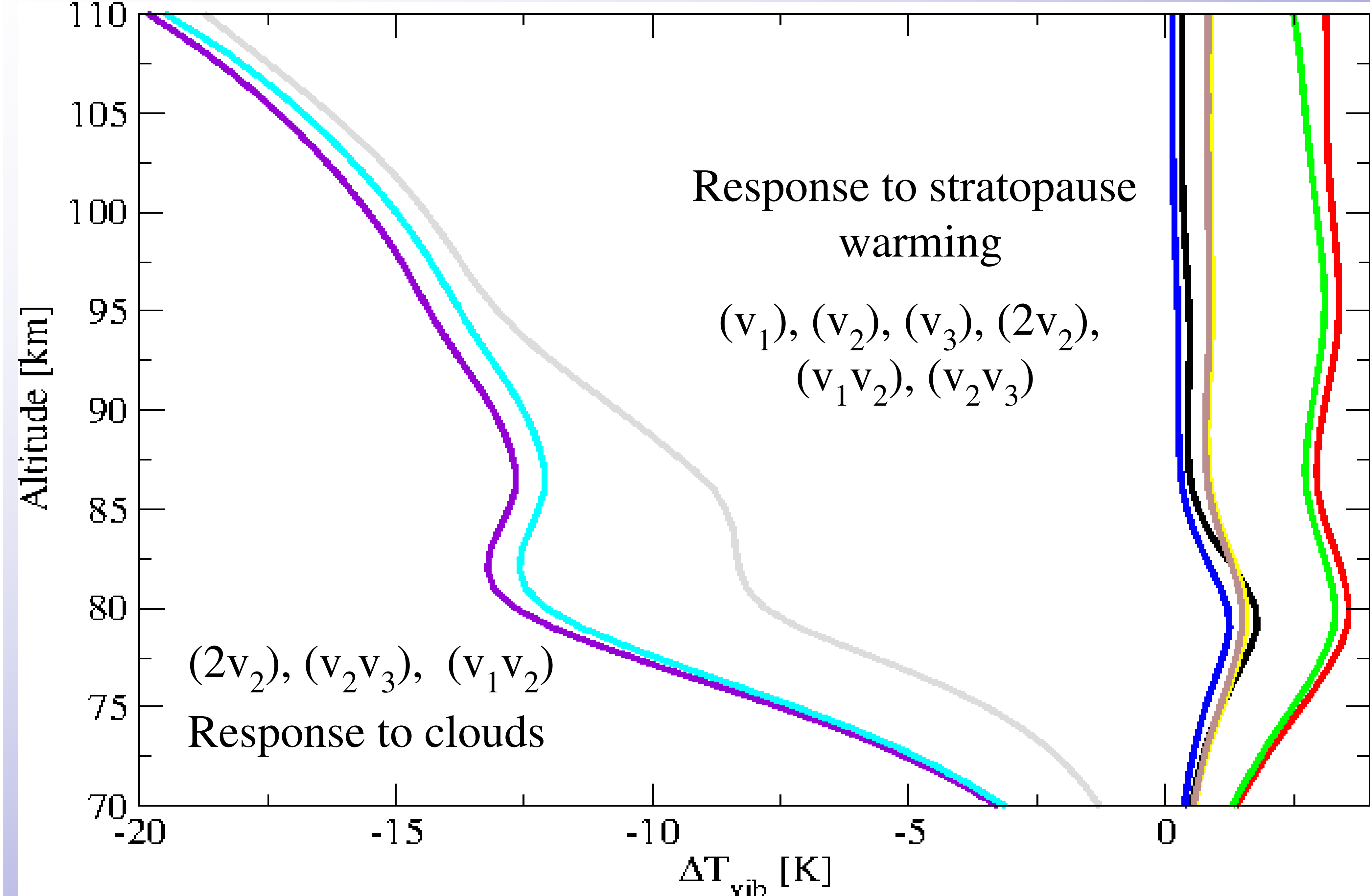
O_3 cooling/heating rates



MLT sensitivity to clouds, stratopause T, and solar pumping changes



O_3 vibr. levels, sensitive to changes in other layers



Take home messages

- ✓ O_3 is an important component of the MLT
- ✓ O_3(9.6μm) IR cooling/heating in 65-105 km altitude range is -1...+3 K/day
- ✓ Energetic effects of direct radiative coupling with tropo- and stratosphere are less than 1 K/day
- ✓ Changes in lower atmosphere affect vibrational levels, which are pumped by radiation coming in optically thin lines.
- ✓ Adequate model of nascent population of O_3 molecule formed in three-body recombination is still required
- ✓ Collisional rate calculations are needed.