MIPAS Phase F: WPs# 5240, 3600 and 8000

Updates of Tvibs (v3) and non-LTE improvements

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Summary and Major conclusions

We report here on the update of the vibrational temperatures (version 3) of previous version (Technical reports: `TN_IAA_VTs1_IGext_VTs_v2_5ref_Nov2009` and `TN_IAA_VTs2_IGext_VTs_v2_Addendum_5ref_Nov2009`). The reference atmospheres have not been updated. The corresponding changes in the NLTE errors have also been estimated.

The major changes can be summarized as:

- General updates as described in Funke et al., JQSRT, 2012.
- Overall update of spectroscopic and energy levels
- Absorption of upwelling flux (clouds, surface albedo, etc.)
- More energy levels included
- CO2 NLTE updates as described in Jurado-Navarro et al., JGR, 2015. They include:
- Inversion of collisional rates, including the temperature dependence and CO2 vmr from band D spectra. It resulted in improved NLTE CO_2 populations.
- Other "minor" non-LTE updates were included
- O3 NLTE updates (see López-Puertas et al., AMT, 2018):
  – Revision of kvt: O3(v3) + M(N2, O2) => O3(v3-1): Small effect
  – Revision of k1: O+O2+M: Small effect
  – Neglect the removal of O3(v3) by O chemical loss => larger (significant) O3 Tvibs (2-6 K) in the mesosphere

In general, most of these changes affect only to the non-LTE retrievals of species but marginally at the spectral regions/bands were the retrieval is performed under LTE, as in ORM.

The major resulting changes in the vibrational temperatures are:

- H2O-CH4 daytime VTs are smaller ($\sim$1-2 K) at z>60 km
- CO2: Small changes (1-2 K larger) in the Tvibs of the 4.3 and 10 μm bands above around 60 km.
- O3: larger O3 Tvibs (2-5 K) in the mesosphere, z>60km
- CO: No effect in main isotope; smaller VTs for the minor isotopes.
- OH(v): Smaller VTs because of rotational NLTE included (adjusted to MIPAS band A OH emission): Impact on CO2 4.3 μm at night-time
- No significant changes for the rest of species: N2O, NO2, NO, HCN, HNO3.

1 The H_2O and CH_4 NLTE models

The major changes can be summarized as:

- New rate for quenching of O2(1) by O, a factor of ~(3-5) larger (Kalogerakis et al., 2006)
- New rate for H2O-O2 VV rate kvv = 1.0e-12 $cm^3 s^{-1}$ (smaller, MIPAS)
- A new model for O2(v). Provides a larger excitation of O2(1) from O3 photolysis (Previous ϵ=4; now: z-dependent, ϵ=7-8 in the lower mesosphere)
- Minor change: the temperature dependency of CO2(020) + O2 $<=>$ CO2 + O2 (1) at T$<$ 300 K: $\sqrt{T}$
- New rate for CH4-O2 VV exchange (Boursier et al., 2007).
- Revision of the O2(v) model and O2(1) + O rate

See the detailed changes in the vibrational temperatures in the attached Annex.

2 CO_2 NLTE model

The major changes are described in Jurado-Navarro et al., JGR, 2015, and are summarized below:

- Inversion of Kvv and Kvt collisional rates, including their temperature dependence
- Near-IR solar flux of the 2.7 μm bands increased in 1.7%.; and that at 4.3 μm bands reduced in 0.2%
- Further V-V coupling (v1+v2=1,2) for isos=2-6: CO2(main)(001) + CO2(iso)(v1,v2,0) $<=>$ CO2(main) + CO2(iso)(v1,v2,1)
- Fixed bug in the collisional rate N2(1) + O $<=>$ N2 + O. It was a factor of 5 too large
- Fixed error affecting the population of the CO2 628 (010) and (020) (15 μm) levels
- Line-by-line calculation of the CMs of the 3 2.7 μm levels
- Angular integration increased from 4 to 8 points in the bands affecting the 2.7 μm levels
- Included HITRAN 2012 CO2 spectroscopy

See the detailed changes in the vibrational temperatures in the attached Annex.

Summary of CO_2 results:

– Many changes done in the CO2 non-LTE modelling.
– New set of collisional rates derived from MIPAS spectra
– Small changes (1-2 K larger) in the Tvibs of the 4.3 and 10 μm bands of CO2 above around 60 km.

3 O_3 NLTE model

The major changes are described in Jurado-Navarro et al., JGR, 2015, and are summarized below:

- Included the thermal relaxation by O: O3*(v1,v3) + O => O3(v2)
- The chemical quenching of O_3 by O: O3*(v1,v3) + O => O3 + O has been removed. This leads to larger O_3 Tvibs
- Total quenching by O still within measurements errors (West et al., 1976; 1978)

See the detailed changes in the vibrational temperatures in the attached Annex. In summary:
– The revision of kvt: O3(v3) + M(N2, O2) => O3(v3-1) has a small effect
– The revision of k1: O+O2+M has a small effect
– The neglection of the removal of O3(v3) by O chemical loss leads to larger (2-5 K) O3 Tvibs in the mesosphere.

4 NLTE model of other species

– CO: No effect in main CO(1) isotope. Smaller VTs for the minor isotopes because tropospheric upwelling flux is smaller because of inclusion of tropospheric clouds.
– OH(v): Smaller VTs because of rotational NLTE included (adjusted to MIPAS band A OH emission). It has some impact on CO2 4.3 μm at night-time.
– No significant changes for the rest of species: N2O, NO2, NO, HCN, HNO3.

5 Revision of NLTE errors after these new VTs

The figures showing the new NLTE errors compared to previous ones are shown in the attache annex.

ANNEX I:

Detailed changes in VTs and NLTE errors as presented at

QWG #40 (Firenze, 2-4 Nov, 2015)

MIPAS Phase F: WPs# 5240 & 3600: Updates of Tvibs (v3)

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Tvibs history

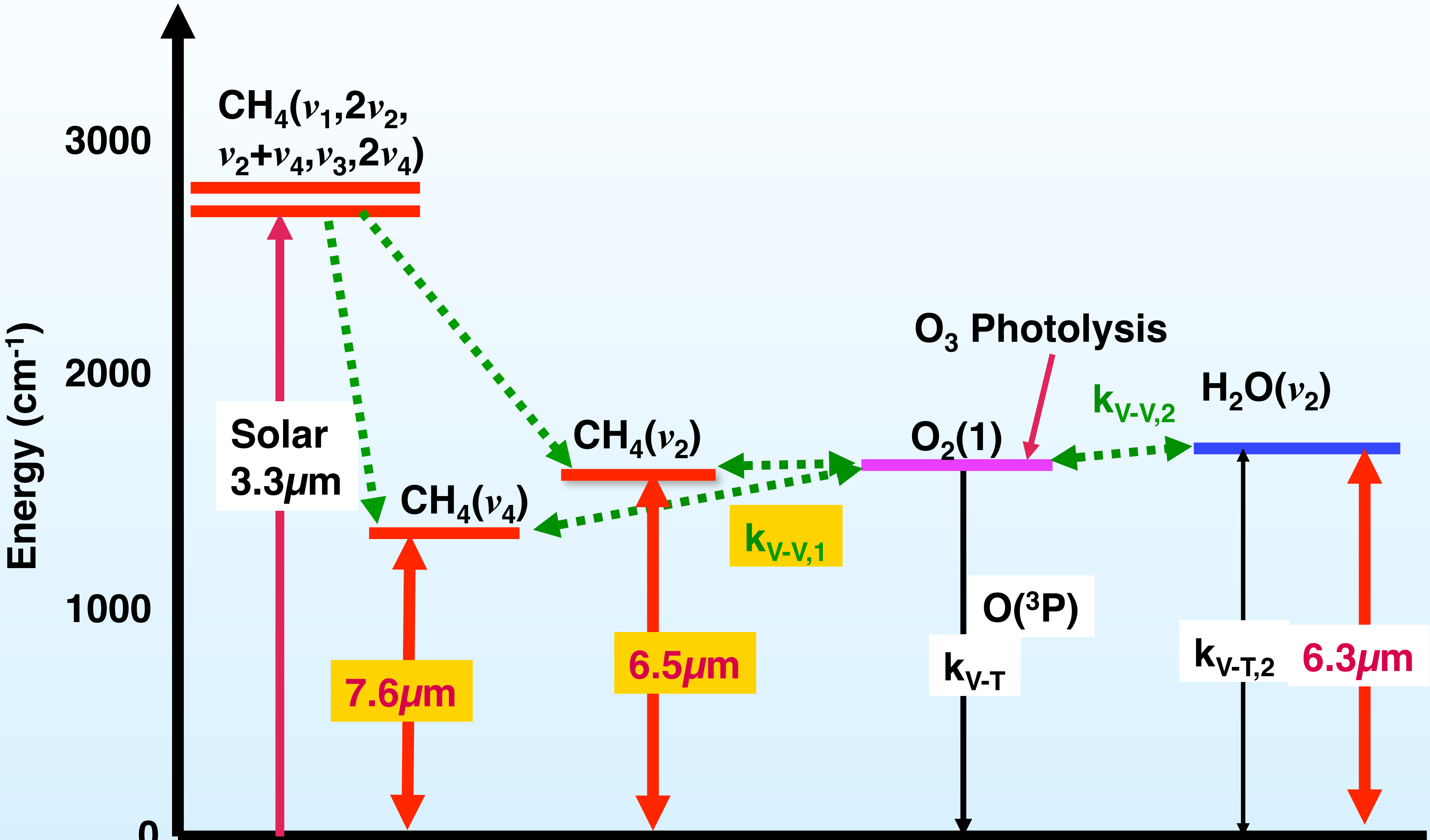
- **NLTE Study (1997) (before QWG)**
- **> 5 ref atm (Nov 2009)**
- **> ig2 (Nov 2009)**
- **> ig2_v2 (Jul 2011)** (Inconsistent ref. atm., No NLTE updates)
- **> Version 3 (5 ref. and 48 ref. atms) (Sep. 2015)**

NLTE updates for VTs v3

- General updates (Funke et al., JQSRT, 2012)
  - Overall update of spectroscopic + Energy levels
  - Absorption of upwelling flux (clouds, surface albedo, etc.)
  - More energy levels
- CO2 NLTE updates (Jurado-Navarro et al., JGR, 2015)
  - Inversion of collisional rates, including the temperature dependence + CO2 vmr from band D spectra => Improved NLTE
  - Other “minor” non-LTE updates
- O3 NLTE updates (Presentation at 38th MIPAS QWG)
- Most of these changes affect only to the non-LTE retrievals of species

H_2O, CH_4

H2O, CH4 & O2 collisional proc.



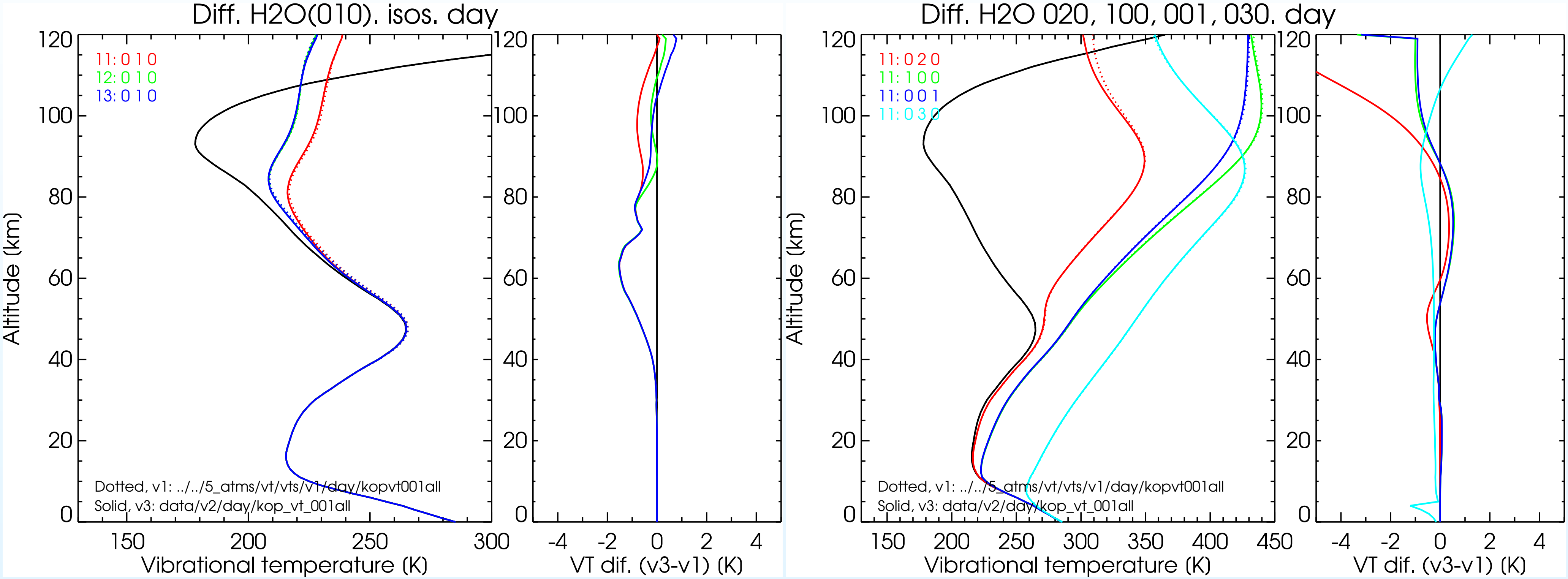
H2O and CH4 VTs

- New rate for quenching of O2(1) by O, a factor of ~(3-5) larger (Kalogerakis et al., 2006)
- New rate for H2O-O2 VV rate kvv = 1.0e-12 cm3s-1 (smaller, MIPAS)
- A new model for O2(v). Provides a larger excitation of O2(1) from O3 photolysis (Previous ε=4; now: z-dependent, ε=7-8 in the lower mesosphere)
- Minor change: Temp. dependency of

  CO2(020) + O2 ←→ CO2 + O2 (1) at T< 300 K: sqrt(T)
- New rate for CH_4-O_2 VV exchange (Boursier et al., 2007).

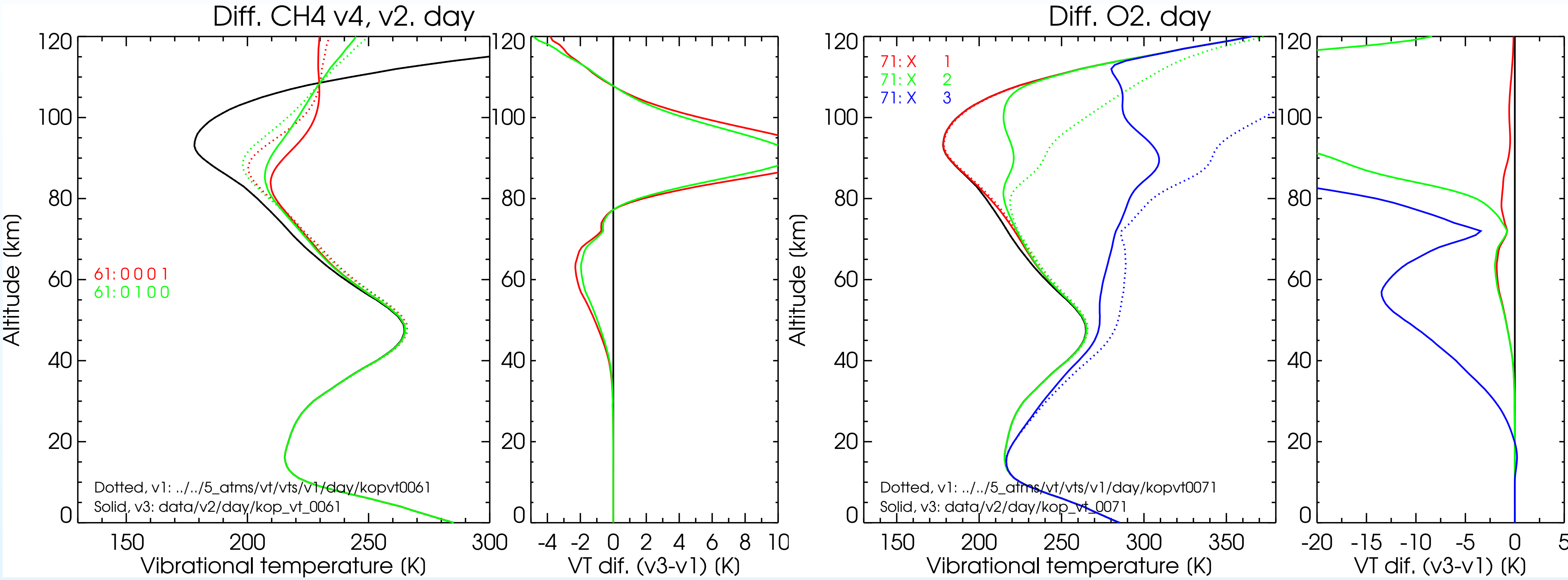
- V3: Revision of the O2(v) model and O2(1)+O rate

Comparison of VTs: H2O(010,020). DAY

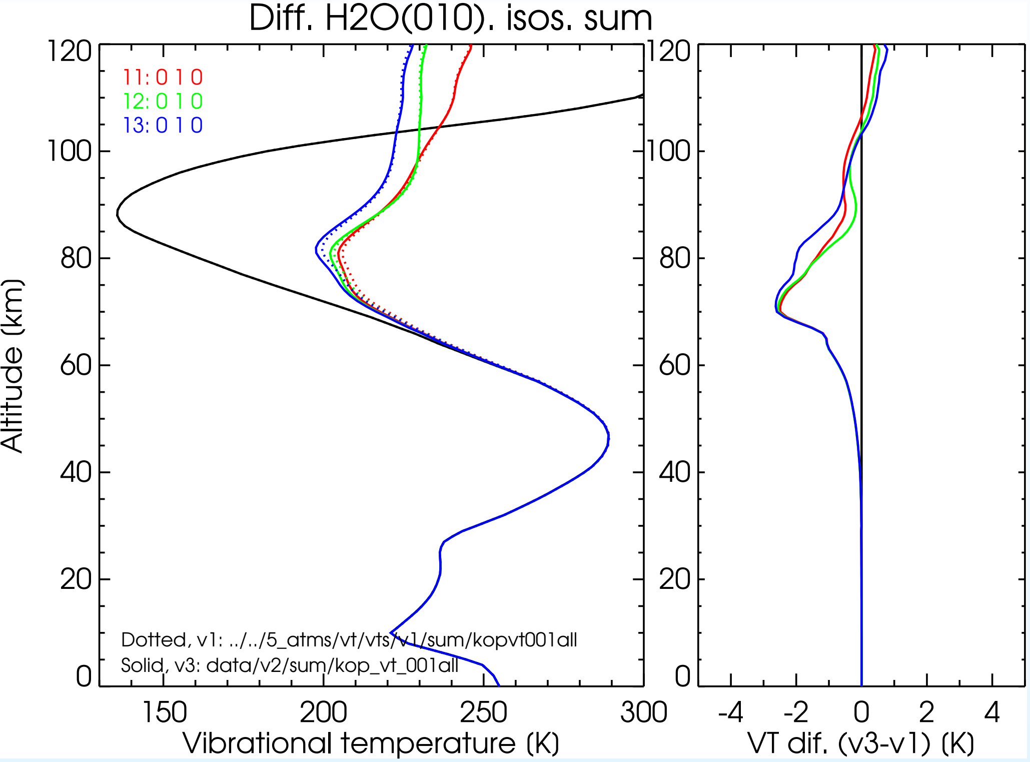


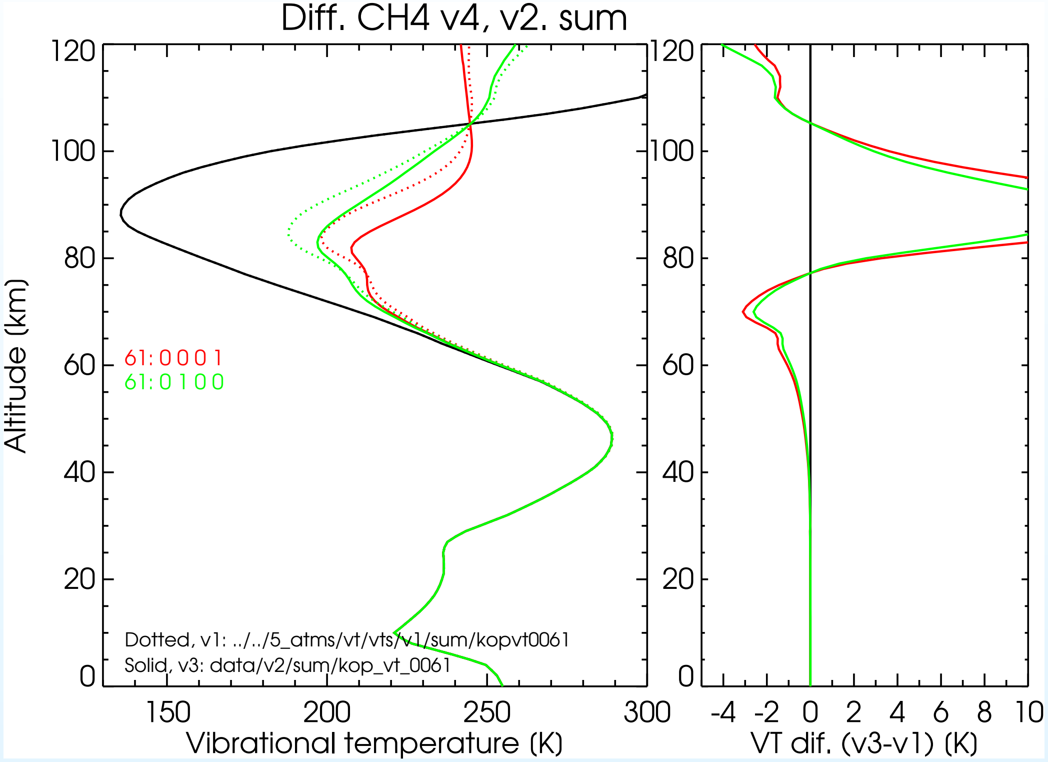
- Previous Tvibs (dotted) and current (solid). Right panels show the differences (New-Old).

Comparison of VTs: CH4(v2,v4), O2(1). DAY

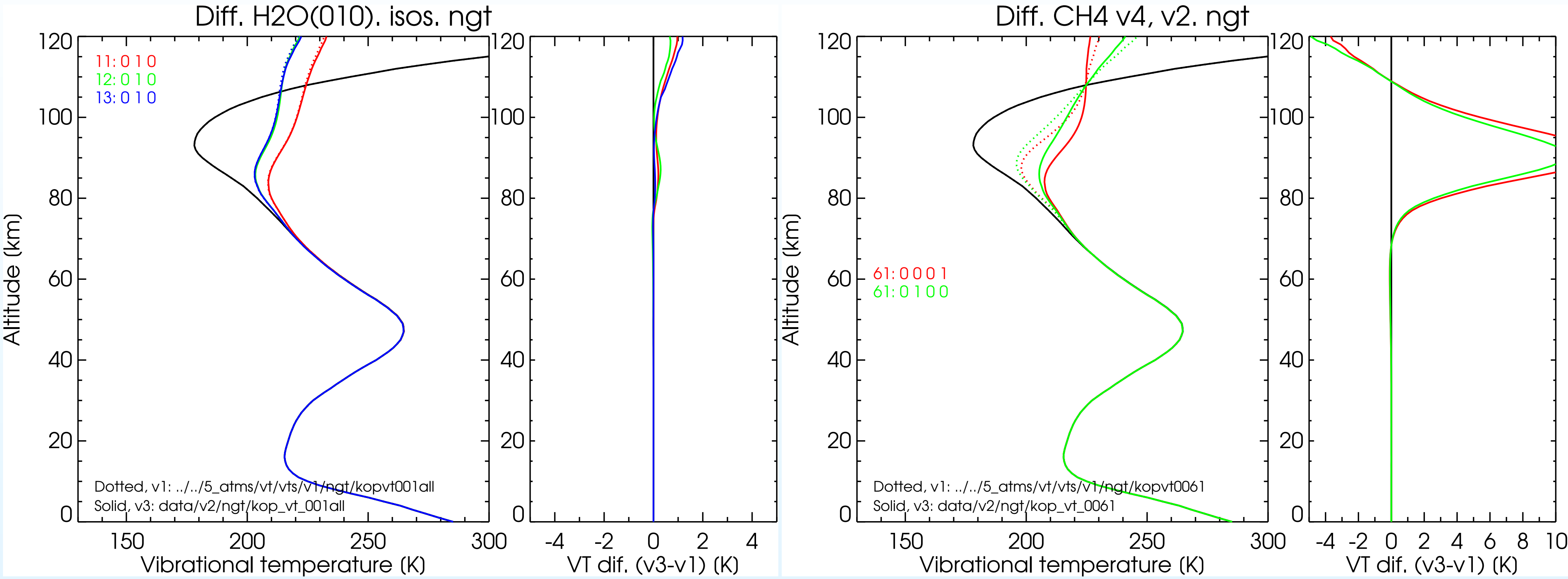


Comparison of VTs: H2O(010), CH4(v2,v4). SUM

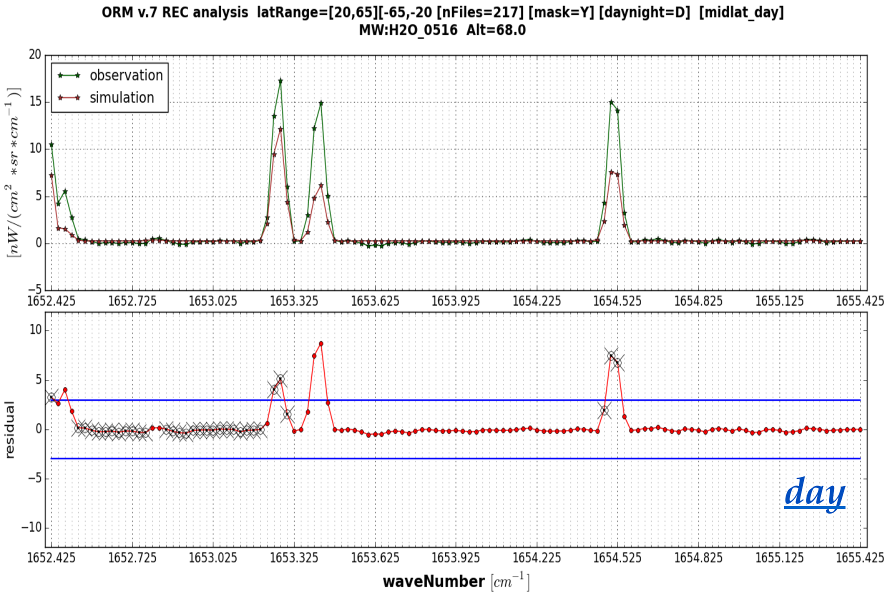


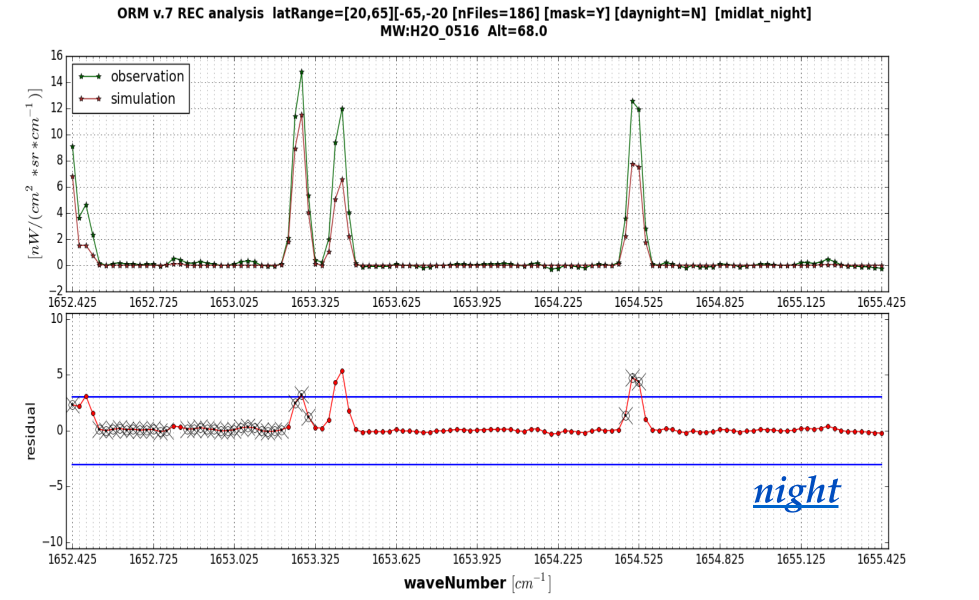


Comparison of VTs: H2O(010), CH4(v2,v4). NGT

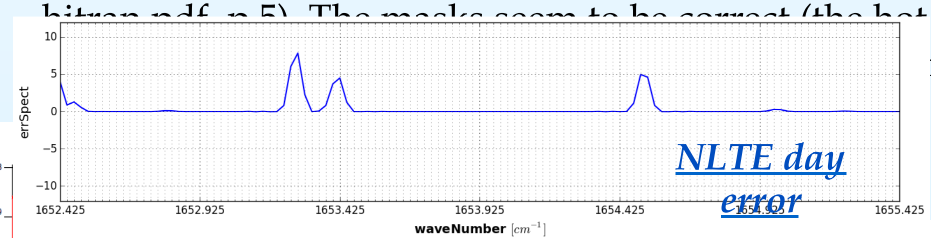


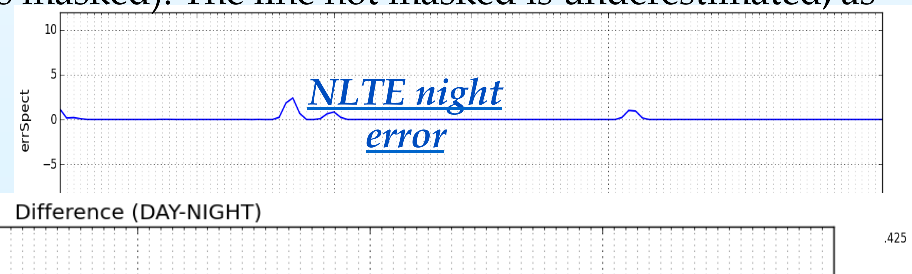
From Piera: H2O MWs at 68 km (2/2)

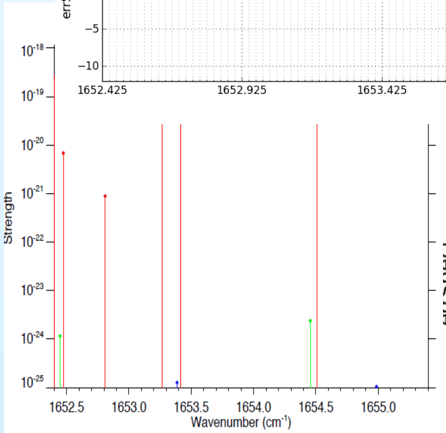


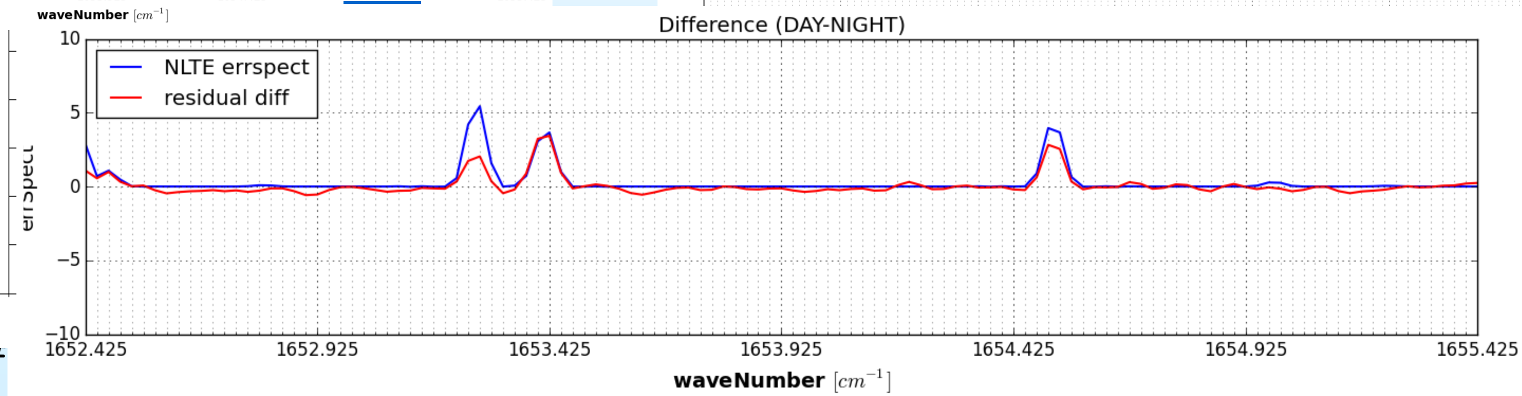


Contribution from 3 fundamental lines and one hot (near 1654.45, overlapped with one fundamental) (see fig. hitran.pdf, p.5). The masks seem to be correct (the hot line is masked). The line not masked is underestimated, as ... m.









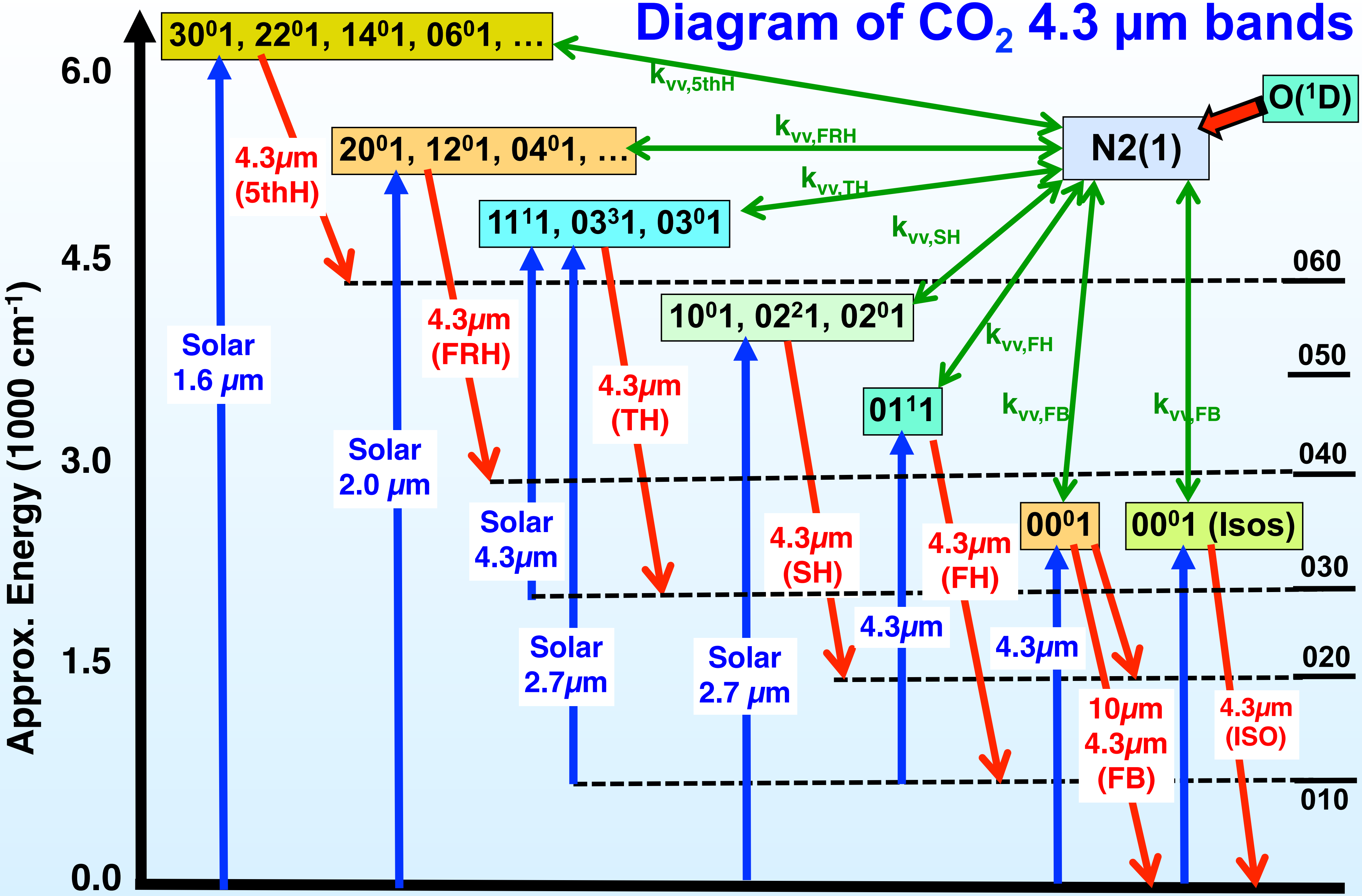
CO_2

Updates in the CO2 NLTE model

- CO2 NLTE updates (Jurado-Navarro et al., JGR, 2015)
  - Inversion of Kvv and Kvt collisional rates, including the temperature dependence
- Near-IR solar flux of the 2.7 µm bands increased in 1.7%.; & 4.3 µm bands reduced in 0.2%
- Further V-V coupling (v1+v2=1,2) for isos=2-6:

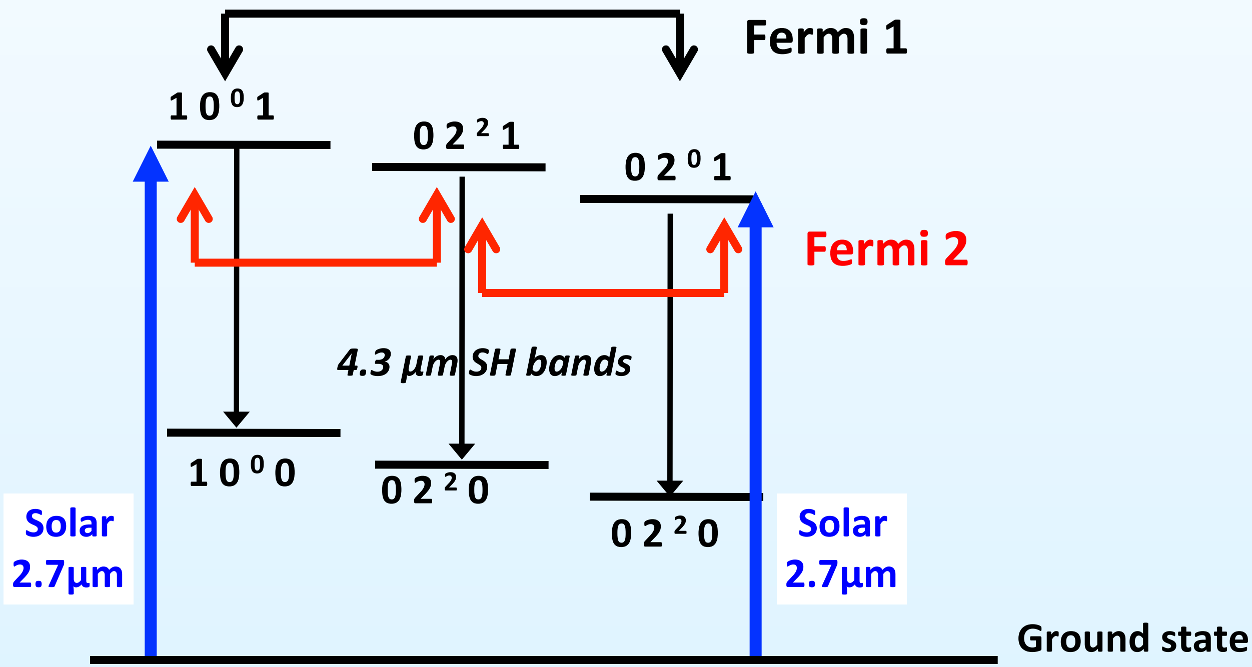
  CO2(main)(001) + CO2(iso)(v1,v2,0) <=> CO2(main) + CO2(iso)(v1,v2,1)
- Bug: Rate of N2(1) + O ⇔ N2 + O was a factor of 5 too large
- Fixed error affecting the population of the CO2 628 (010) and (020) (15 µm) levels
- Line-by-line calculation of the CMs of the 3 2.7 µm levels
- Angular integration increased from 4 to 8 points in the bands affecting the 2.7 µm levels
- Included HITRAN 2012 CO2 spectroscopy

Diagram of CO_2 4.3 μm bands



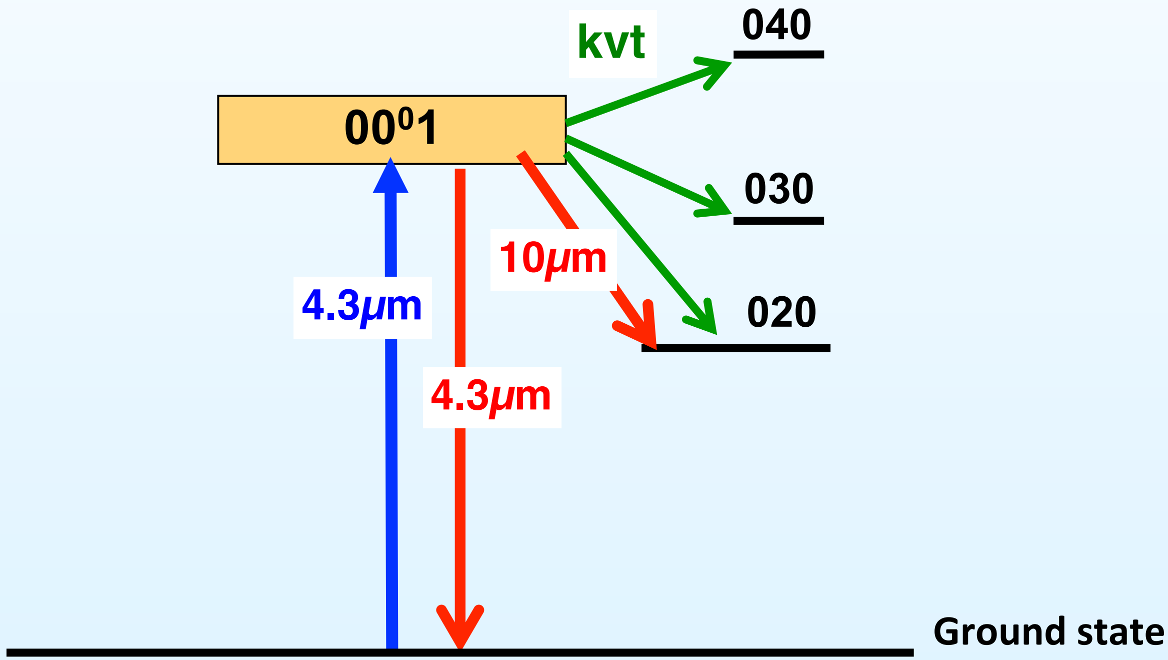
Collisional processes: Fermi coupling

- Near resonant levels (Fermi coupling). Affects mainly the SH bands.
- Kvv Fermi1; Δv_d=0; Δl=0: $CO_2(v_1,v_2,l,1)+N_2$ <=> $CO_2(v_1',v_2',l',1)+N_2$
- Kvv Fermi2; Δv_d=0; Δl=±2: $CO_2(v_1,v_2,l,1)+N_2$ <=> $CO_2(v_1',v_2',l',1)+N_2$

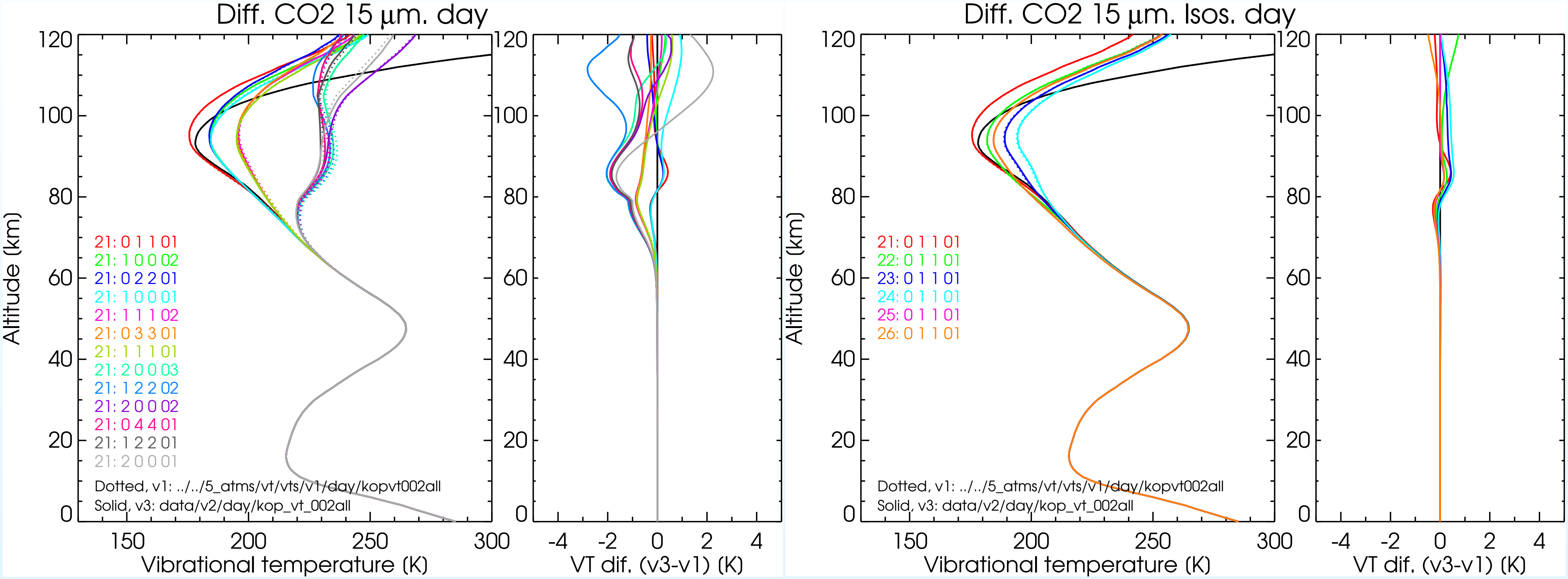


Col. processes: Deactivation of CO2(001)

- Major channel of thermalization of solar energy
- **Kvt:** ; $\Delta v_d=0$; $\Delta l=0$: $CO_2(001)+N_2$ <=> $CO_2(nv_1+mv_{2,}0)+N_2$

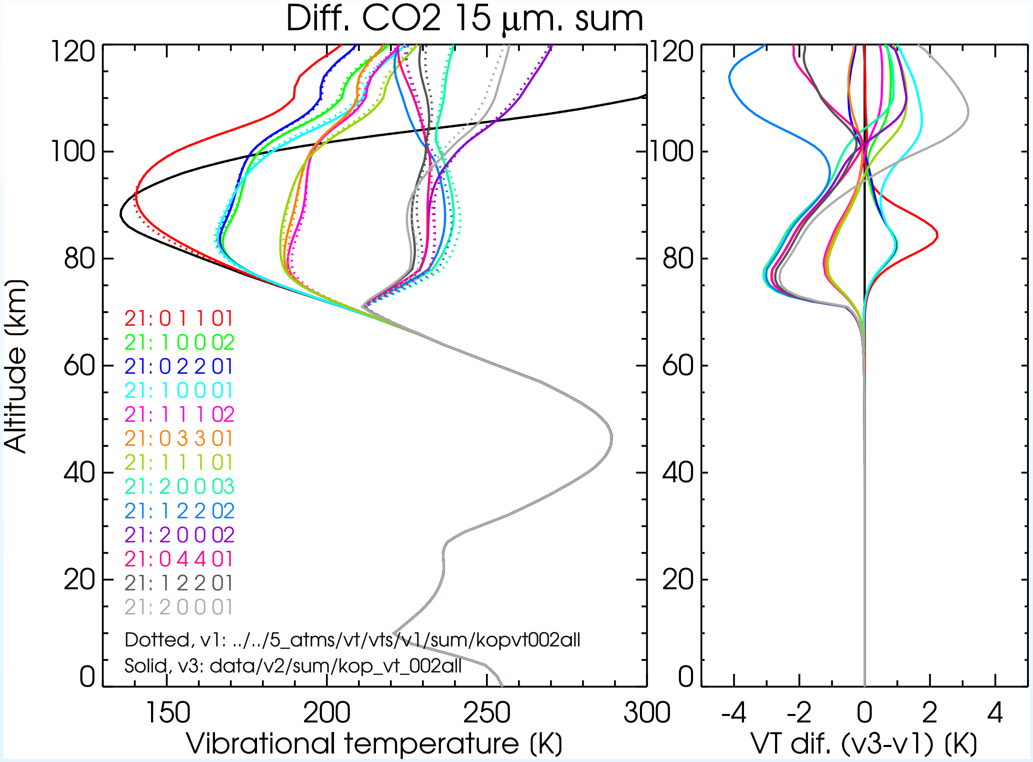


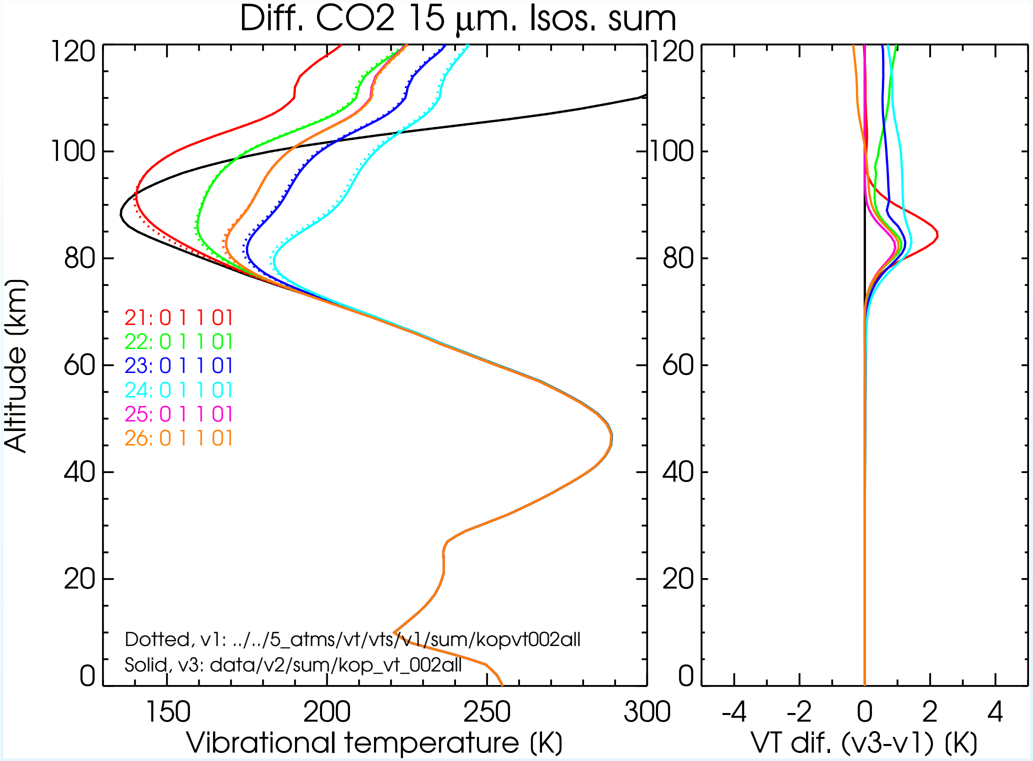
Comparison of VTs: CO2 15 µm levels, DAY



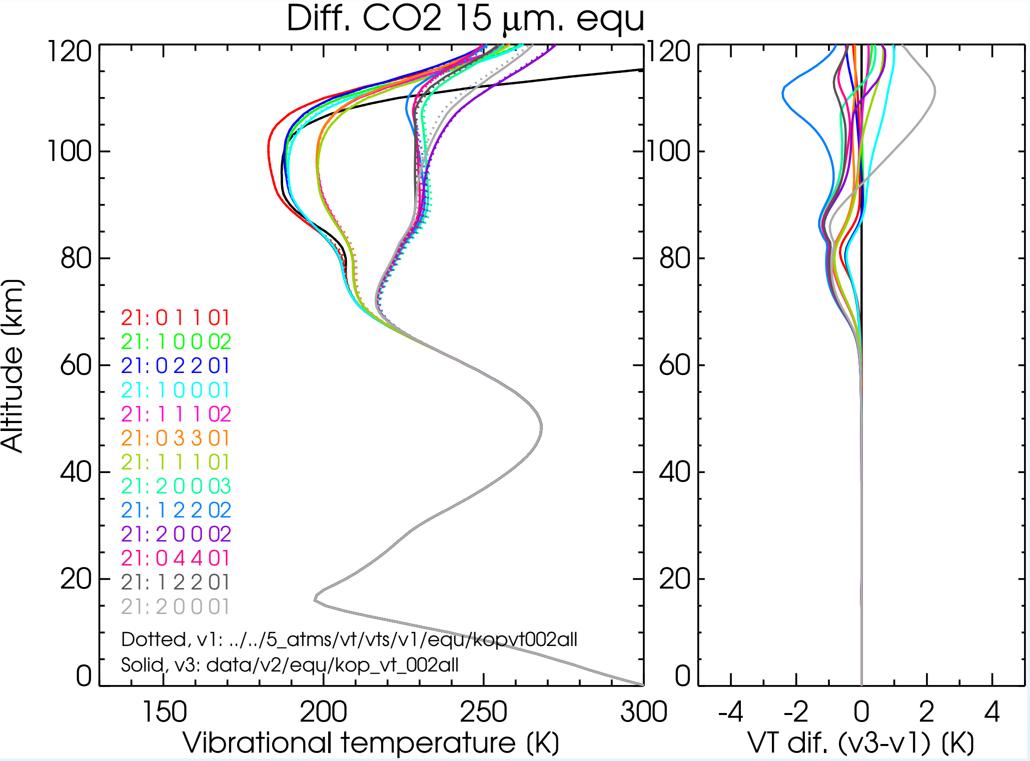
- Previous Tvibs (dotted) and current (solid). Right panels show the differences (New-Old).

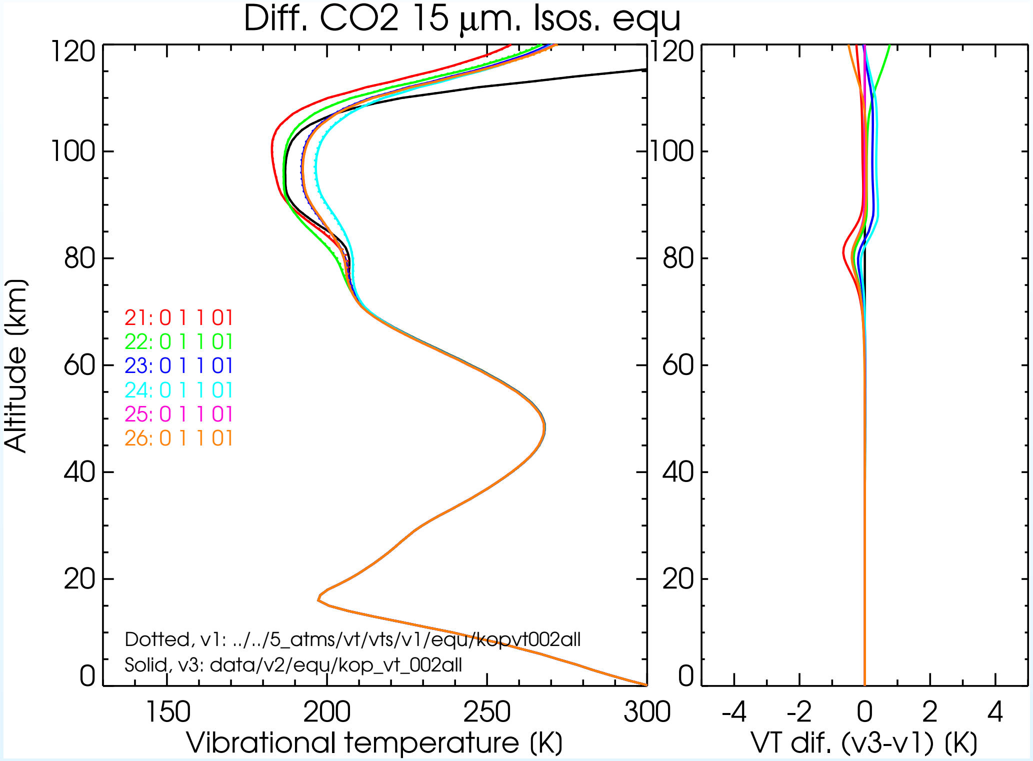
Comparison of VTs: CO2 15 µm levels, SUM



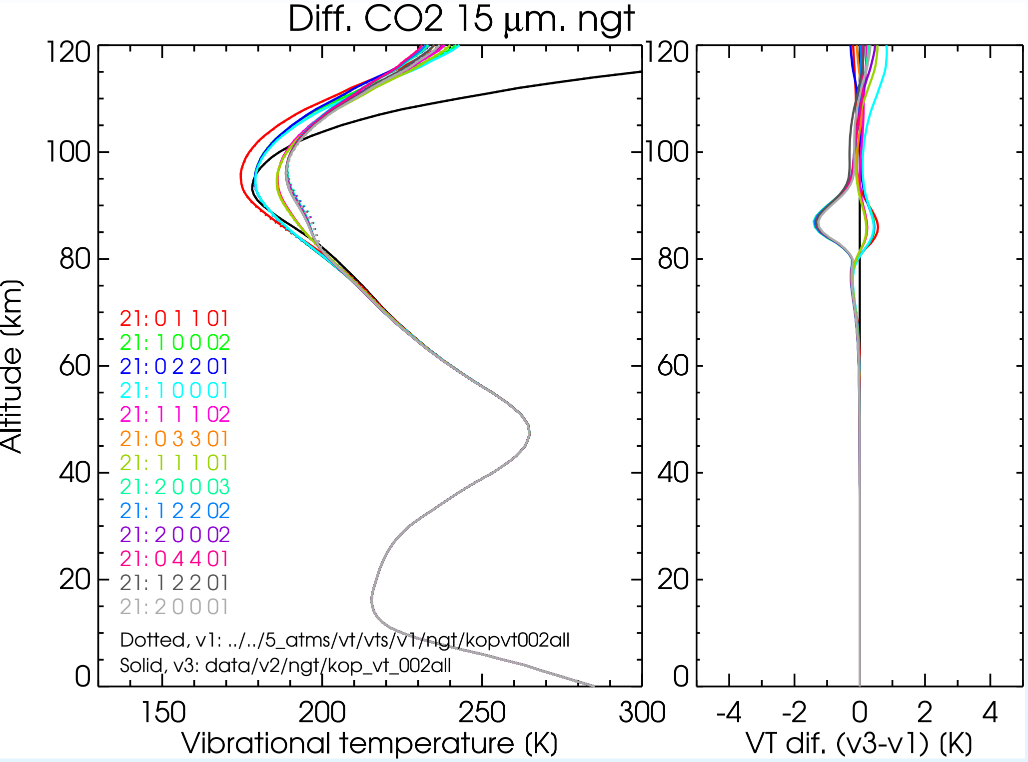


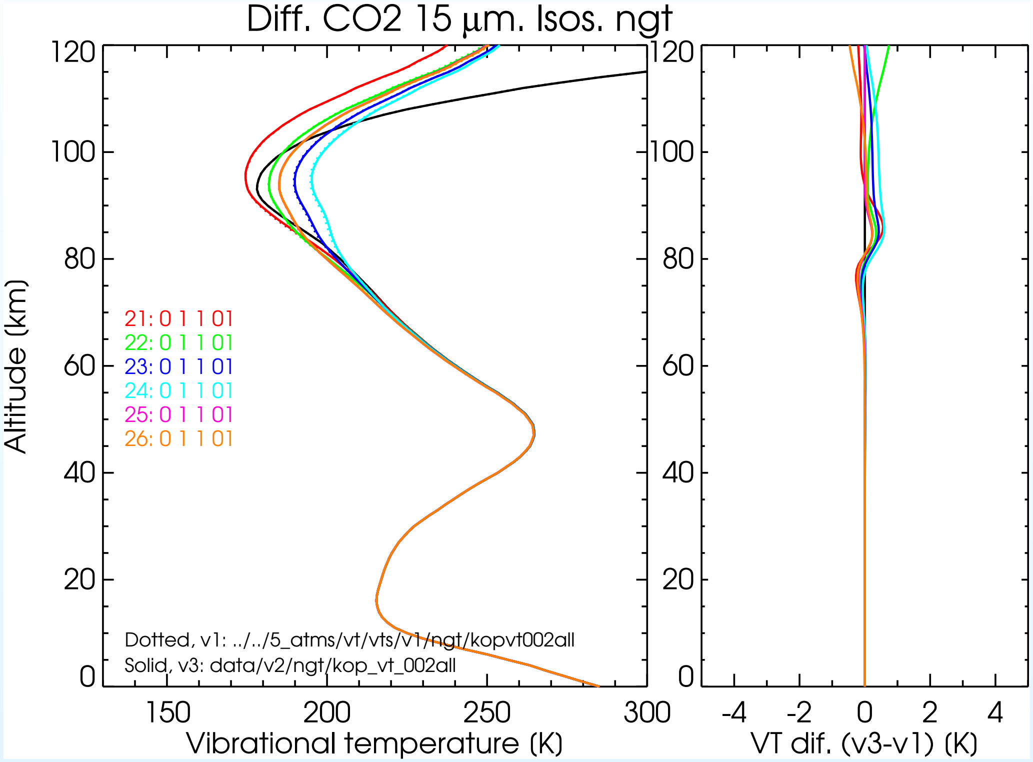
Comparison of VTs: CO2 15 levels, EQU



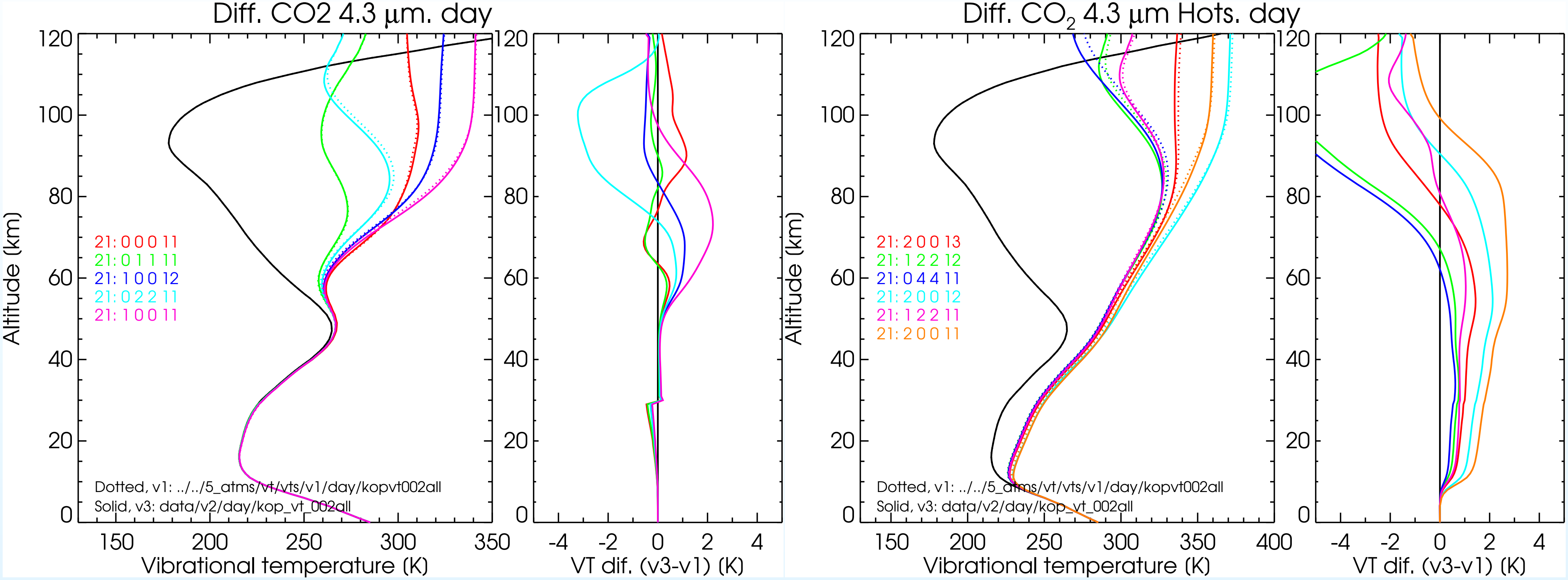


Comparison of VTs: CO2 15 levels, NGT

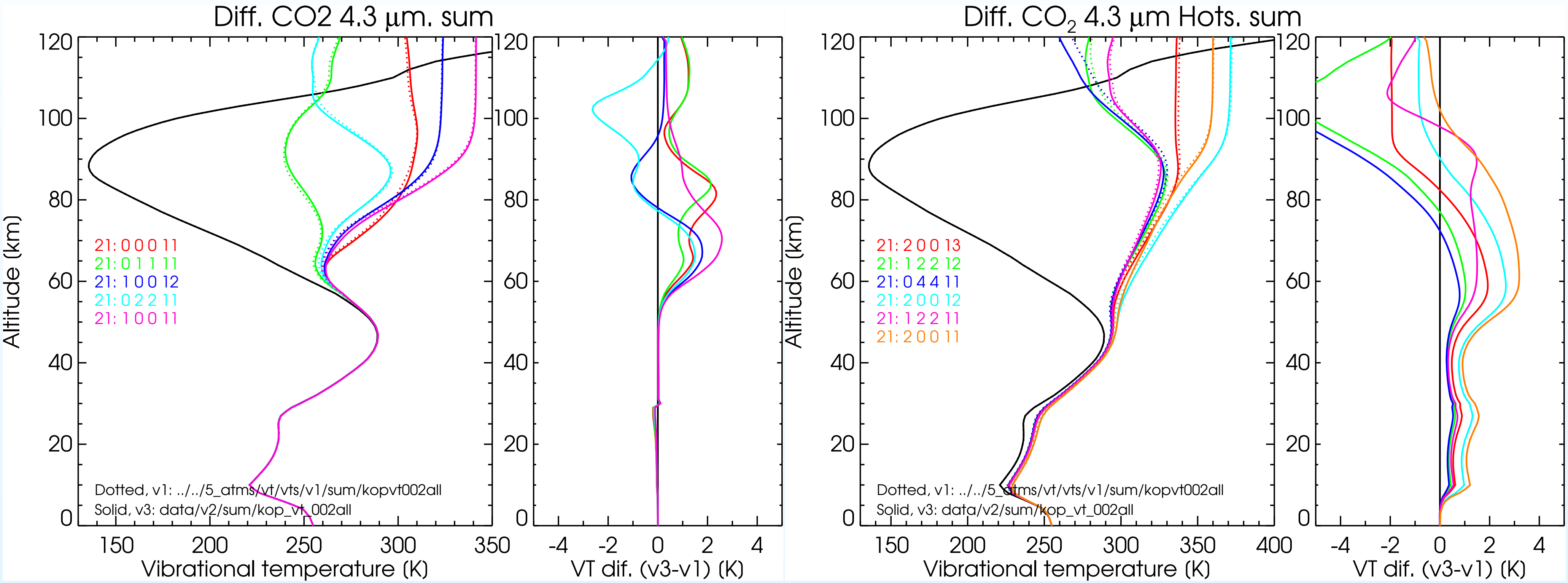




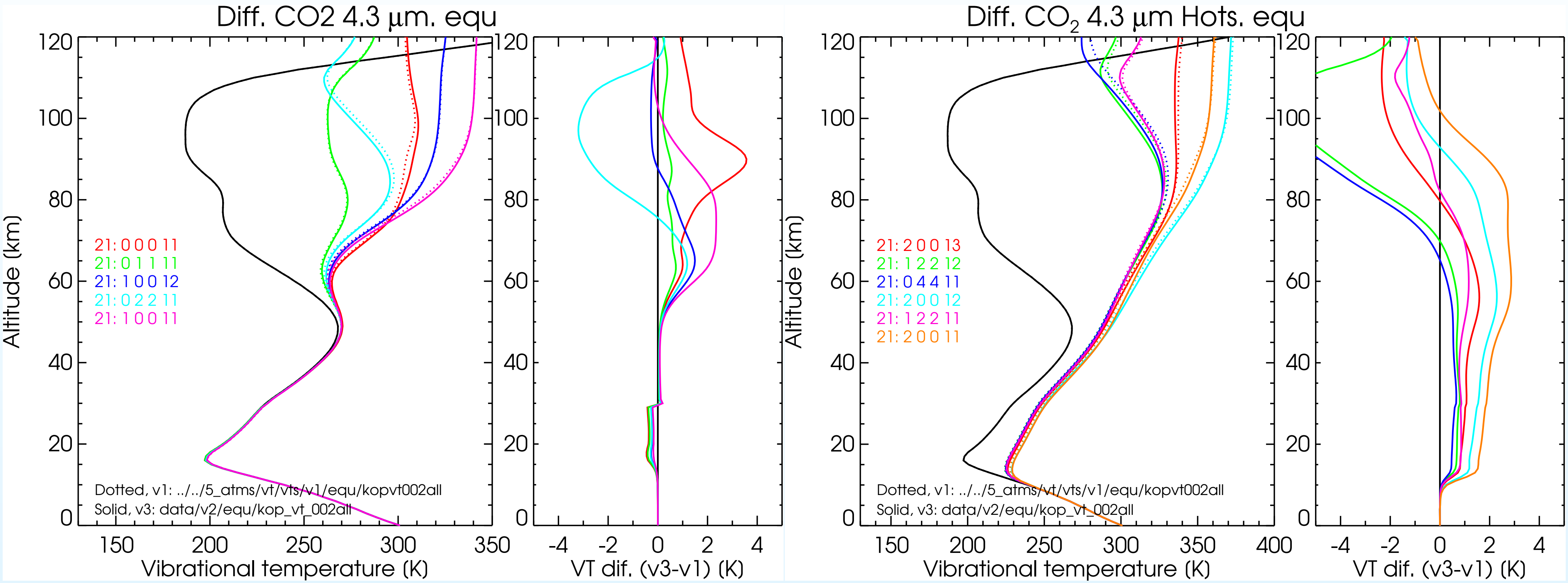
Comparison of VTs: CO2 4.3 µm levels, DAY



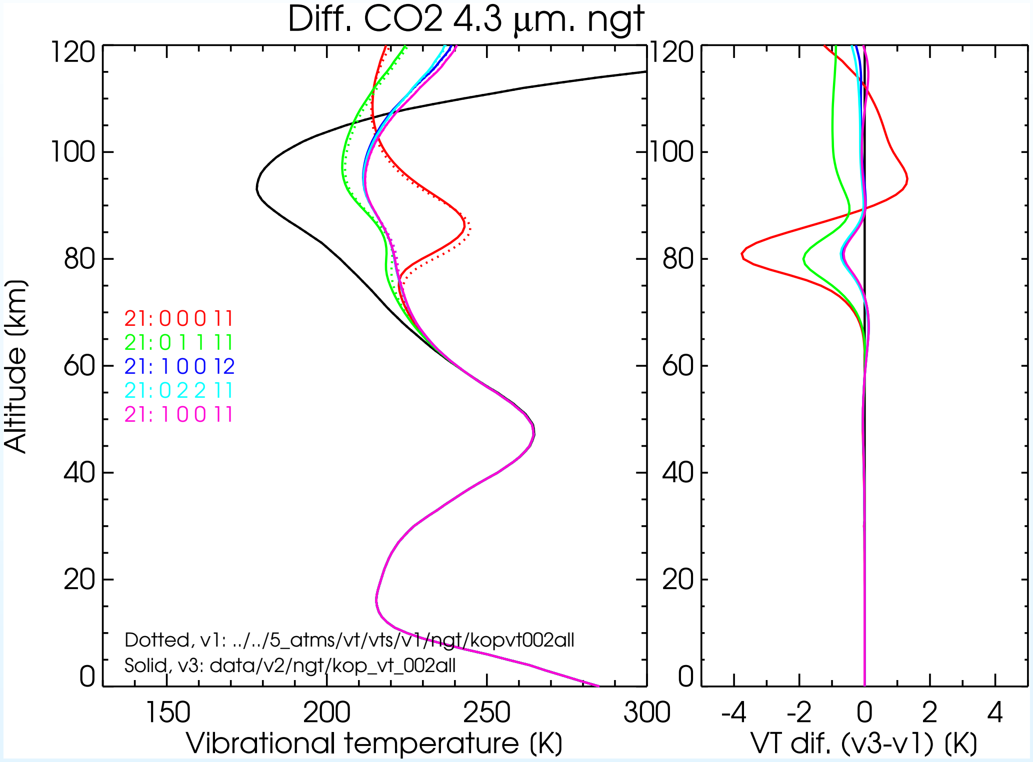
Comparison of VTs: CO2 4.3 µm levels, SUM

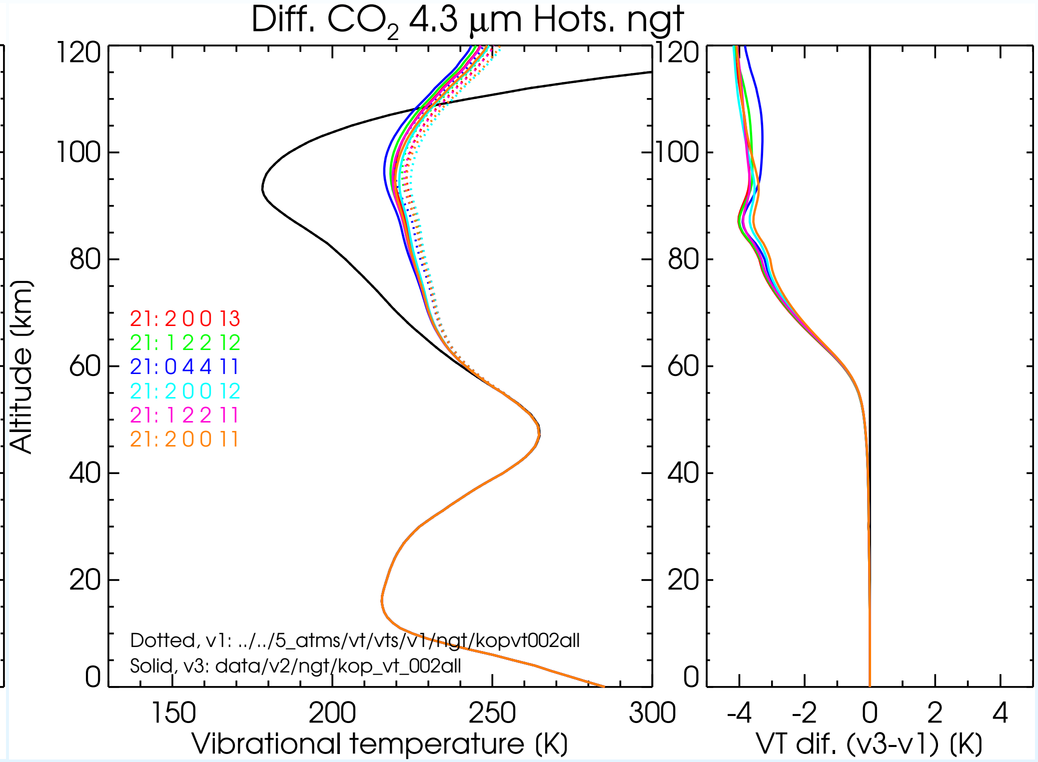


Comparison of VTs: CO2 4.3 µm levels, EQU

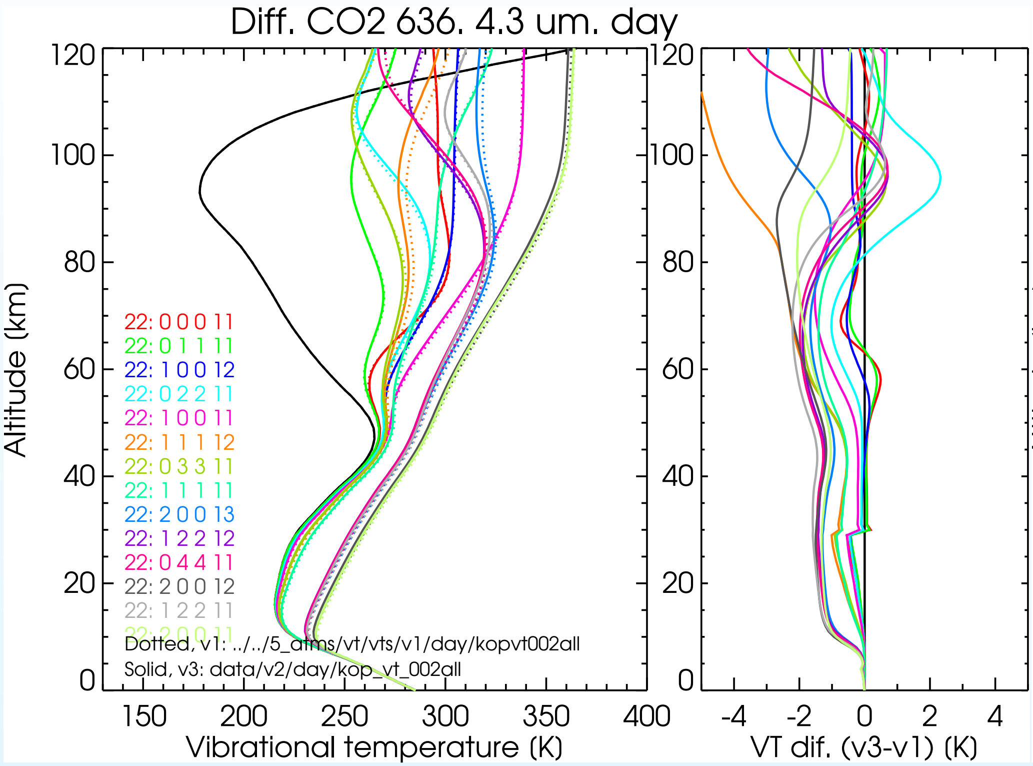


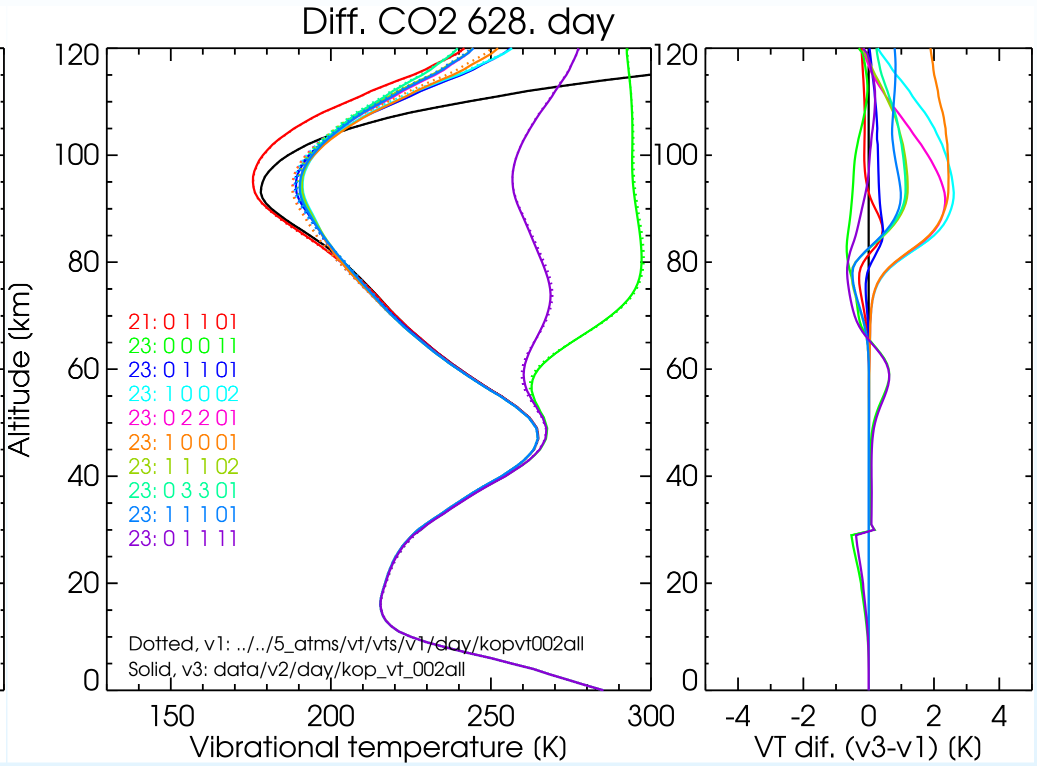
Comparison of VTs: CO2 4.3 µm levels, NGT





Comparison of VTs: CO2 4.3 µm, 636, 628, DAY





Summary of CO_2

- Many changes done in the CO_2 non-LTE modelling
- New set of collisional rates derived from MIPAS spectra
- Small changes (1-2 K larger) in the Tvibs of the 4.3 and 10 μm bands of CO_2 above around 60 km.

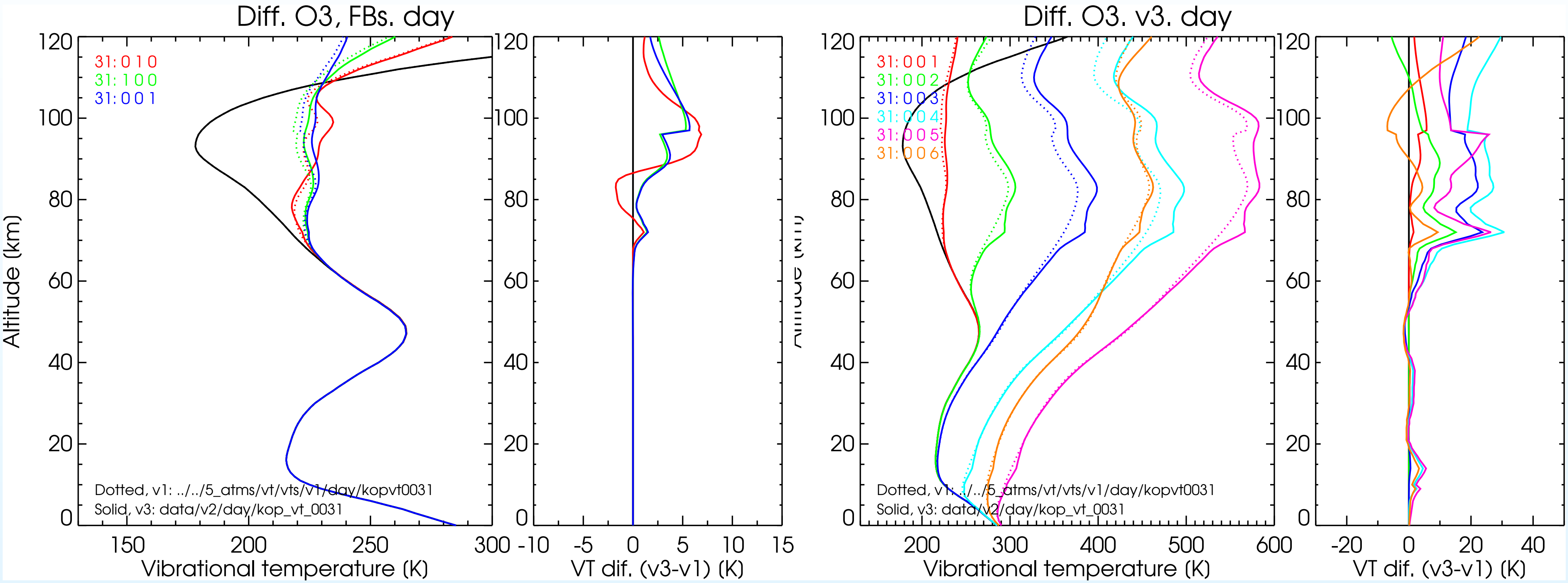
03

Upgrades in the O3 NLTE model

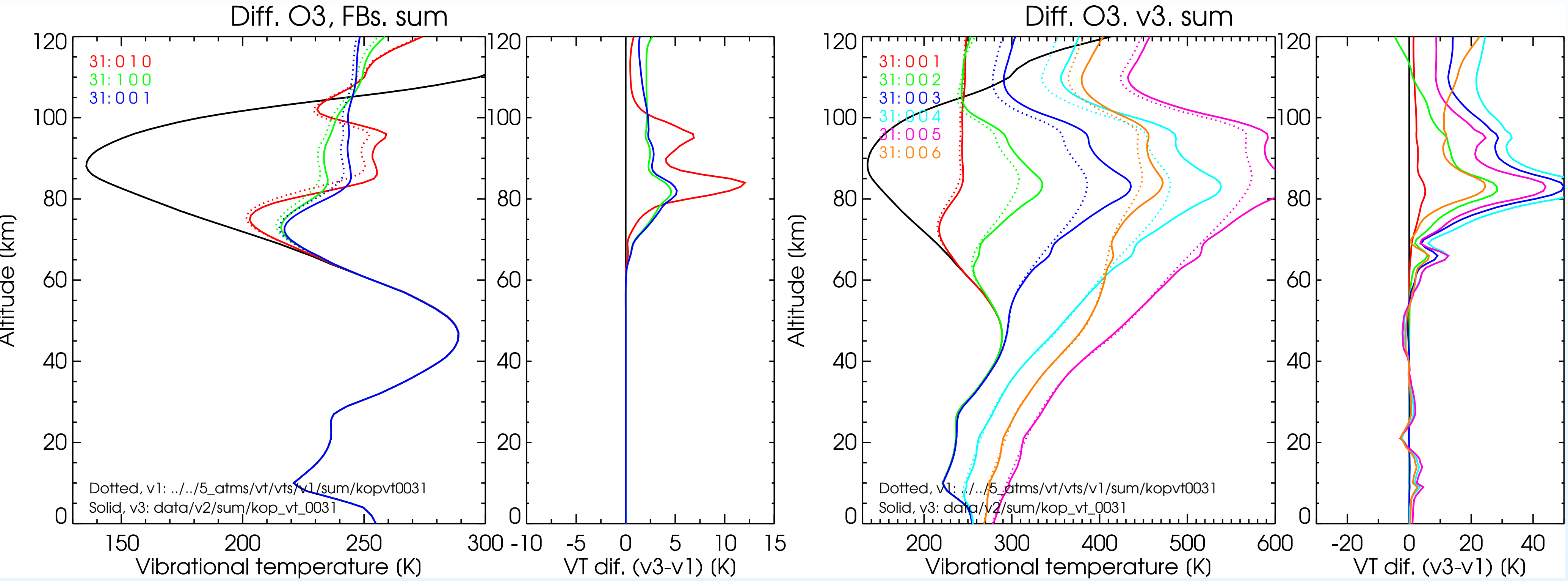
- Thermal relaxation by O: O_3*(v1,v3) + O => O_3(v2)
- Chemical quenching by O: O_3*(v1,v3) + O => O_3 + O => Removed => larger Tvibs

  Total quenching by O still within measurements errors (West et al., 1976; 1978)

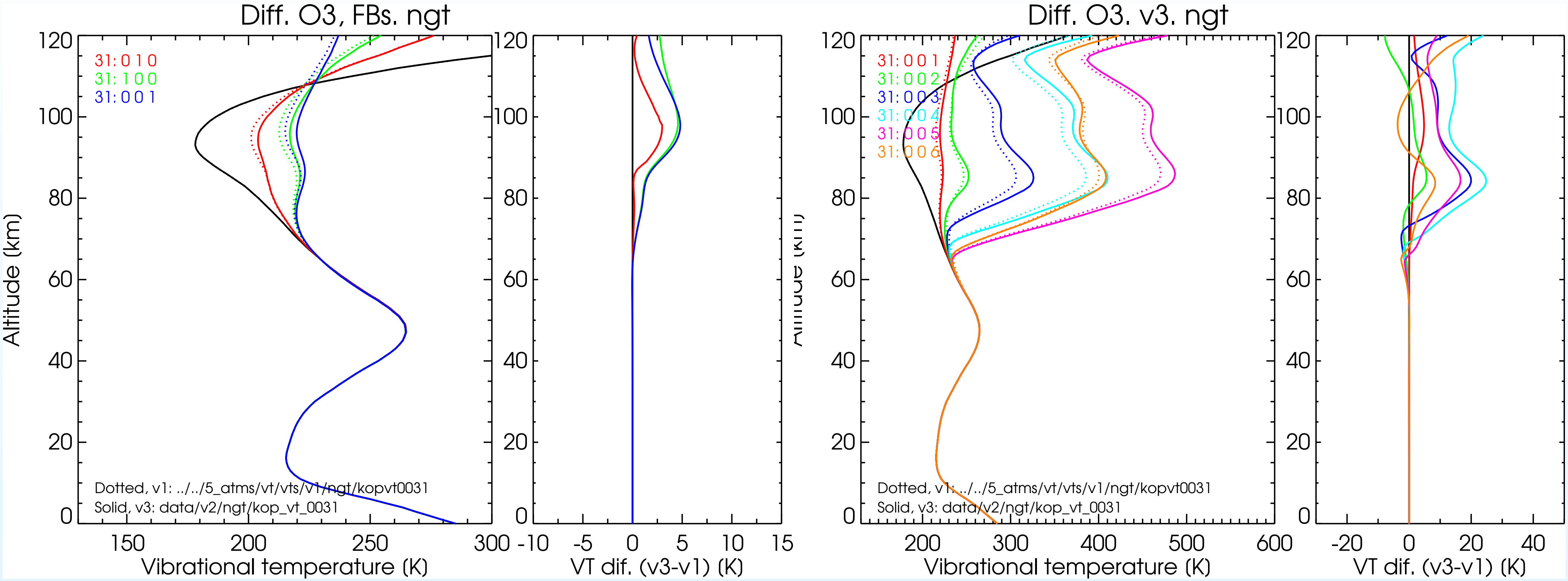
Comparison of VTs: O3 FBs +v3 hots, DAY



Comparison of VTs: O3 FBs +v3 hots, SUM



Comparison of VTs: O3 FBs +v3 hots, NGT

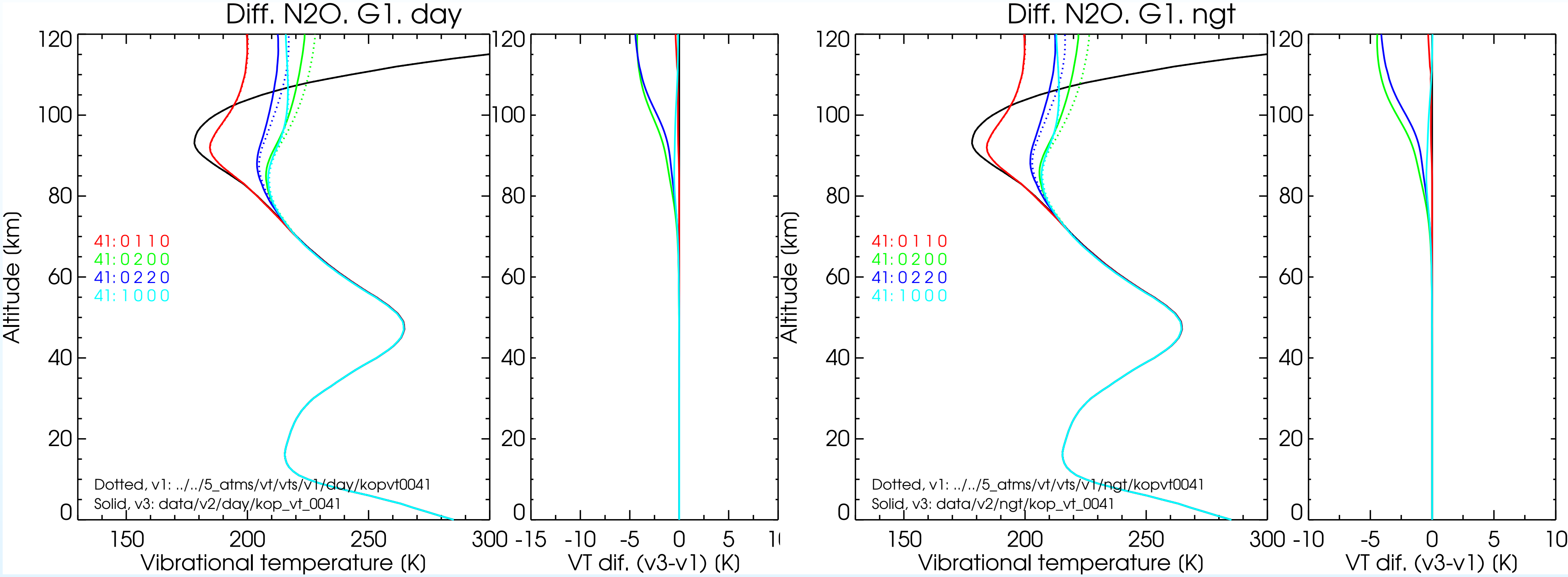


Summary O3

- Changes in NLTE:
  - Revision of k_{vt}: $O_3(v_3)+M(N_2, O_2) => O_3(v_3-1)$: Small effect
  - Revision of k1: $O+O_2+M$: Small effect
  - Neglect the removal of O3(v_3) by O chemical loss => larger (significant) O3 Tvibs (2-5 K) in the mesosphere

N_2O

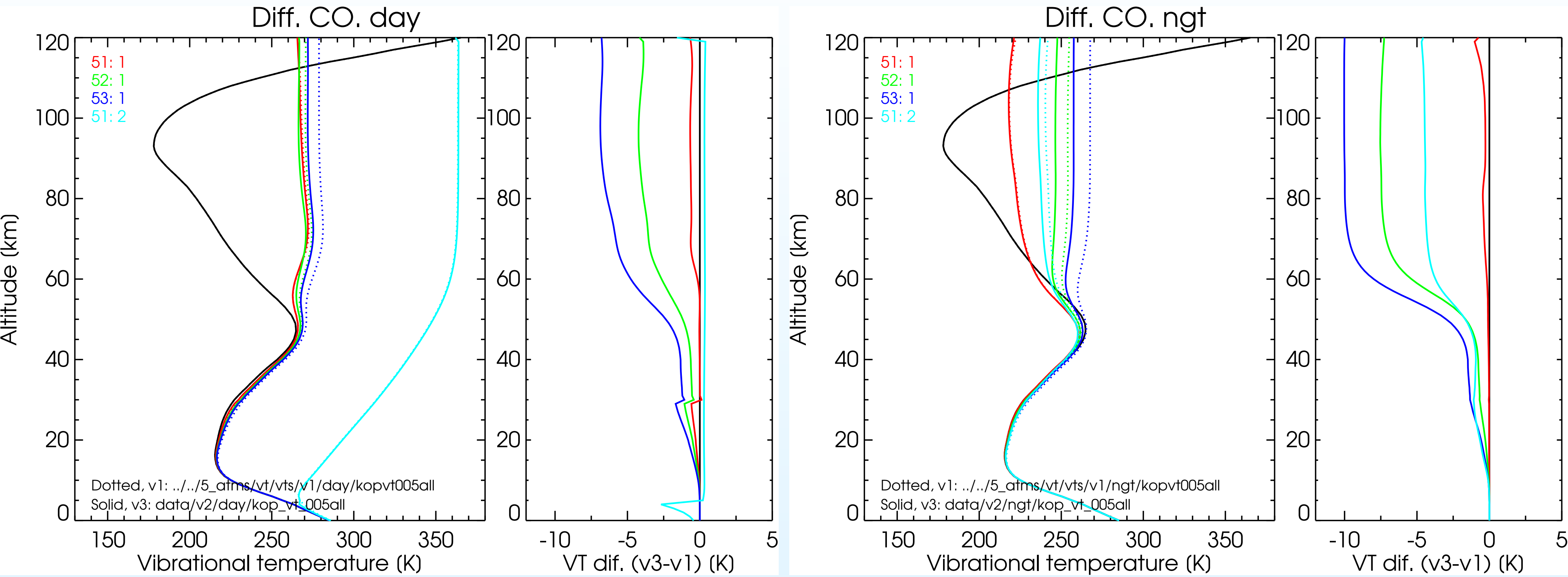
Comparison of VTs: N2O, DAY, NGT



- Negligible changes for N2O.

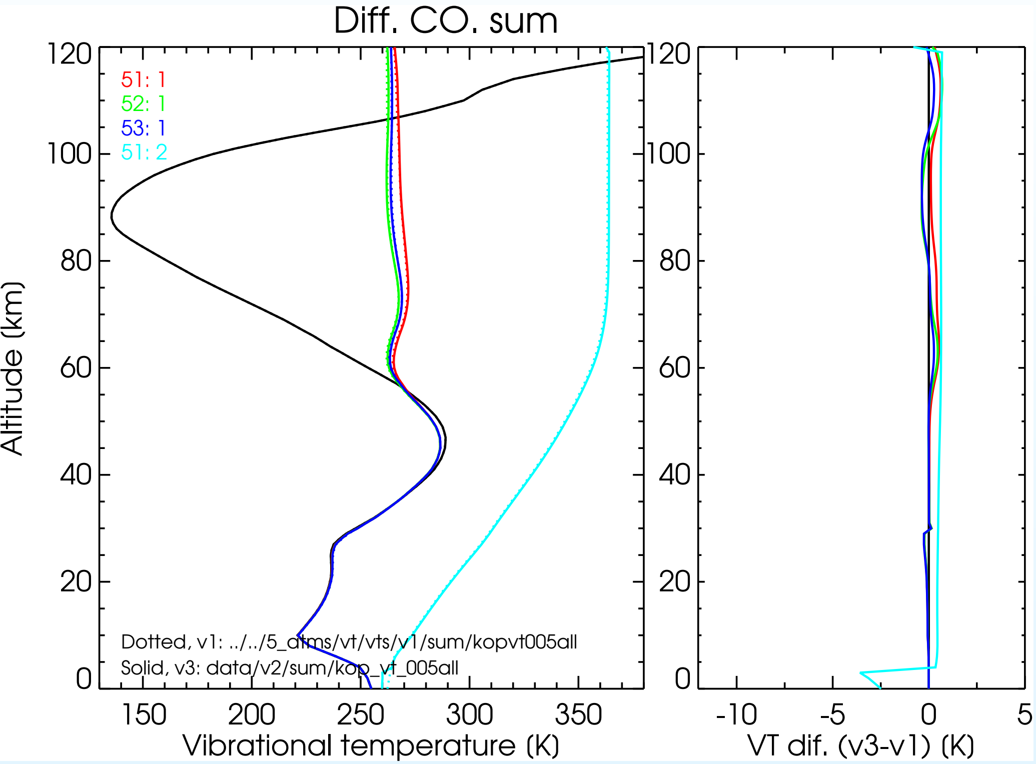
CO

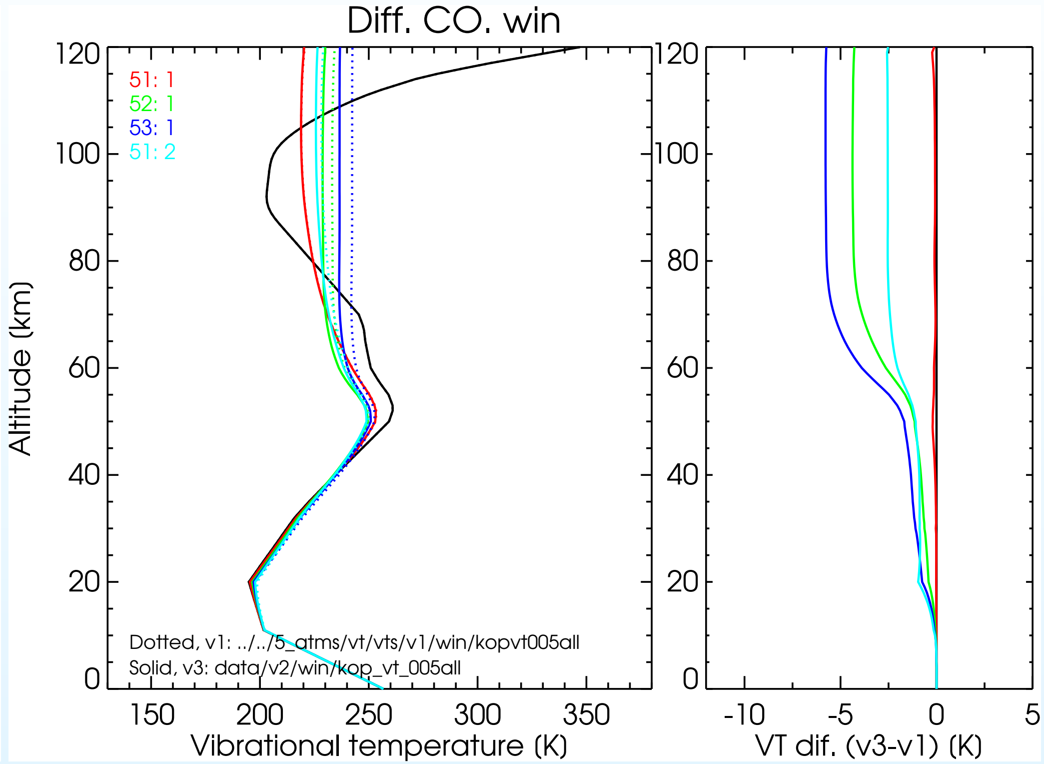
Comparison of VTs: CO, DAY, NGT



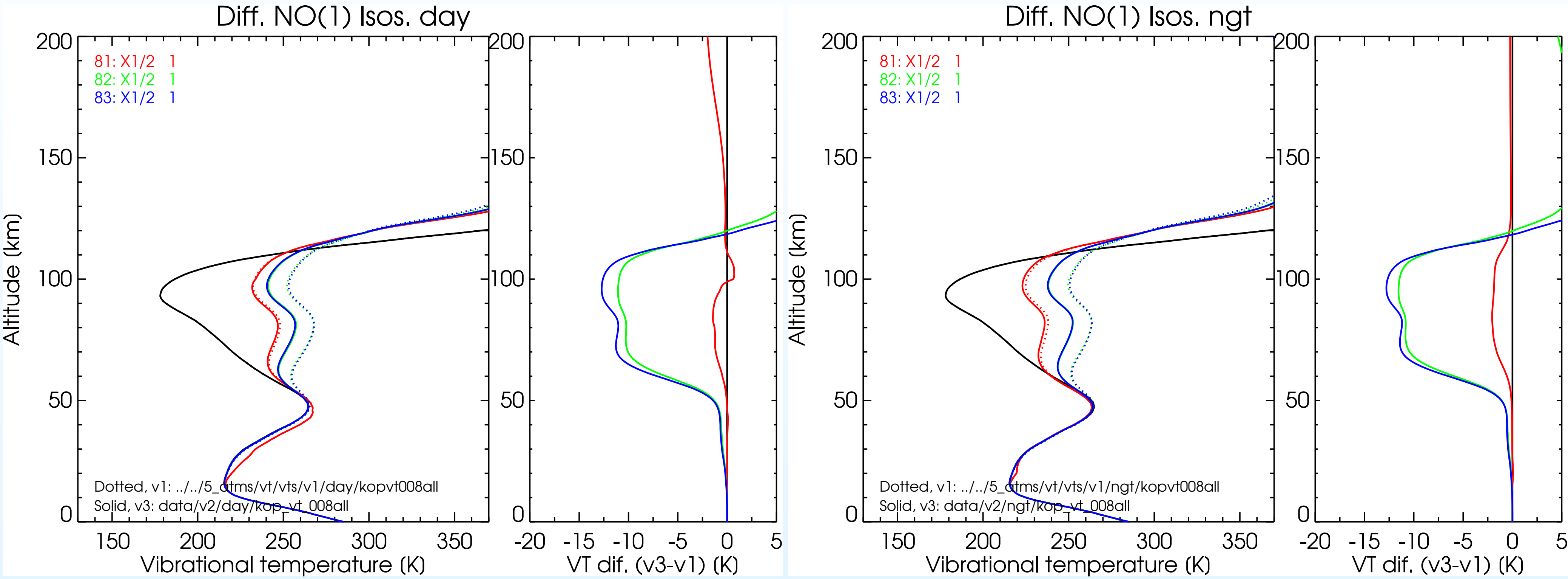
- Negligible changes for CO(1) of main isotope. Smaller VTs for the less abundant isotopes (tropospheric upwelling flux is smaller because of inclusion of tropospheric clouds)

Comparison of VTs: CO, SUM, WIN



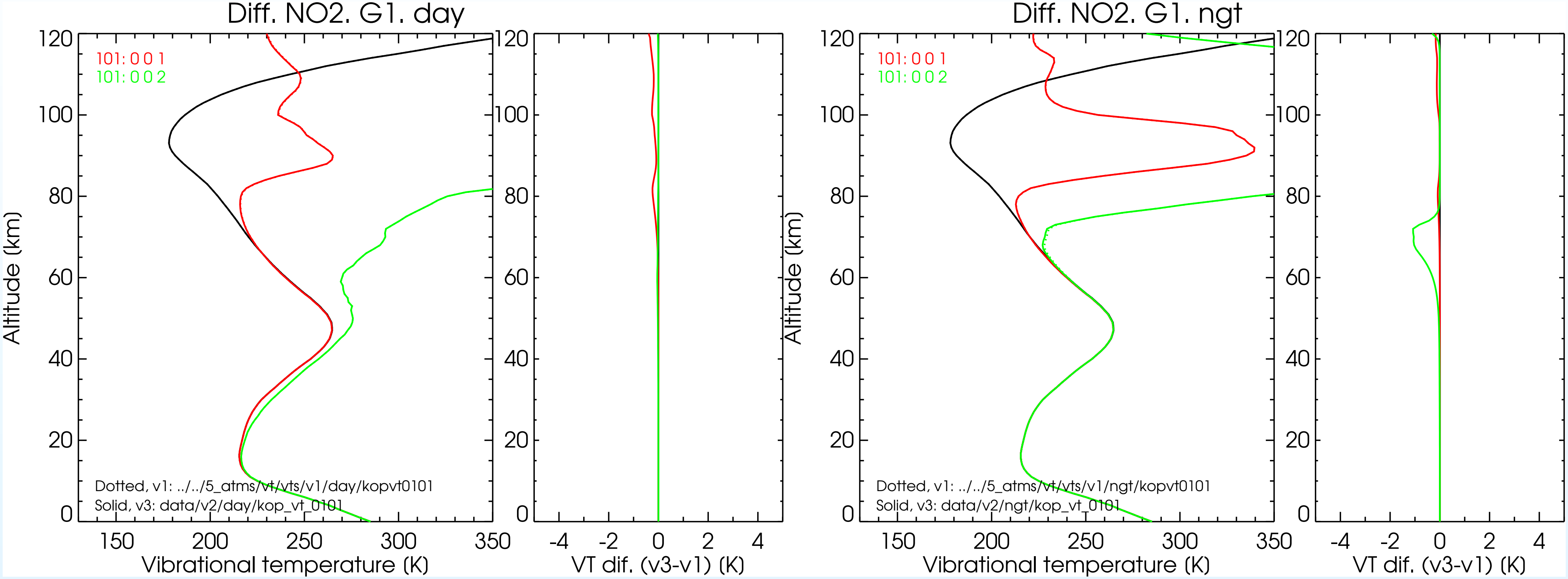


Comparison of VTs: NO, DAY, NGT



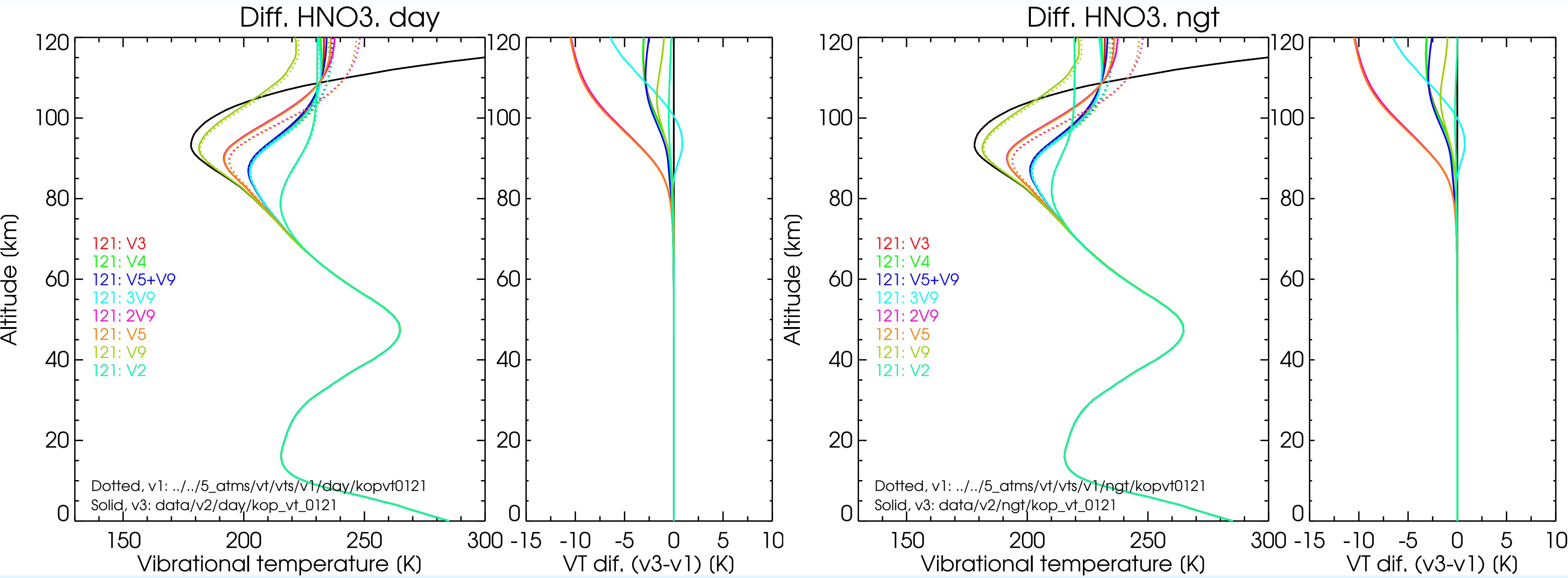
- Negligible changes for NO(1) of main isotope. Smaller VTs for the less abundant isotopes (tropospheric upwelling flux is smaller because of inclusion of tropospheric clouds)

Comparison of VTs: NO2, DAY, NGT



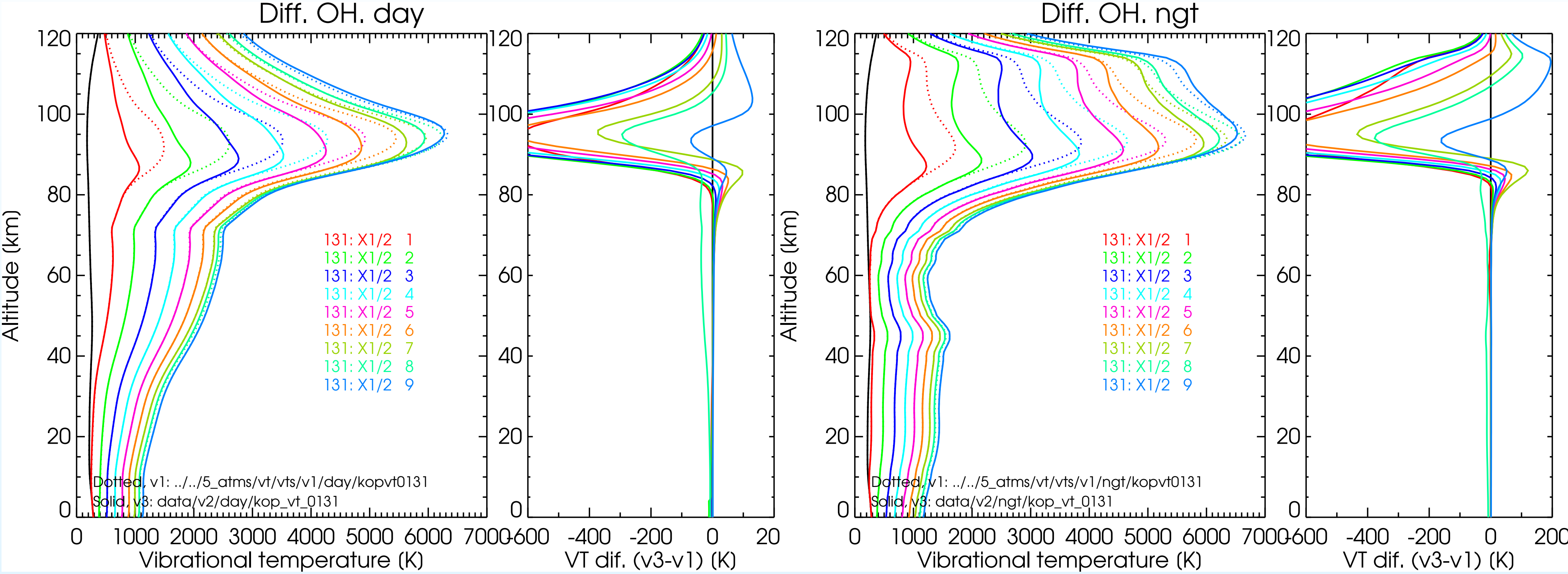
- Negligible changes for NO2.

Comparison of VTs: HNO3, DAY, NGT



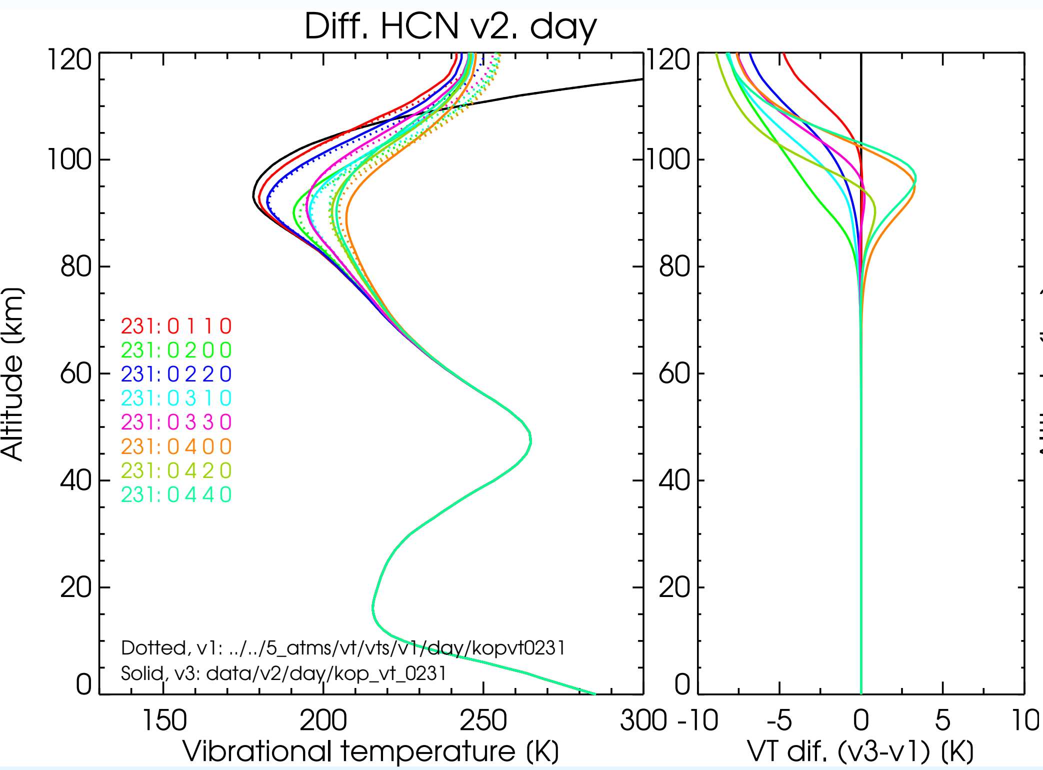
- Negligible changes for HNO3

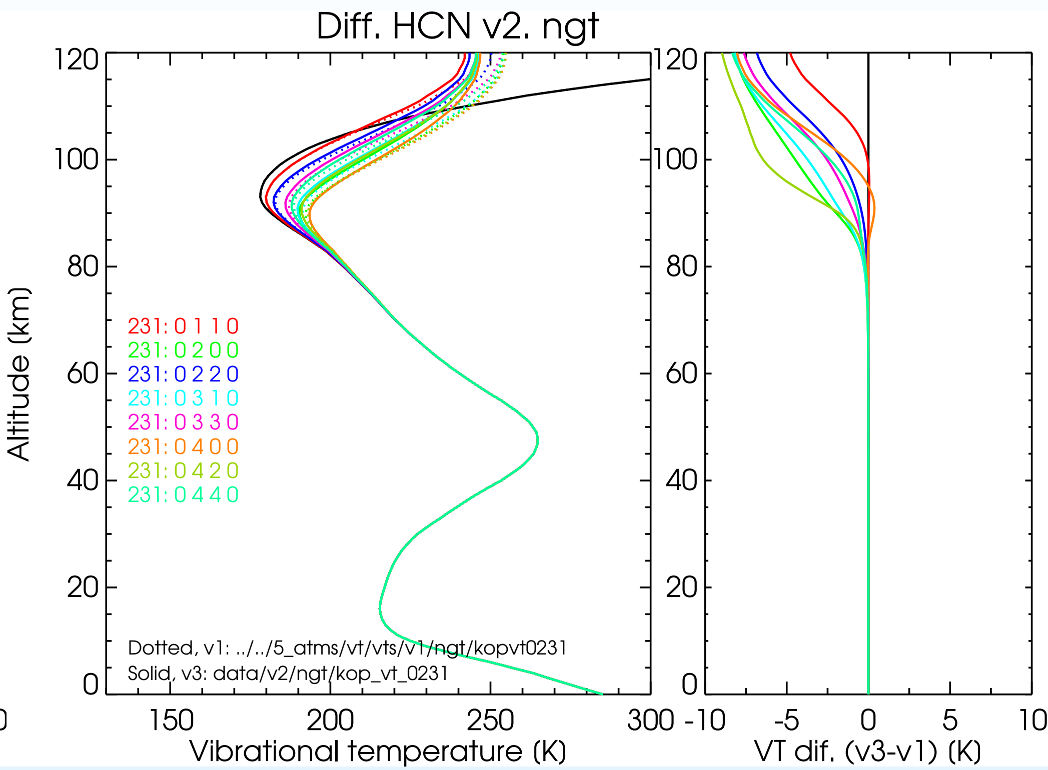
Comparison of VTs: OH, DAY, NGT



- Smaller VTs because of rotational NLTE included (adjusted to MIPAS band A OH emission)

Comparison of VTs: HCN, DAY, NGT

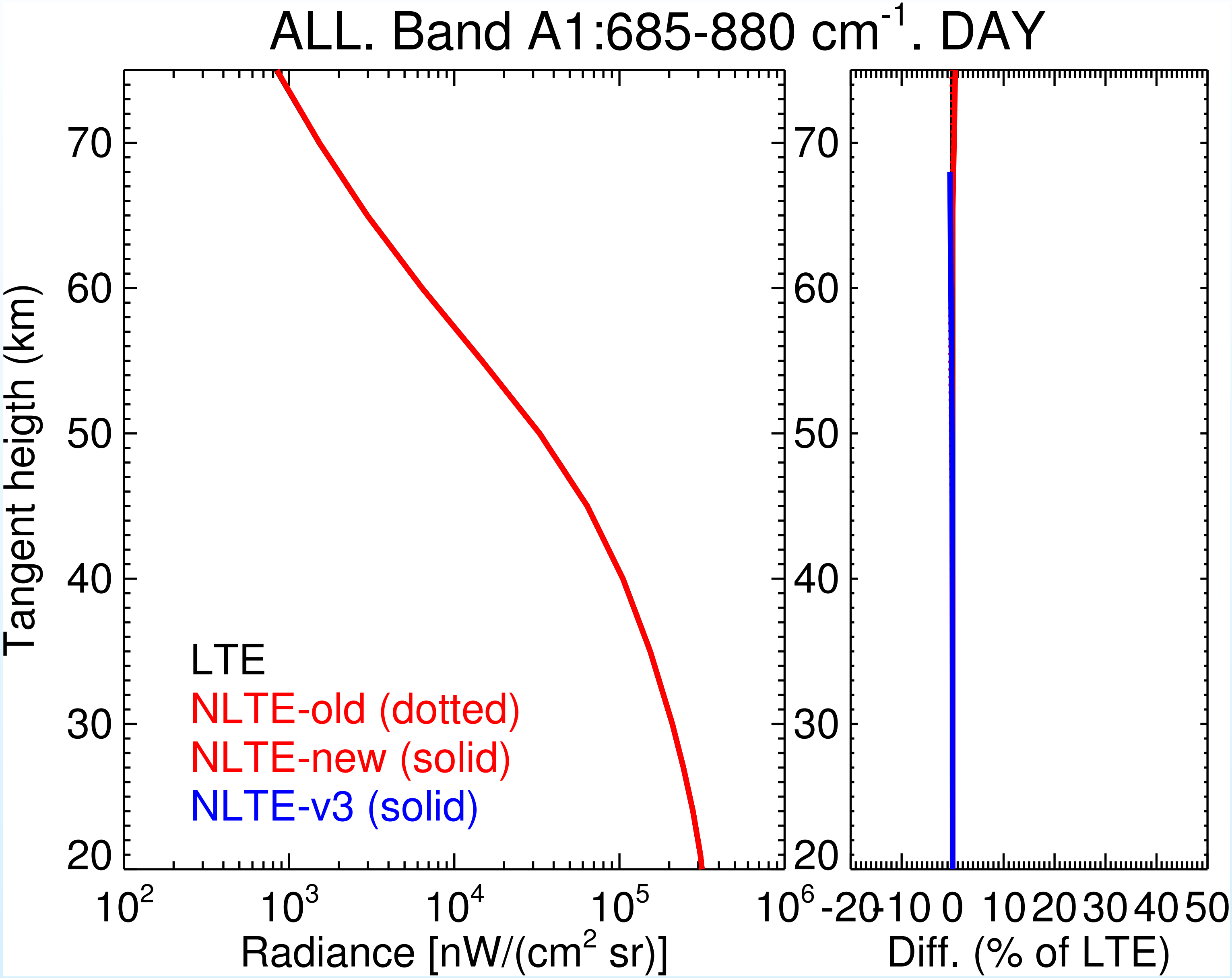




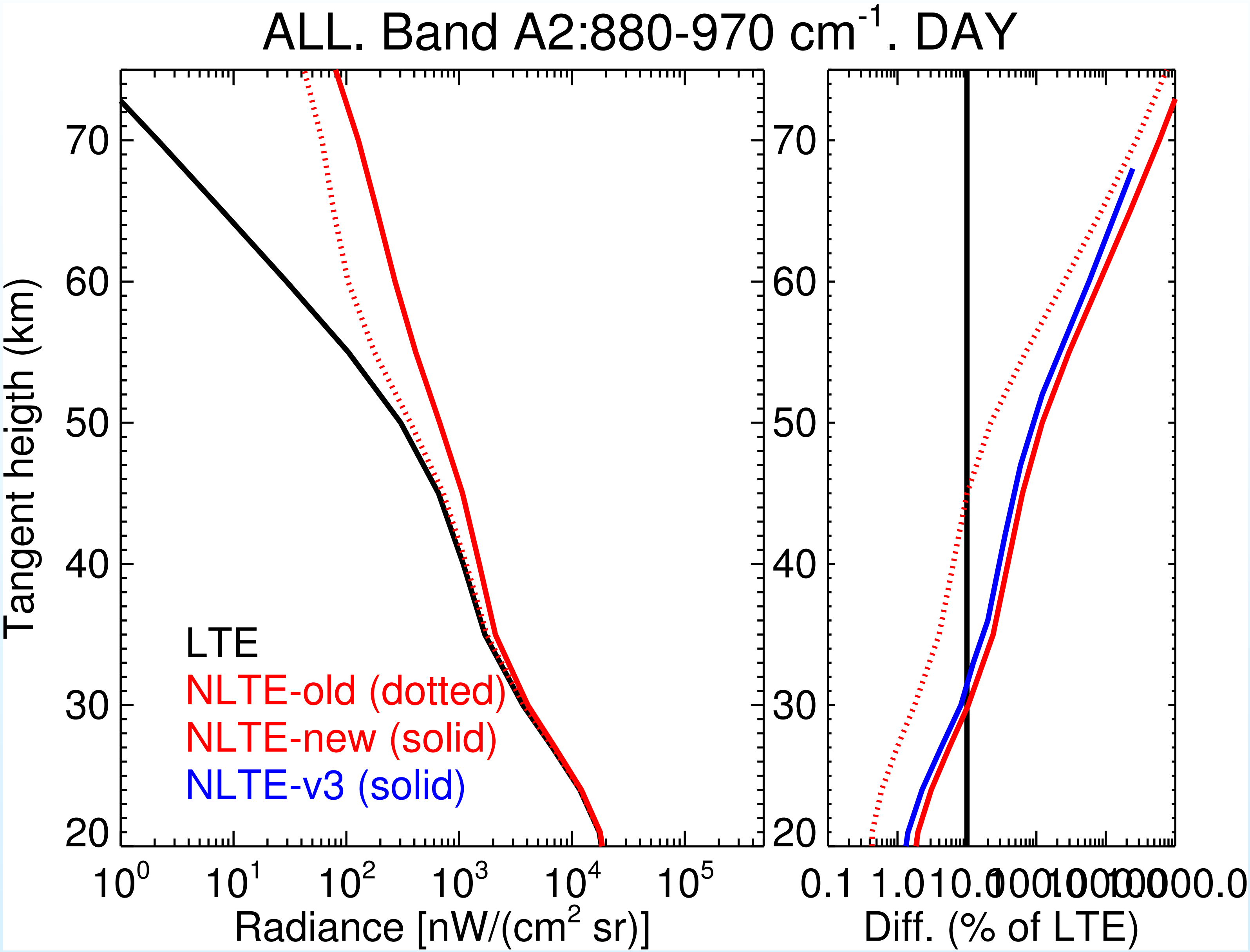
- Negligible changes for HCN

NLTE error (v3)

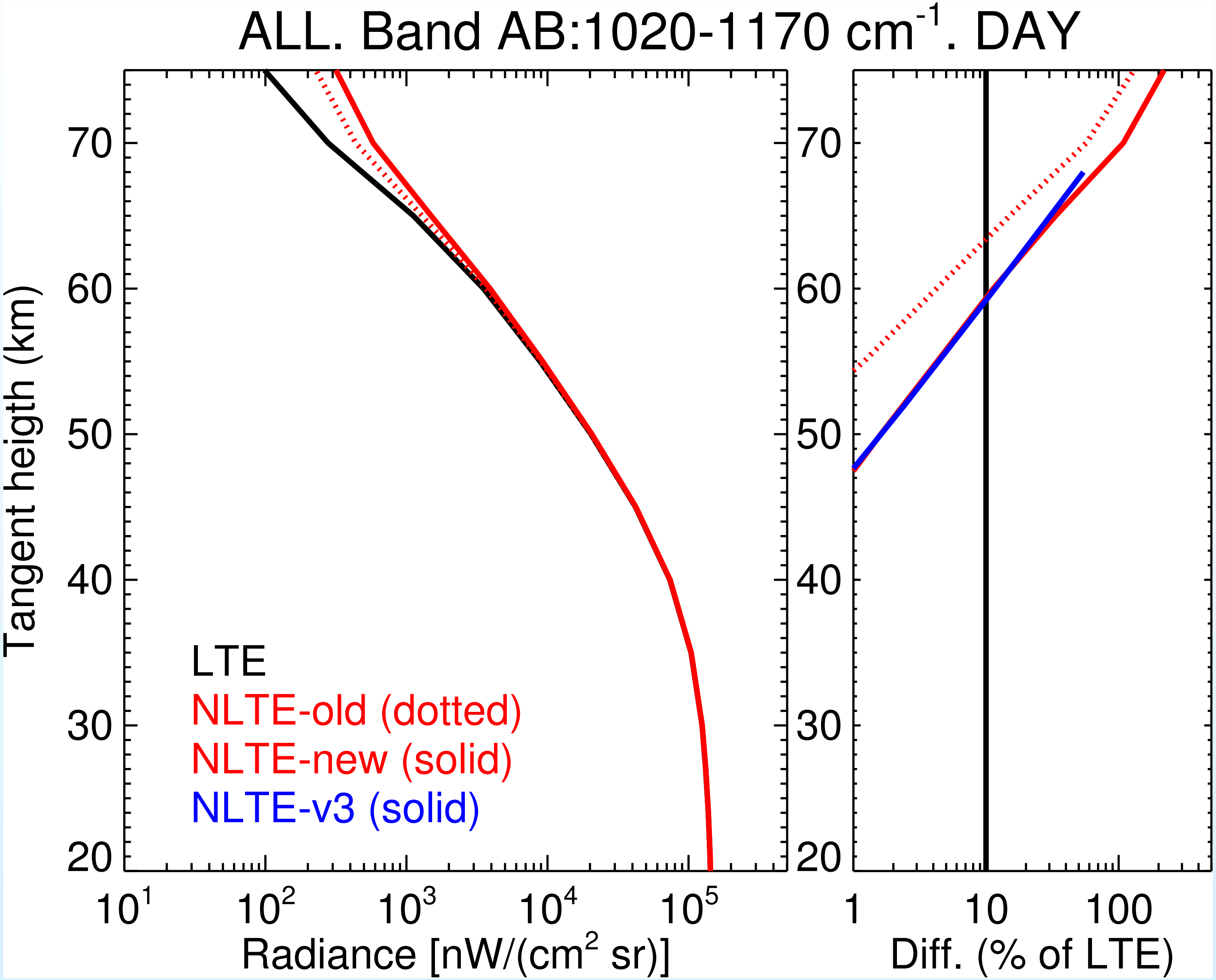
NLTE error (v3): Band A1, Day



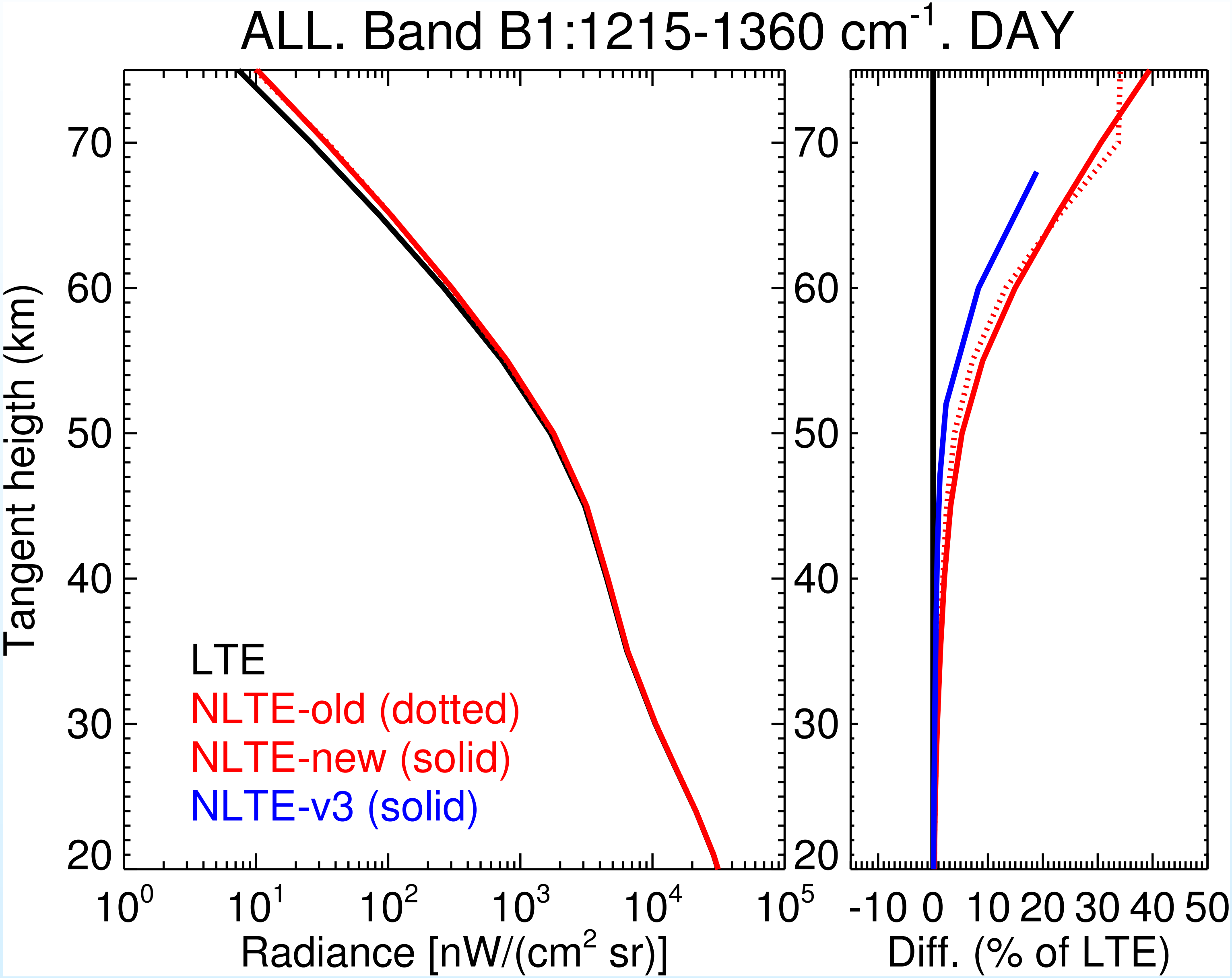
NLTE error (v3): Band A2, Day



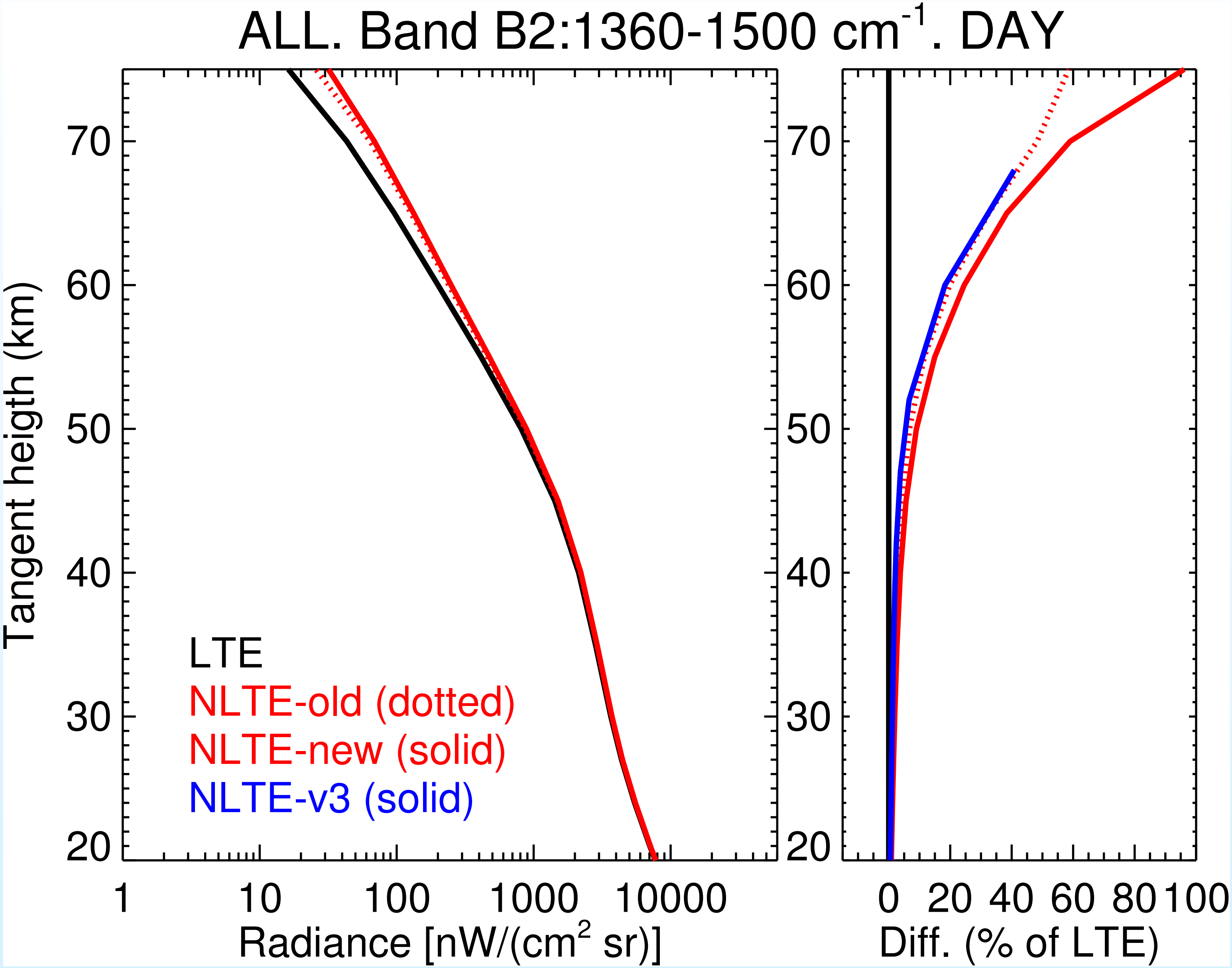
NLTE error (v3): Band AB, Day



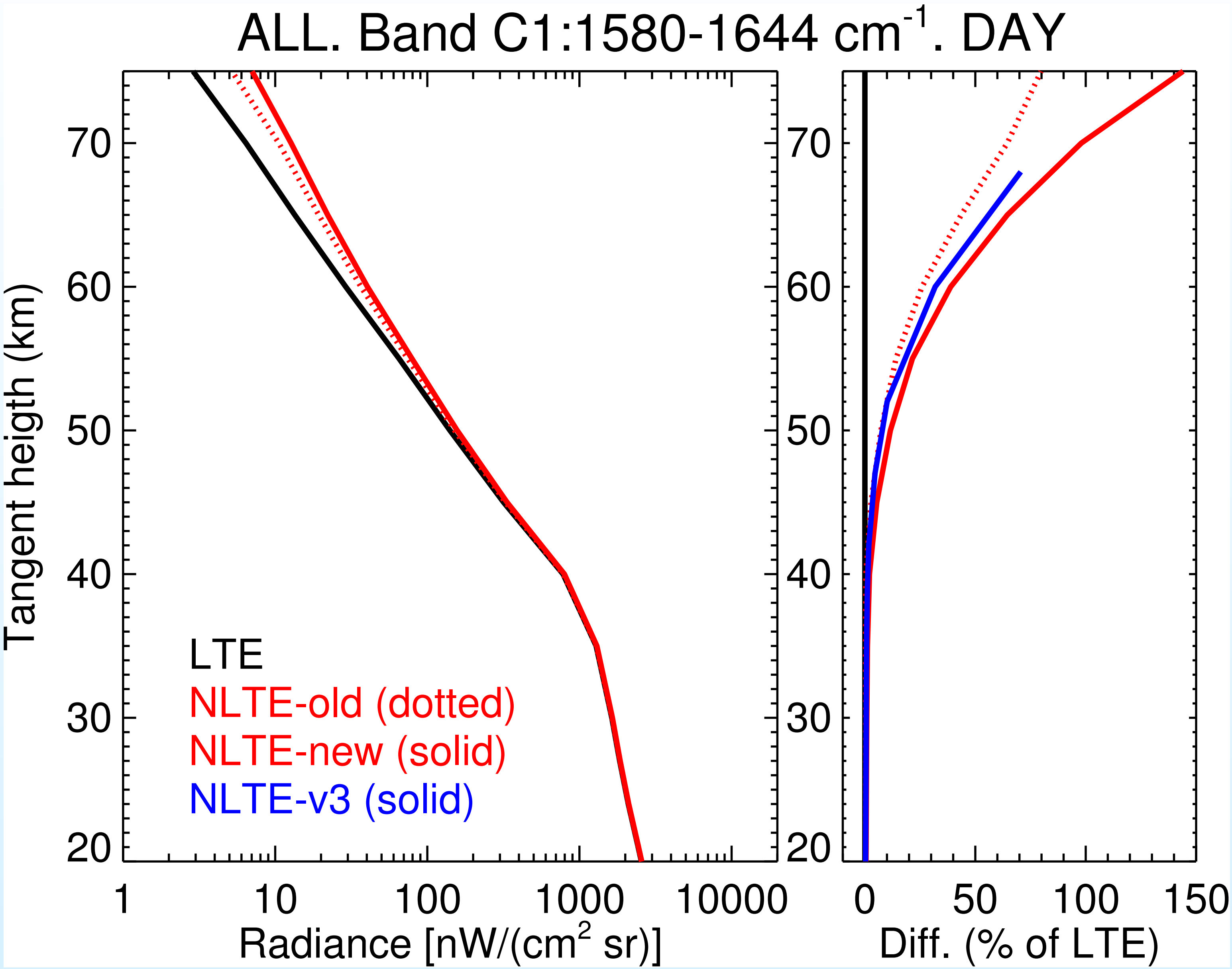
NLTE error (v3): Band B1, Day



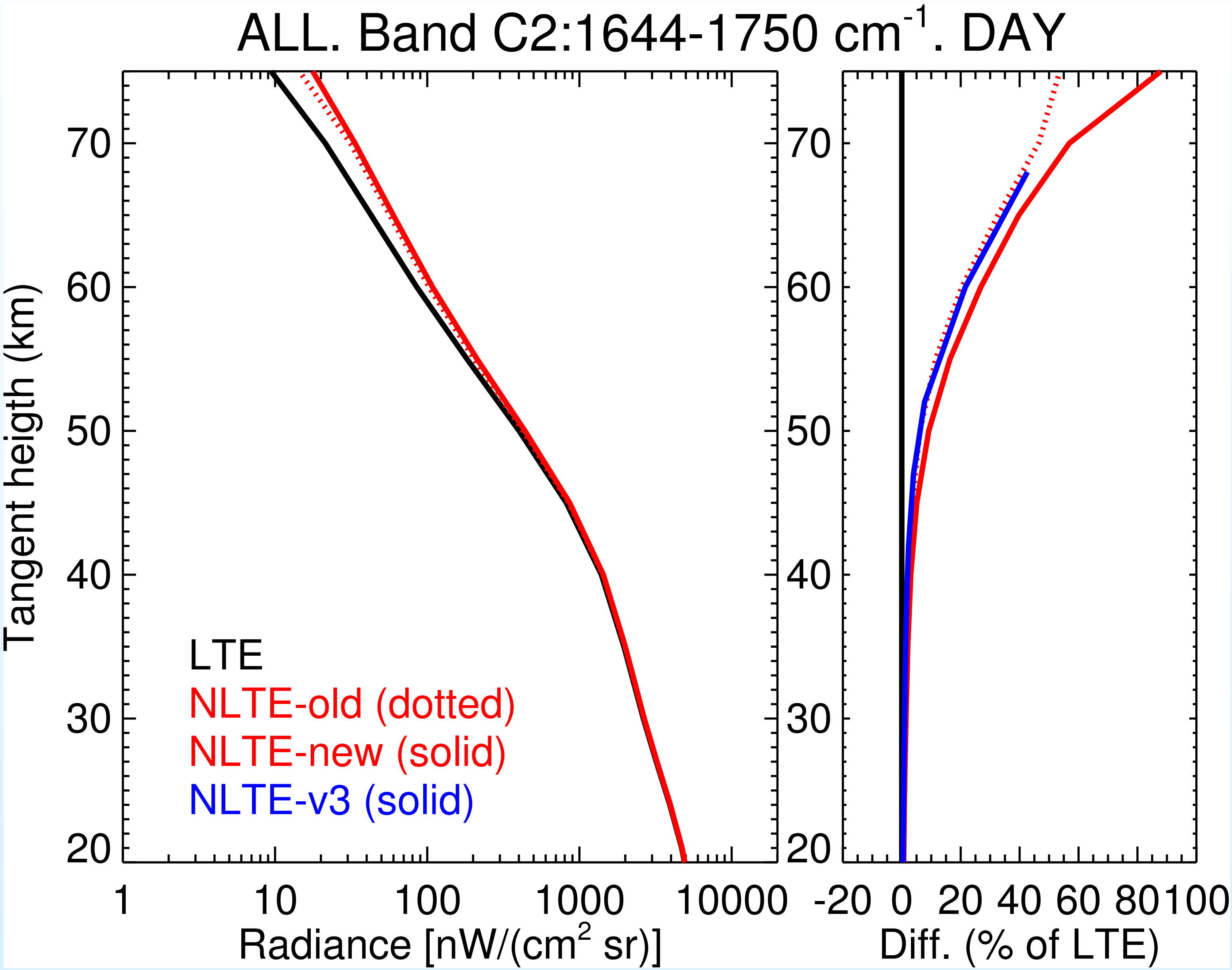
NLTE error (v3): Band B2, Day



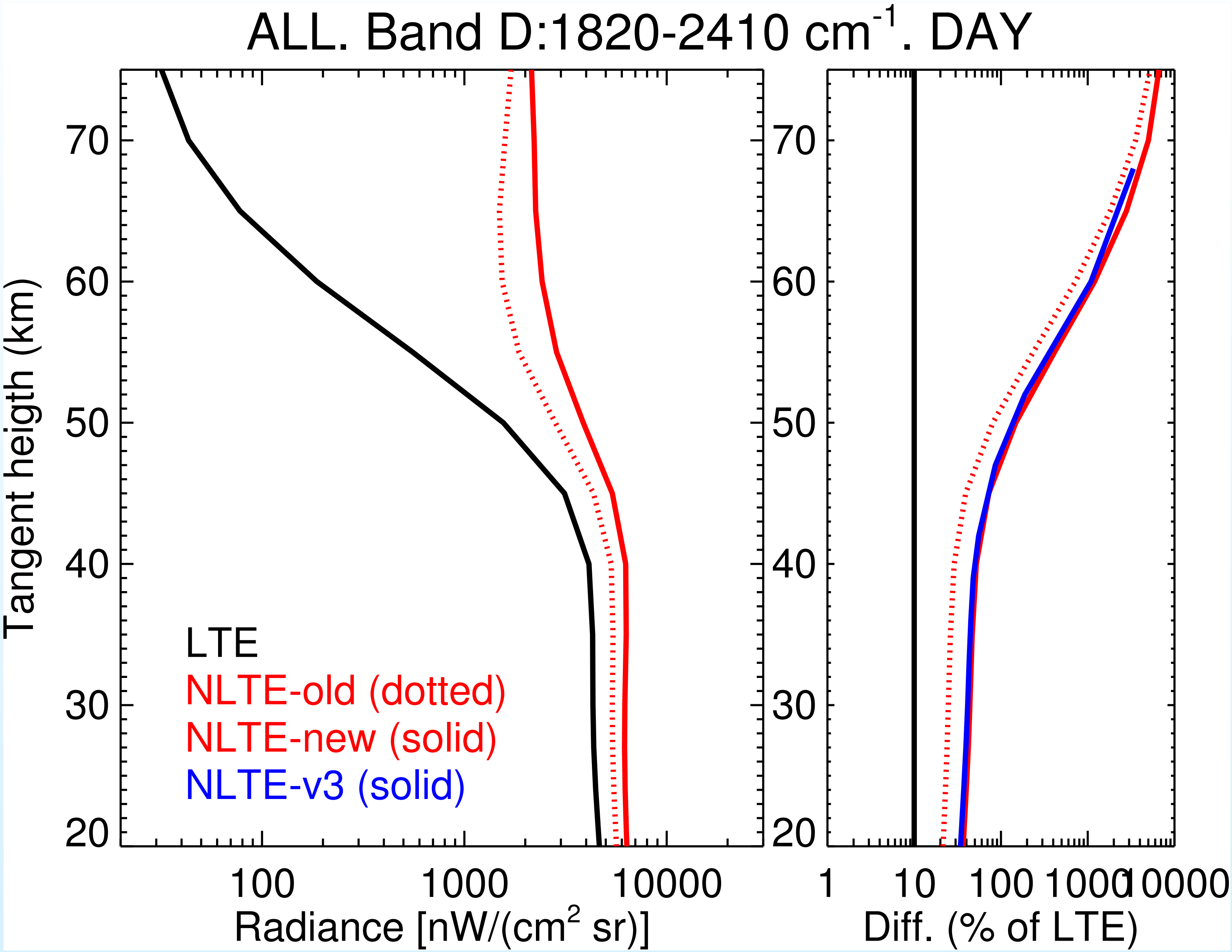
NLTE error (v3): Band C1, Day



NLTE error (v3): Band C2, Day



NLTE error (v3): Band D, Day



Summary

- H2O-CH4 daytime VTs are smaller (~1-2 K) z>60 km
- CO2: Small changes (1-2 K larger) in the Tvibs of the 4.3 and 10 μm bands above around 60 km.
- O3: larger O3 Tvibs (2-5 K) in the mesosphere, z> 60km
- CO: No effect in main isotope; smaller VTs for the minor isotopes.
- OH(v): Smaller VTs because of rotational NLTE included (adjusted to MIPAS band A OH emission): Impact CO2 4.3 μm at night-time
- NO significant changes for the rest of species: N2O, NO2, NO, HCN, HNO3.

Work to be done:

- Check if new CH4 VTs are consistent with the MIPAS study (L-P. et al., GRL, 2005). Revise H2O NLTE
- Revise New non-LTE errors calculated by Anu
- Write TN