Modelling Non-LTE effects

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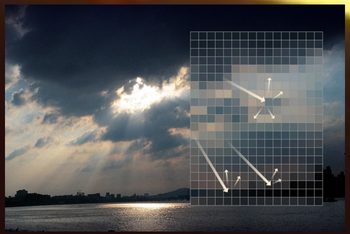


Collaborators:

Bernd Funke (IAA), Marty Mlynczak (NASA Langley), Marco Matricardi (ECMWF)

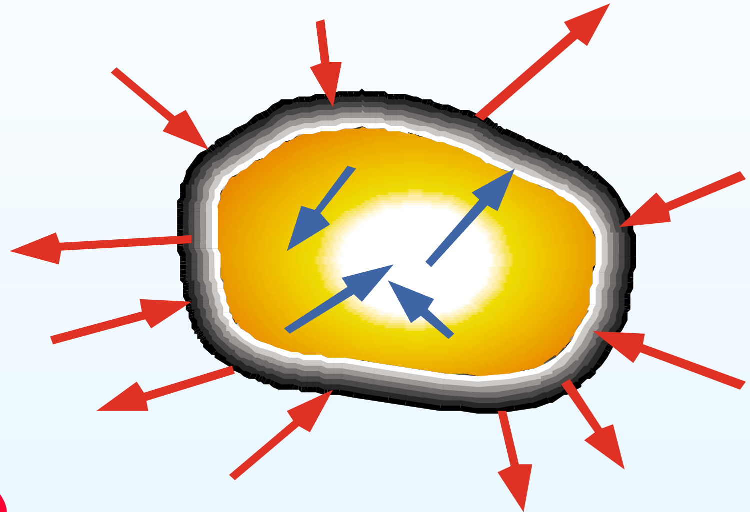
Outline

- Introduction to Non-LTE
- Retrieval of temperature and species under non-LTE:
  - **Limb emission IR** sensors: MIPAS, SABER
  - **Nadir emission IR** sensors: AIRS, IASI
- Non-LTE in heating/cooling rates:
  - Near-IR CO2 heating
  - Non-LTE IR cooling (CO2, O3, H2O, NO, O) (mesosphere & thermosphere)
  - Parameterizations for GCMS
- Summary/Future prospects

Introduction to non-LTE

NLTE: Basics (I)

- Gas parcel (atoms+molecules)
- Three energies at work: kinetic; internal (rot., vib., elec.); and radiation



- **Thermodynamic Equilibrium (TE)**
  - A gas parcel enclosed and isolated => Therm. Equil., T
  - Molecular velocities: Maxwell distribution
  - Excited states: Boltzmann law
  - Radiation properties: $k_v(T)$, $J_v(T)=B_v(T)$
  - Radiative field: Planck function, $B_v(T)$

NLTE: Basics (II)

- **Local Thermodynamic Equilibrium (LTE)**
  - In the atmosphere a kinetic (translational) a **local** $T_k(z)$ can be defined
  - Molecular velocities: Maxwell distribution at $T_k(z)$
  - Excited states: Boltzmann relation at $T_k(z)$, e.g.

$$\frac{n_1}{n_0} = \frac{g_1}{g_0} \exp\left(-\frac{h\nu}{k\, T_k(z)} \right)$$

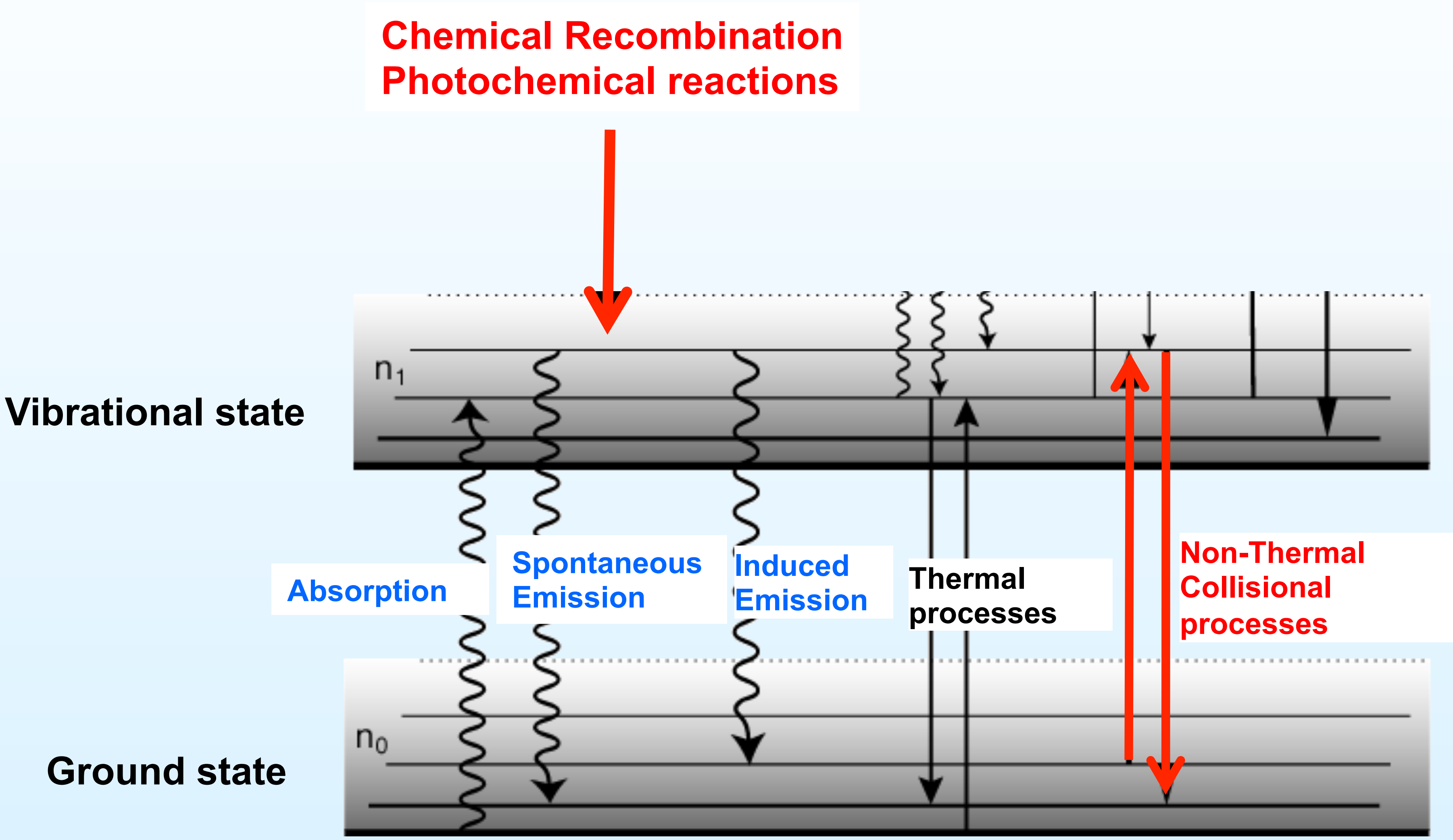
  - Radiation properties: $k_\nu(T_k)$, $J_\nu = B_\nu(T_k)$
  - Radiative field is NOT described by $B_\nu(T_k)$

- **Non-Local Thermodynamic Equilibrium (NLTE)**
  - A translational $T_k(z)$ is also defined
  - Excited states: Boltzmann relation at $T_\nu(z)$, e.g.

$$\frac{n_1}{n_0} = \frac{g_1}{g_0} \exp\left(-\frac{h}{k\, T_\nu(z)} \right)$$

  - Radiation properties: $k_\nu(T_k, T_\nu)$, $J_\nu = B_\nu(T_\nu)$
  - Radiative field is NOT described by $B_\nu(T_k)$

Non-LTE: A two-levels system (I)



Non-LTE: A two-levels system (II)

- **Statistical Equilibrium Equation (SEE)**

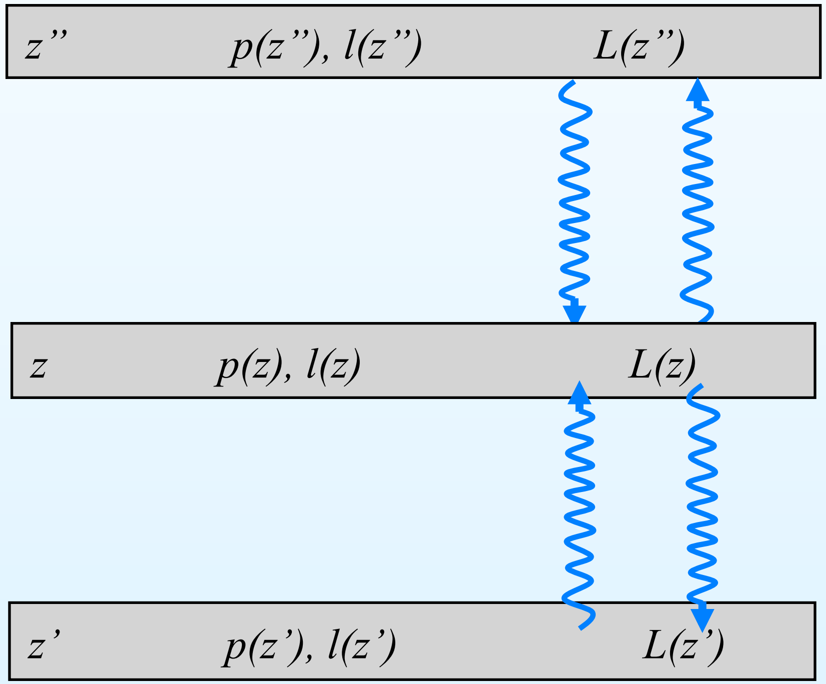
$$\frac{n_1(z)}{n_0(z)} = \frac{B_{01}\overline{L}(z) + p_T(z) + p_{NT}}{A_{10} + l_T + l_{NT}}$$

$$\overline{L}(z) = \frac{1}{2K}\int_{-1}^{+1}\int_{\Delta\nu} L(z,\mu,\nu)\; k(z,\nu)\; d\nu\; d\mu$$

- **Radiative transfer equation (RTE)**

$$\frac{dL(z,\mu,\nu)}{dz} = -\frac{k(z,\nu)}{\mu}\left[L(z,\mu,\nu) - J(z,\nu)\right]$$

$$J(z,\nu_0) = \frac{2h\nu_0^3}{c^2}\left[\frac{n_0(z)\;g_1}{n_1(z)\;g_0} - 1\right]^{-1}$$



=> Output: Non-LTE populations $n_1(z)$, and Heating/Cooling rates $h(z)$

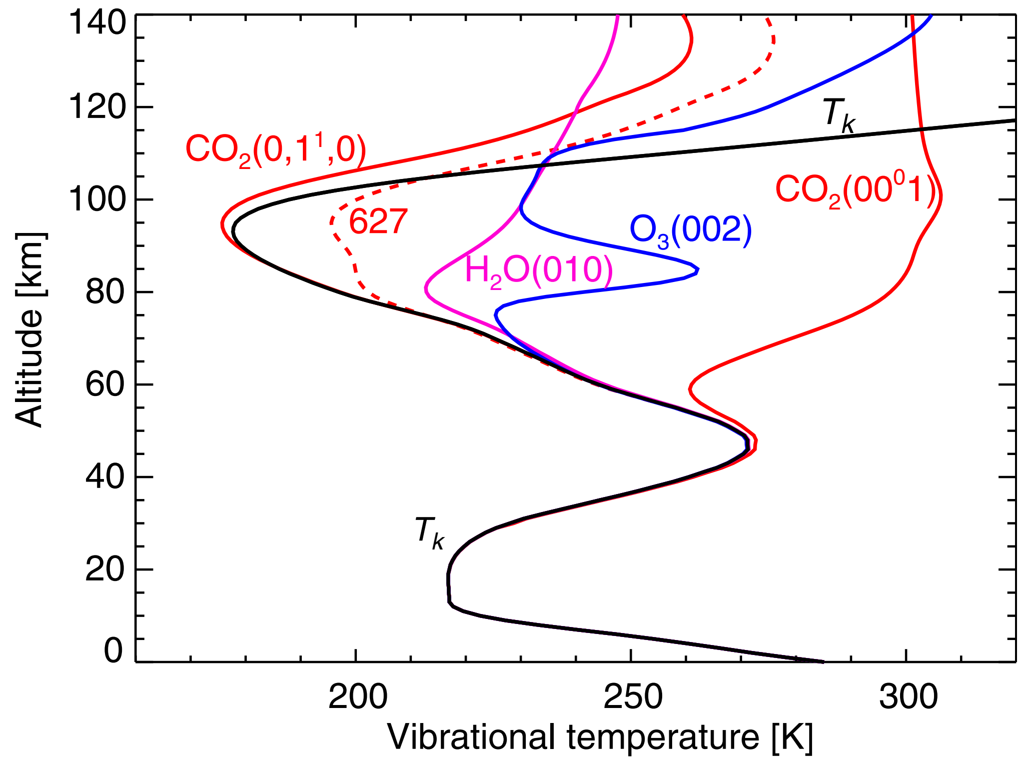
$$h(z) = 4\pi S n_a\left[\overline{L}_{\Delta\nu}(z) - J(z)\right]$$

- **Multilevel case** of *n* energy levels and *m* bands, we need to solve the coupled system of *n* (SSE) x *m* (RTE) equations

Non-LTE: Basic facts, examples

$$\frac{n_1}{n_0} = \frac{B_{01}\bar{L} + p_T + p_{NT}}{A_{10} + l_T + l_{NT}} = \frac{g_1}{g_0}\exp\left(-\frac{h\nu}{k\,T_V}\right)$$

- Thermal collisions keep pop. levels in LTE
- NLTE occurs mainly: 1) At high altitudes
  2) For shorter-λ bands
- It can be caused by:
  - Radiative processes, mainly,
    - Spontaneous emission to space
    - Absorption of radiation: Solar (near-IR), Atmospheric radiation
  - Non-Thermal collisional processes (e.g., V-V, E-Vibrational, etc.)
  - Chemical recombination; Photochemical reactions.



López-Puertas & Funke, Encycl. Atmos. Sci., 2015.

Retrievals from non-LTE IR emissions (limb sensors)

Non-LTE retrievals

- Retrievals of atmospheric parameters (temperature, species abundances) from non-LTE IR emissions

  => A big step forward in last 15 years (SABER and MIPAS)

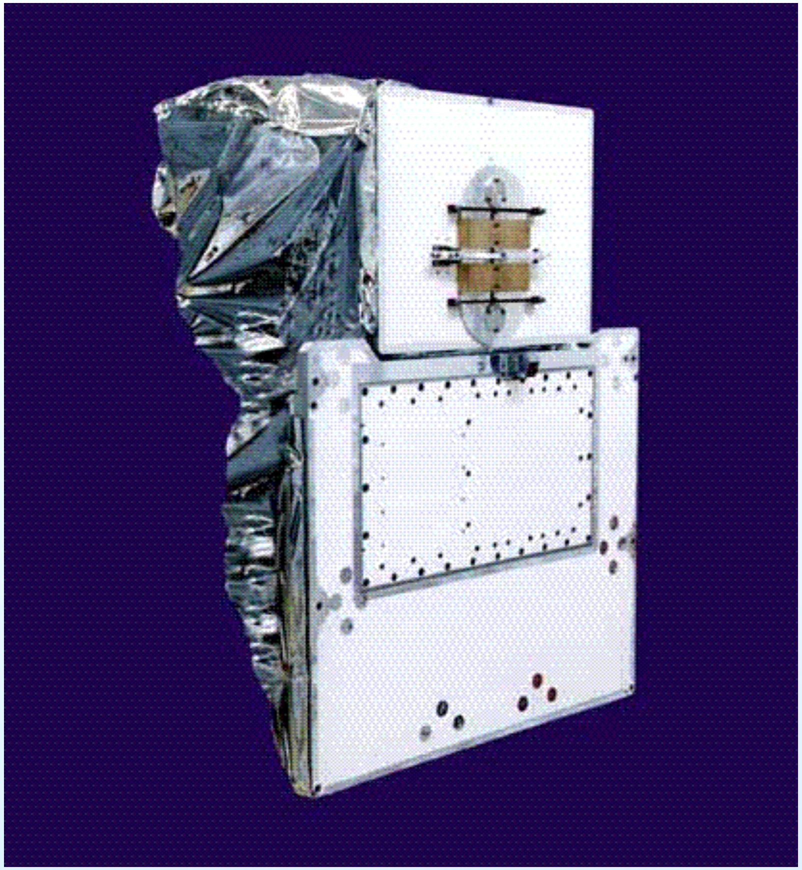
  => In IR retrieval non-LTE seen as a "problem"; but very useful for many species (high SNR)

  => Mainly in emission IR experiments

  => Requires good knowledge of non-LTE processes

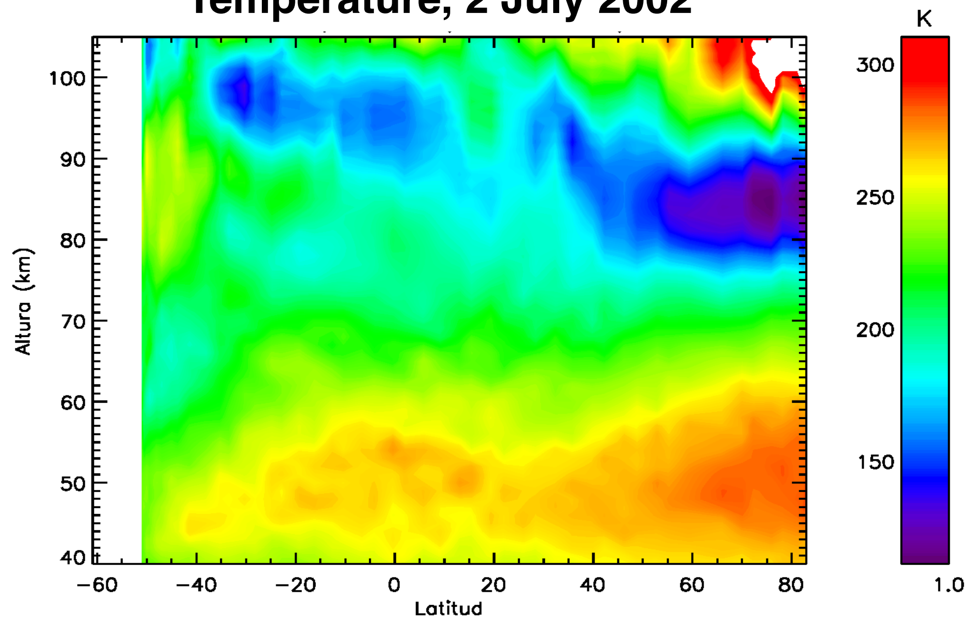
SABER instrument

- Limb viewing, 400 km to Earth's surface
- Ten channels radiometer (1.27-16 μm)
  - CO_2 at 14.9 & 15.3 μm (Temperature)
  - O_3 at 9.6 μm (O_3)
  - $O_2(^1\Delta g)$ 1.27 μm (O_3)
  - CO_2 at 4.3 μm (CO_2)
  - OH(v) 1.6 and 2.0 μm (O, H)
  - NO 5.3 μm (NO cooling)
  - H_2O 6.9 μm (H_2O)
- Over 30 routine data products, Temperature, O_3, CO_2, and NO and CO_2 cooling rates (+ H_2O, in progress)
- Over 15 years in-orbit !!!



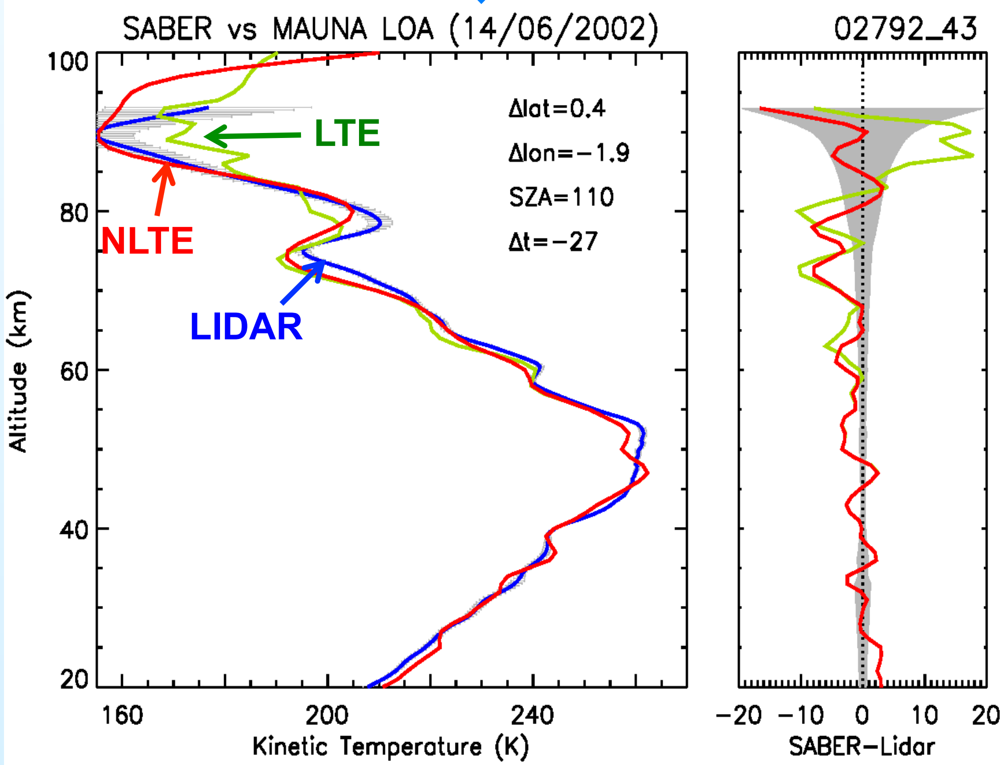
75 kg, 77 watts, 77 x 104 x 63 cm, 4 kbs

Temperature inversion (non-LTE) (SABER)

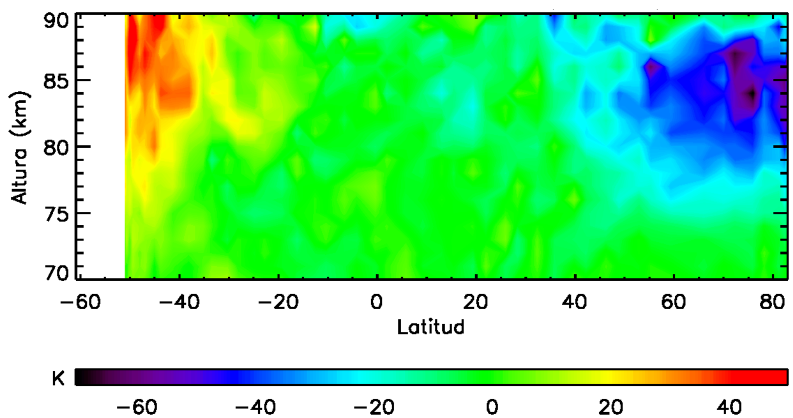


- **From CO2 15 μm emission**

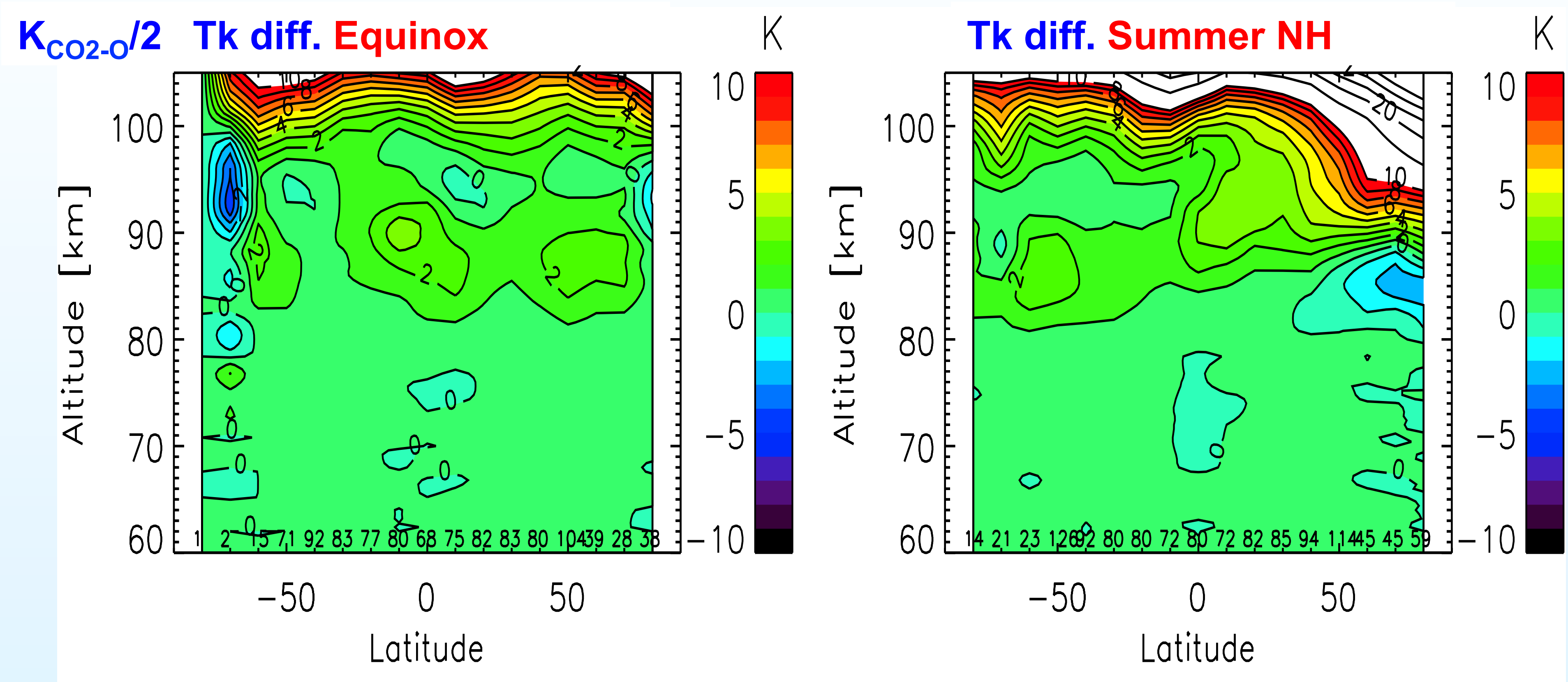
Validation of T_k with Lidars



T(non-ETL)-T(ETL)



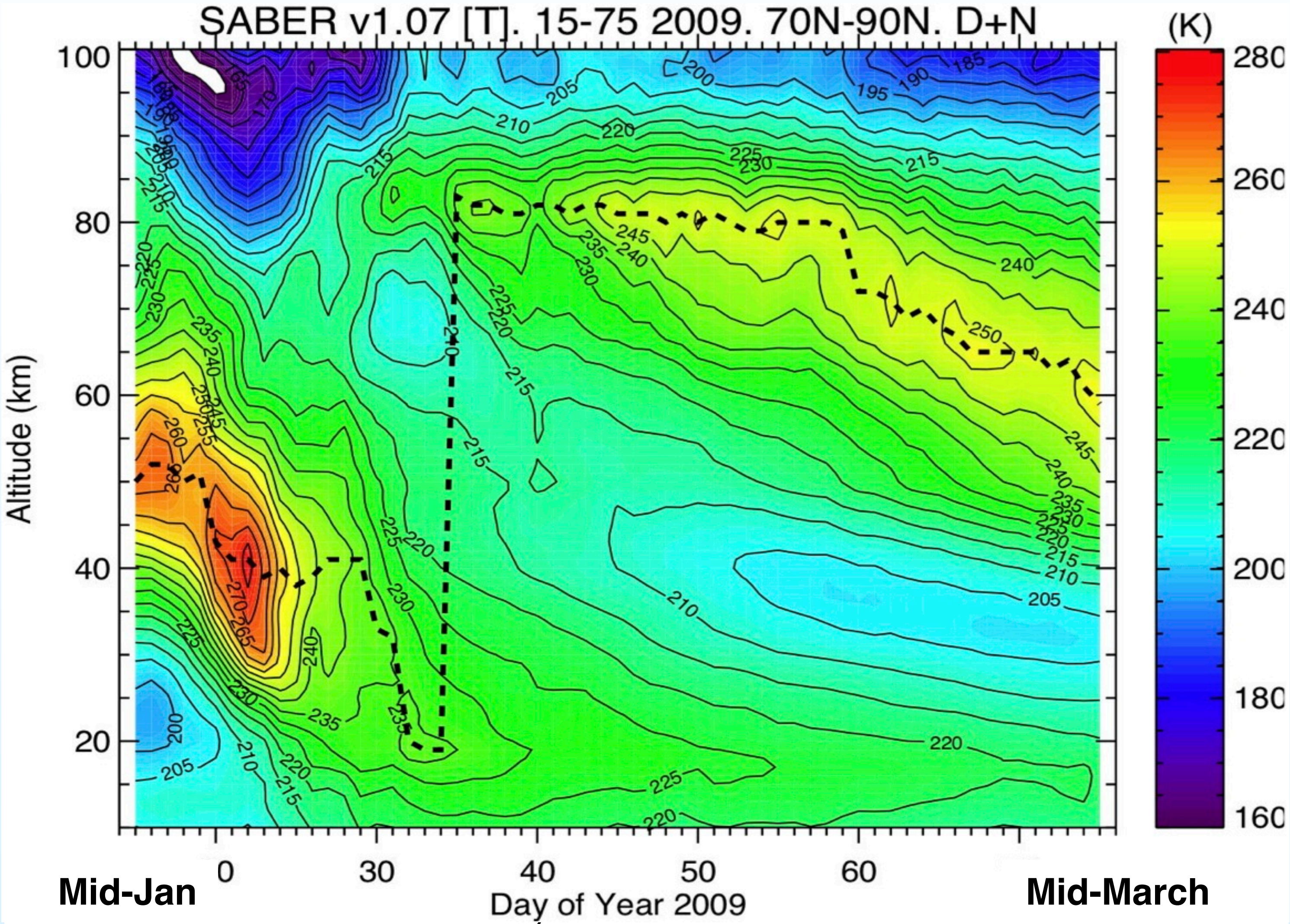
SABER temperatures: Effect of $K_{CO2\text{-}O}$



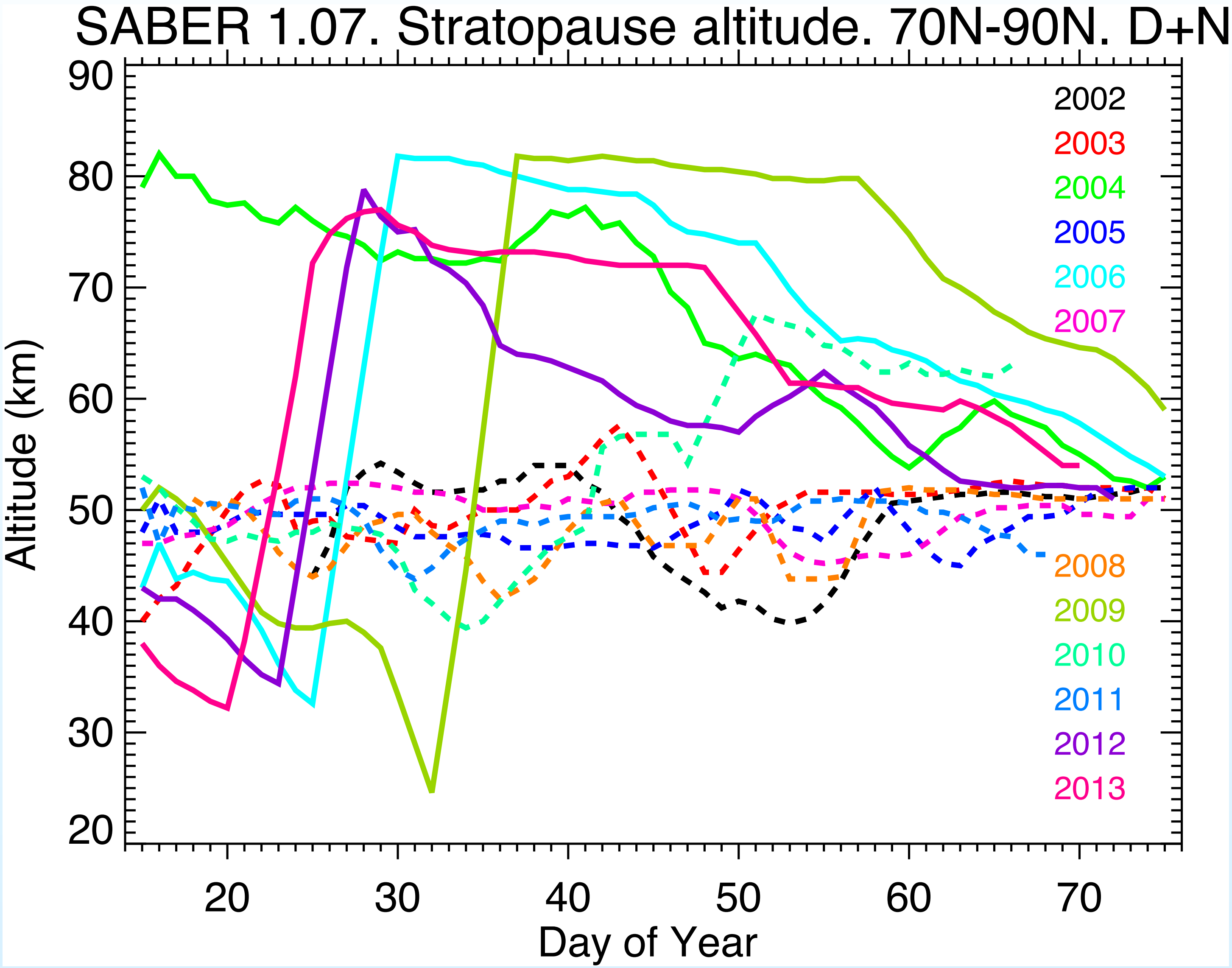
- **Current uncertainties in $K_{CO2\text{-}O}$**: 10-20 K @ 100 km

García-Comas et al., JGR, 2008

Strat-Warm: Elevated Stratopause

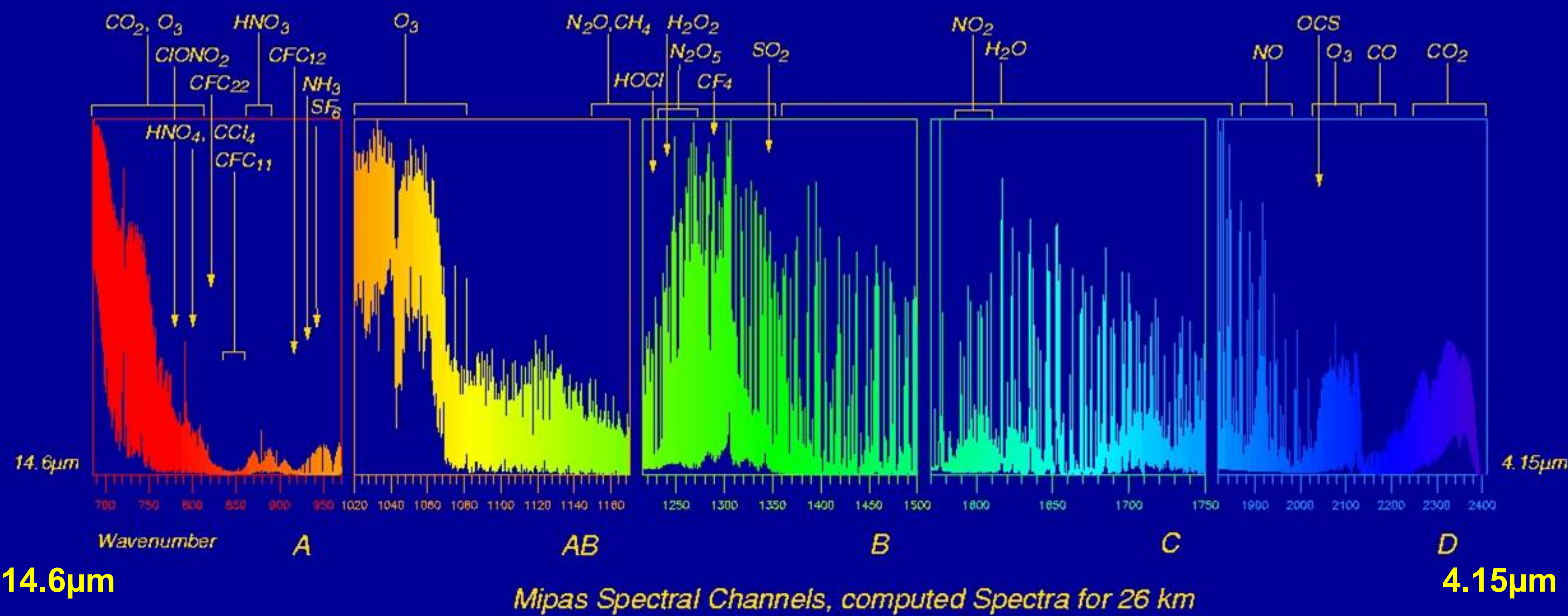


Stratopause in 2002-2013 NH pol. winters



MIPAS

Spectral resolution (apodized): 0.035-0.0625 cm^{-1}



- Michelson interferometer with very high spectral resolution (0.035-0.0625 cm^{-1})
- Wide coverage (15-4.3 µm); High sensitivity (30-3 nW/(cm^2 sr cm^{-1}))
- Global (pole-to-pole) and temporal (day & night) coverage, 5 km to 170 km
- Nominal mode (5-70 km) + Middle and Upper atmosphere modes (20-100km; 40-170km)
- Very useful for investigating non-LTE processes

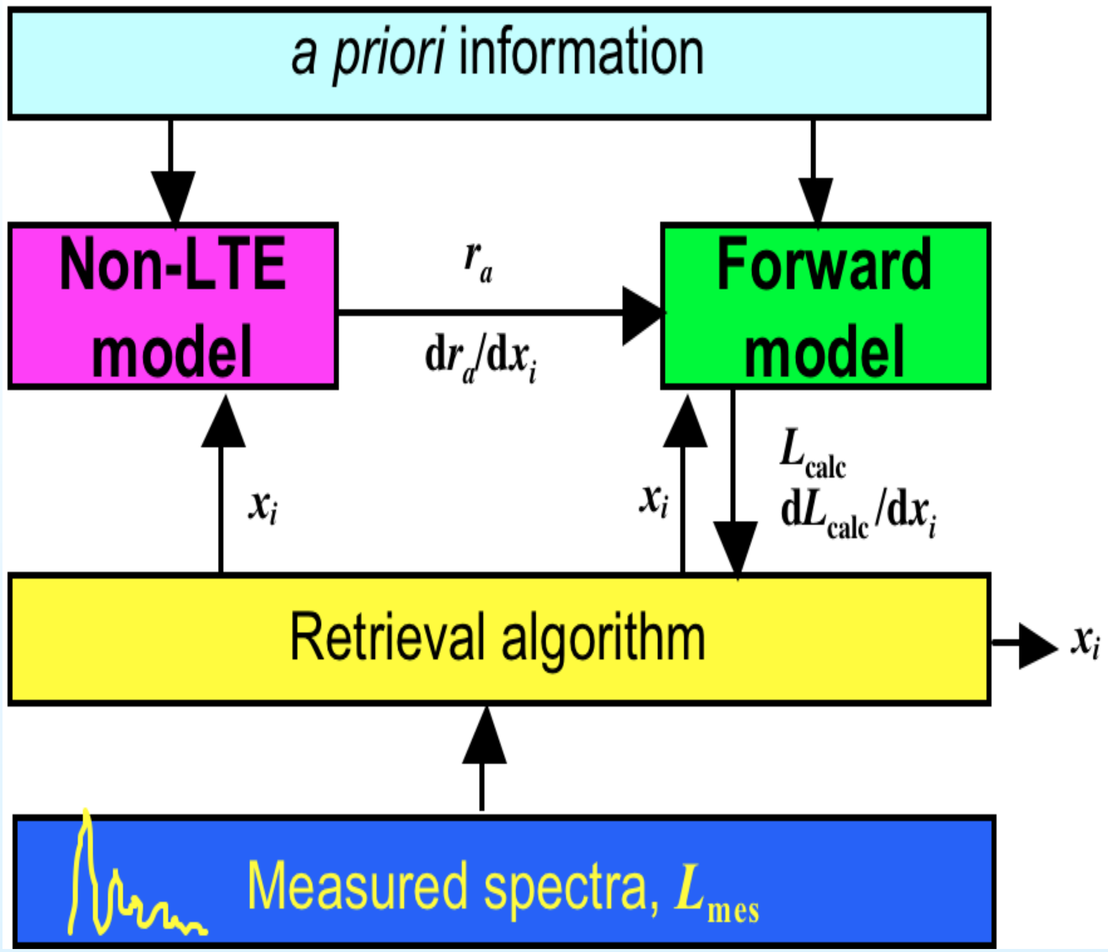
MIPAS non-LTE retrieval scheme

A non-LTE model (GRANADA)

- Calculate Tvibs, Trot, Tspin for all important IR emitters (CO_2, H_2O, O_3, N_2O, CO, CH_4, NO, NO_2, HNO_3, OH)

A forward NLTE code (KOPRA)

- Radiance (limb, nadir)
- Jacobians, if NLTE (Tvibs) parameters are retrieved (i.e., derivatives of radiances and populations wrt non-LTE parameters)



Species retrieved in non-LTE from MIPAS MA+UA modes

SPECIES	Spectral Range [μm]	Altitudes [km]	Reference/Comment
Temperature	15	20-100	García-Comas et al. ACP, 2012; 2014
O_3 [vmr]	12.8, 9.6	20-100	López-Puertas et al., AMT, 2018
H_2O [vmr]	12.5, 6.3	20-90	García-Comas et al. (in prep.)
NO [vmr]	5.3	20-100	Funke et al. (2005a,b; 2014a,b; 2016)
NO_2 [vmr]	6.3	20-60	Funke et al. (2005a,b; 2014a,b; 2016)
CH_4 [vmr]	7.8	20-75	
N_2O [vmr]	7.8	20-55	Funke et al. ACP, 2008.
Temp. & NO [vmr] Therm.	5.3	105-170	Bermejo-Pantaleón et al., JGR, 2011.
CO [vmr]	4.7	20-150	Funke et al. (2007; 2009)
CO_2 [vmr]	10, 4.3	70-110	Jurado-Navarro etal., AMT, 2016; López-Puertas et al., 2017)

NOy: Energetic Particles Precipitation (EPP)

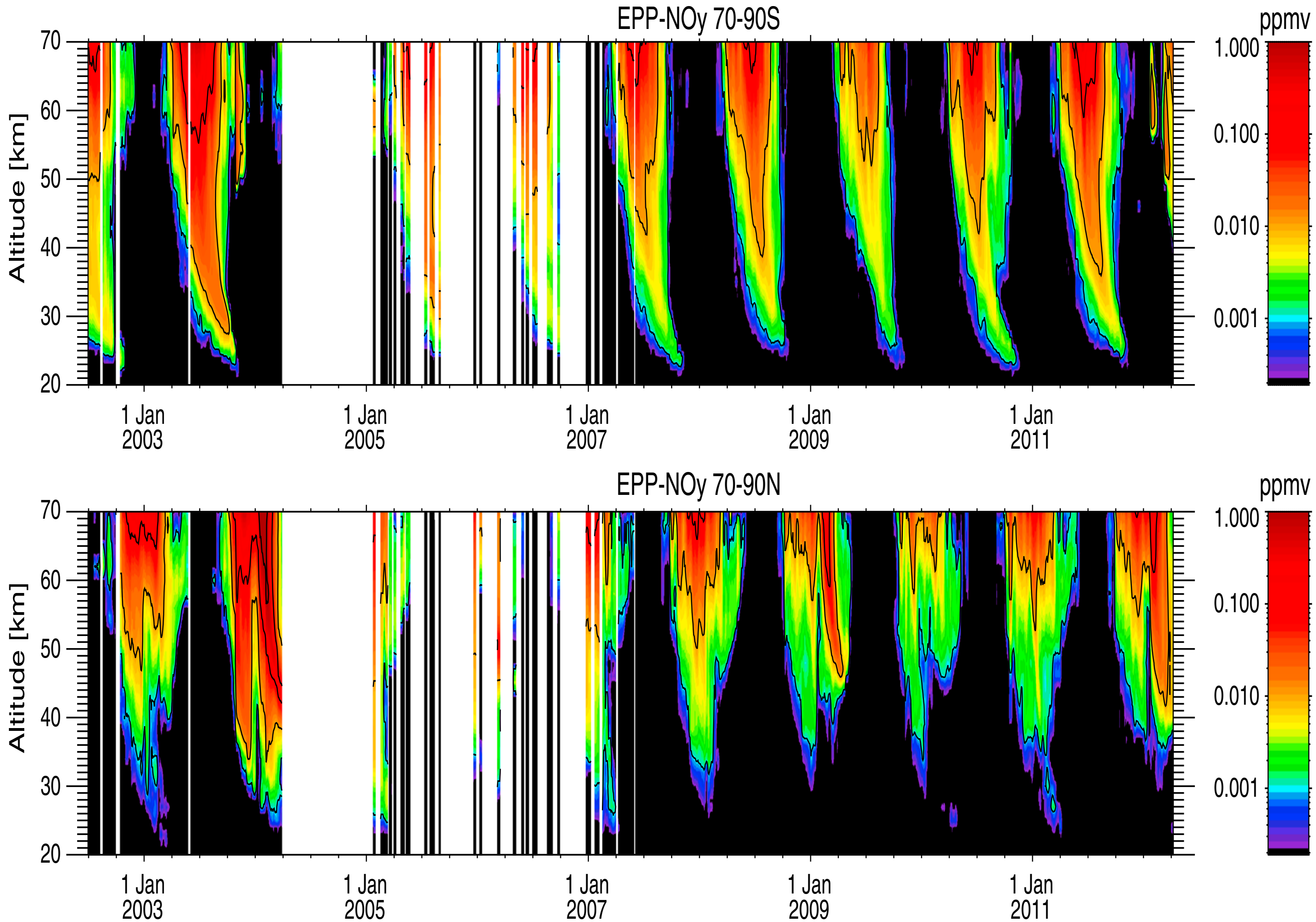
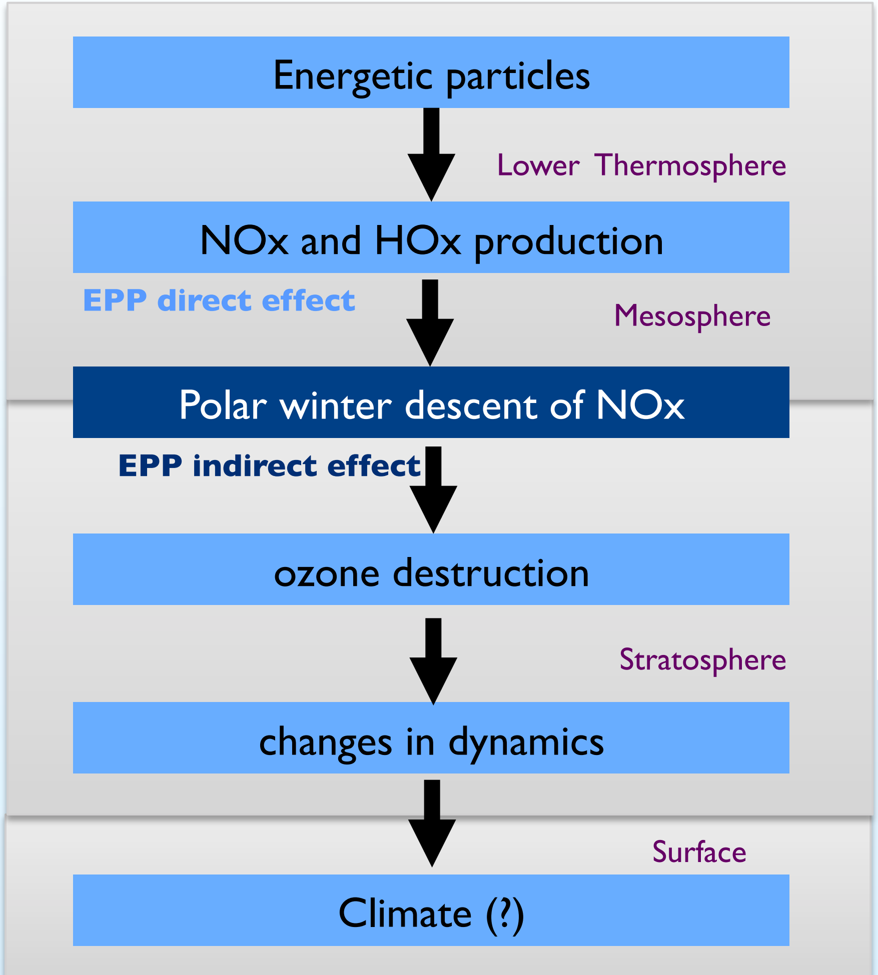
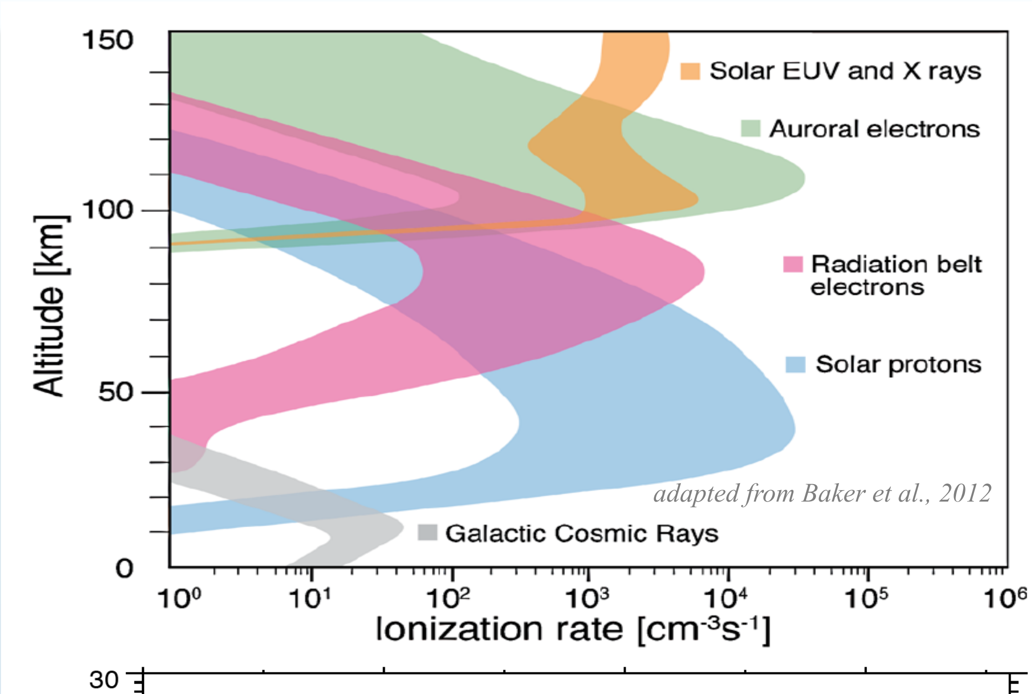


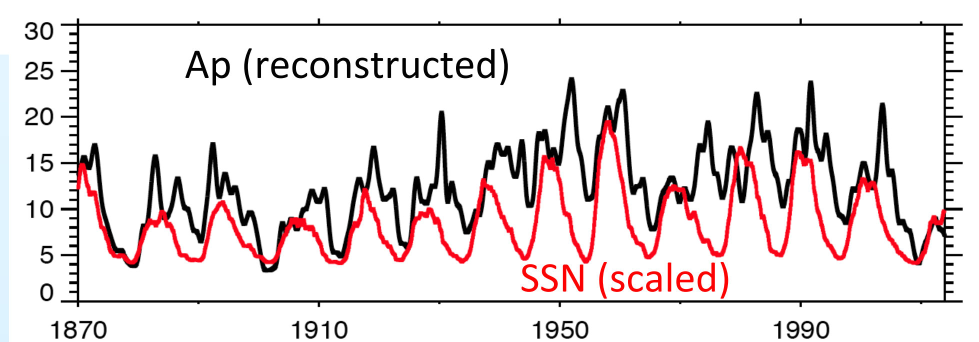
Figure 1. Temporal evolution of the EPP-NO_y VMR at (top) 70–90°S and (bottom) 70–90°N during the Envisat mission lifetime (July 2002 to March 2012).

- Stratospheric and mesospheric reactive nitrogen (NOy) produced by EPP for the MIPAS 10 years record (Funke et al., JGR, 2014).
- NOy descends down to 23 km
- Transport from the lower thermosphere down to the stratosphere depends very much on GW activity
- Effects on O3

EPP: a solar coupling pathway





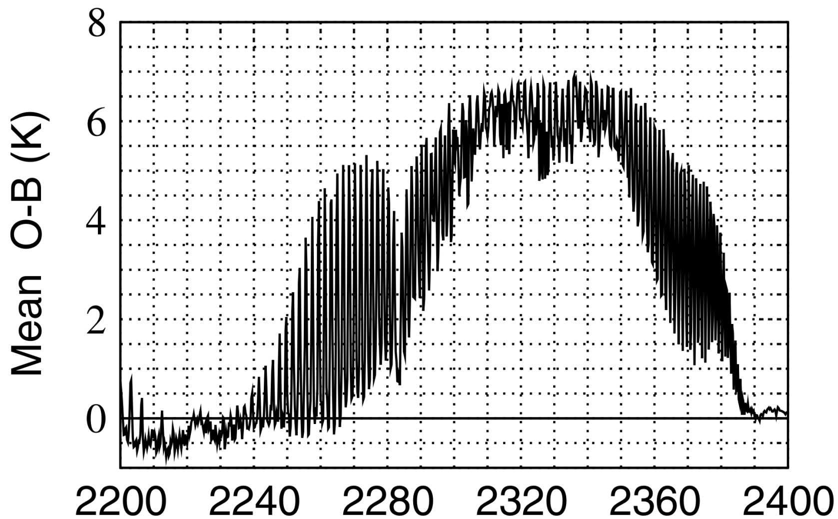


Geomagnetic forcing follows solar cycle, but 2-3 years lagged

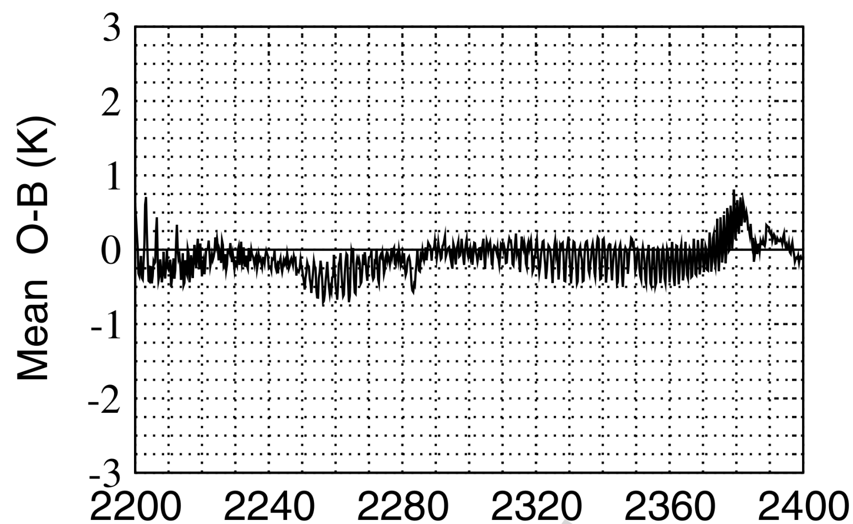
Retrievals from non-LTE emissions (nadir sensors)

IASI Temp. Inver. from 4.3 µm Nadir rad.

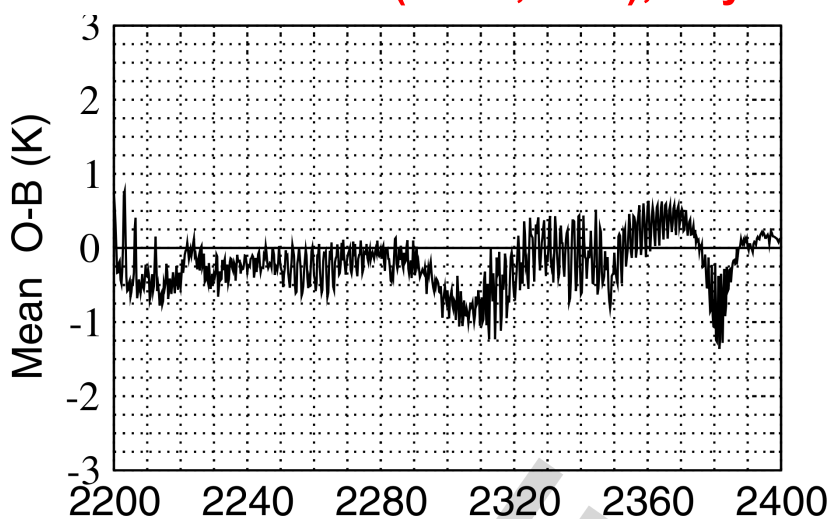
Temp. bias: IASI - RTTOV (LTE); Daytime



Temp. bias: IASI - RTTOV(LTE); Nighttime



T bias: IASI-RTTOV (NLTE, New); Daytime



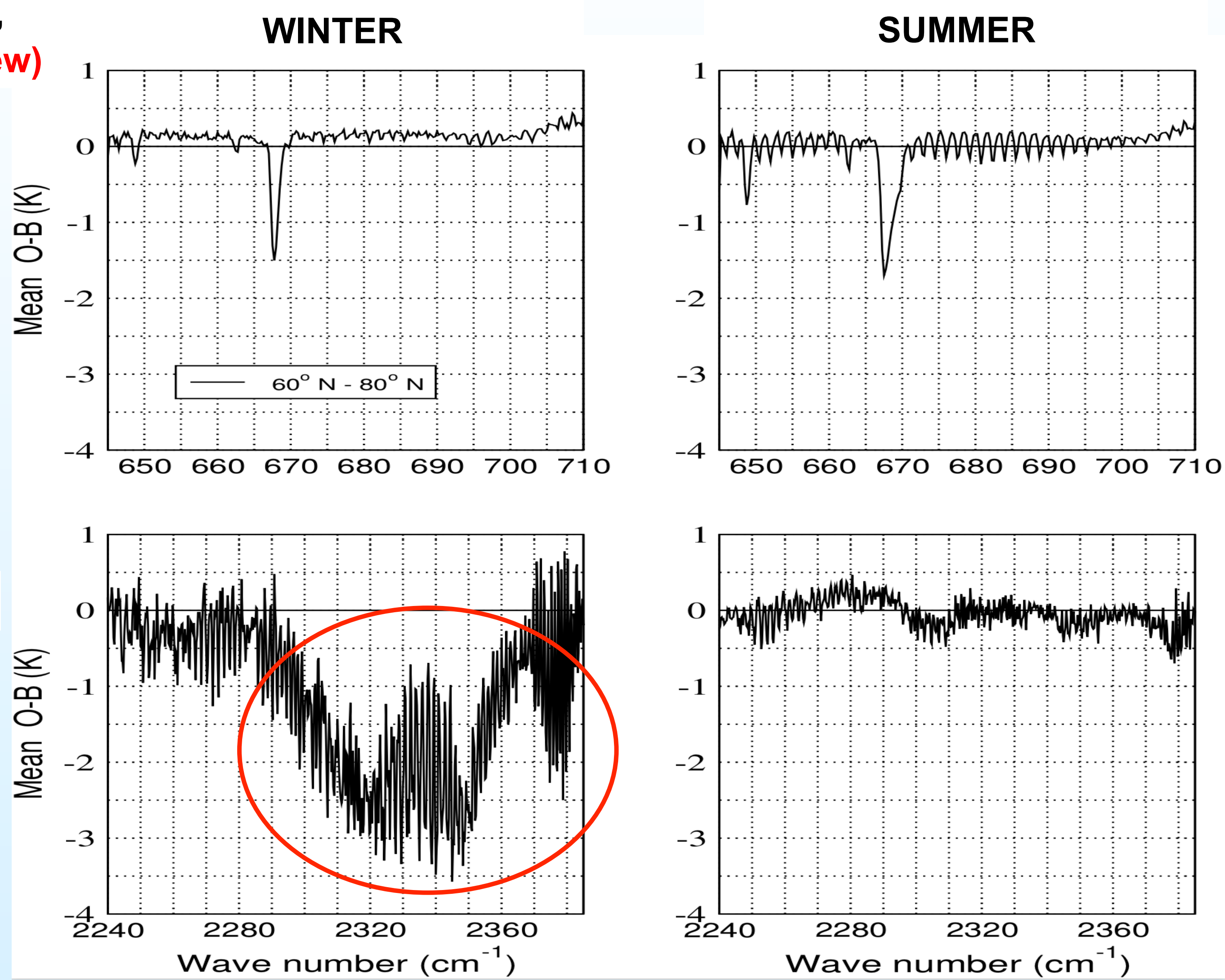
Matricardi et al., JGR, 2018

IASI Temp. Inver. @4.3 μm: Still some problems

Temp. bias, Daytime, IASI - RTTOV(NLTE, New)

15 μm =>

4.3 μm =>

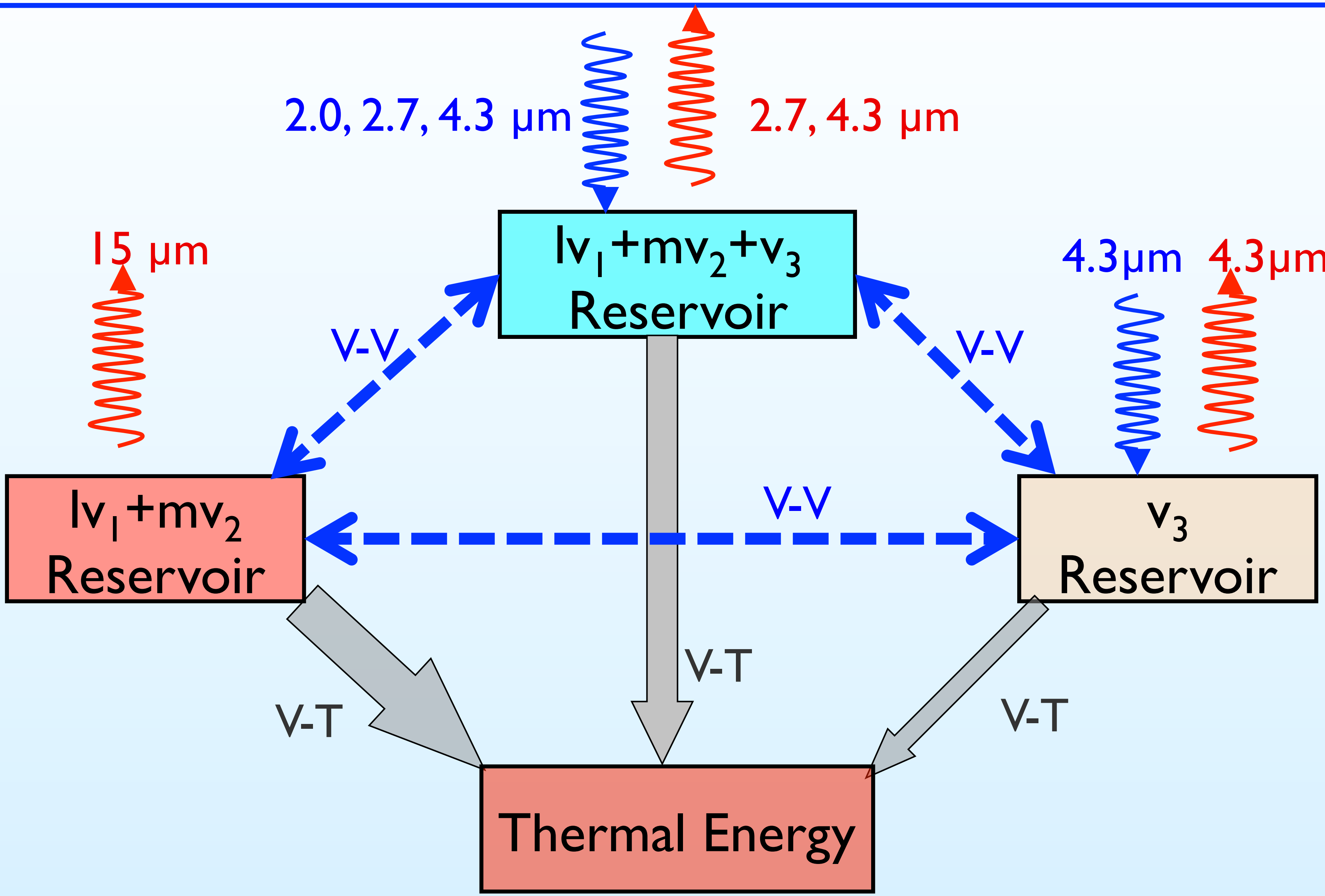


Still some problems in Winter NH, High SZAs !!

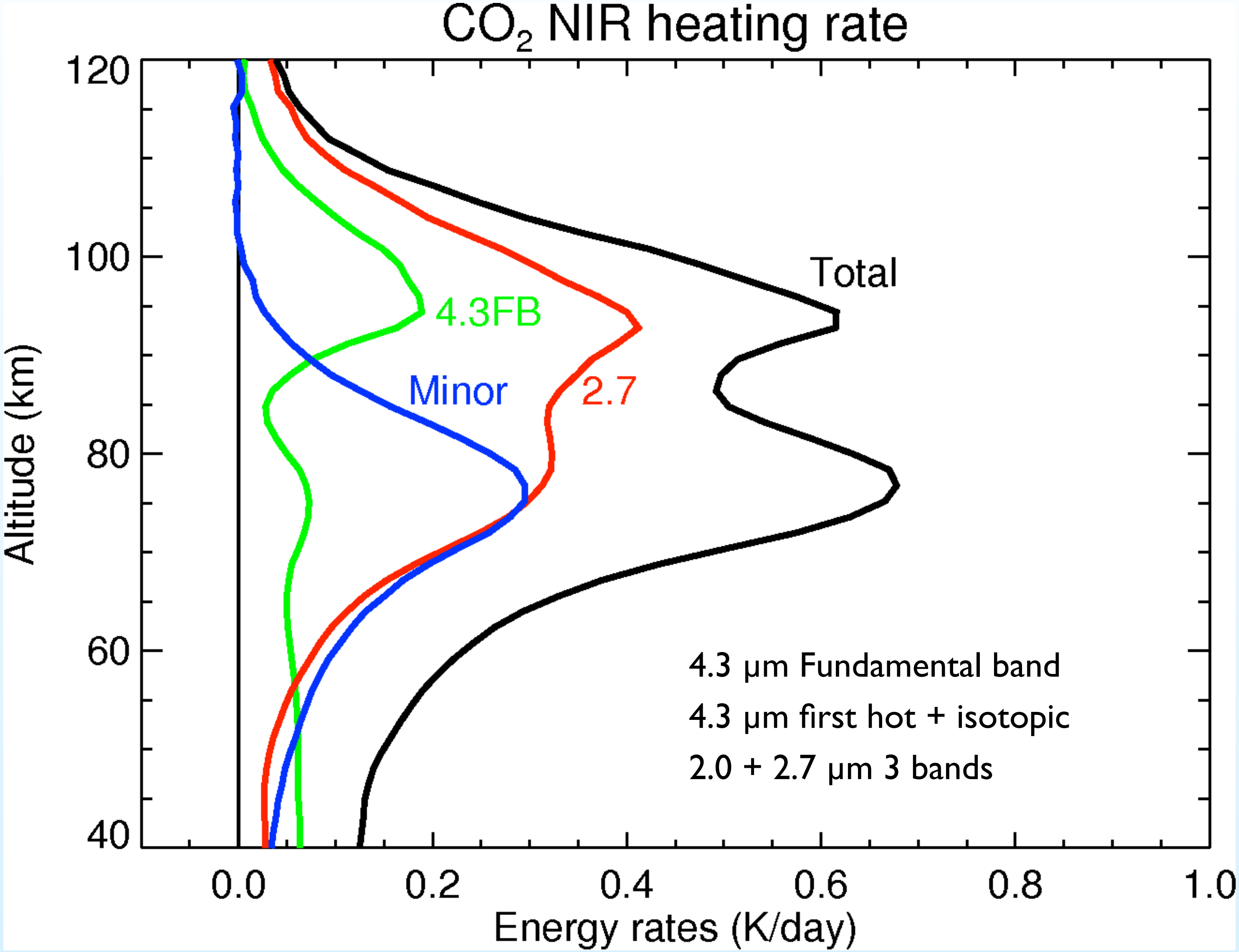
Matricardi et al., JGR, 2018

Near-IR Heating rates

CO2 NIR Heating. Energy pathways



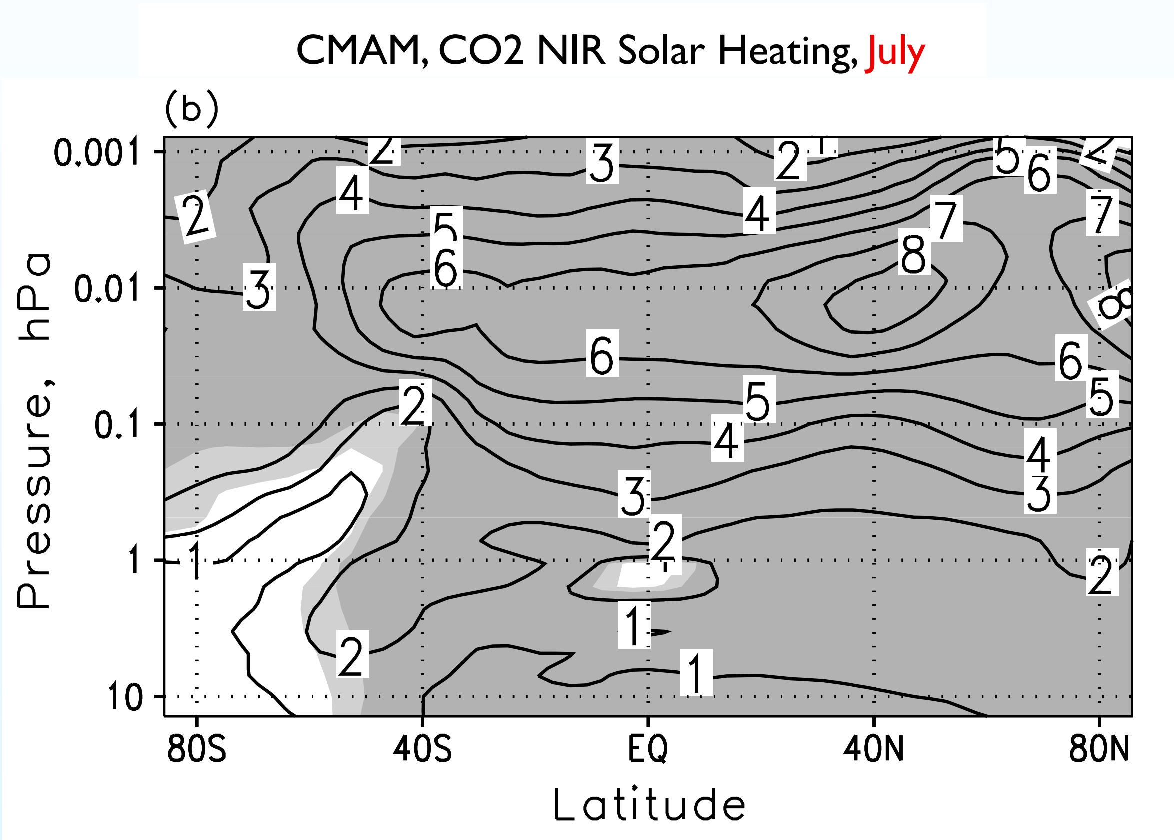
CO2 NIR Heating rates: Contributions



López-Puertas et al., JAS, 1990

CO2 NIR Heating rates: CMAM model

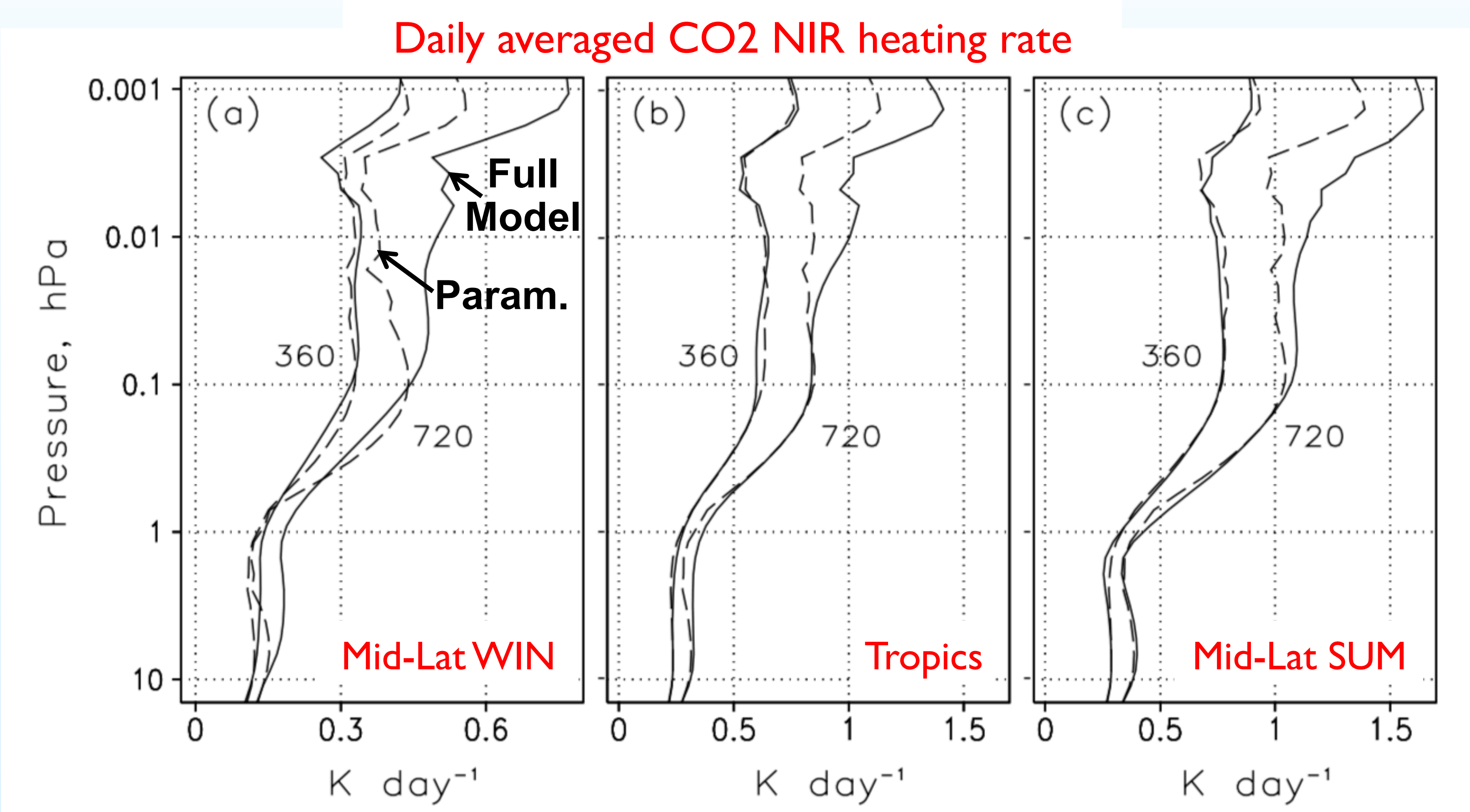
- Results in a significant warming (2-8 K) of the mesosphere.



Fomichev et al., GRL, 2004

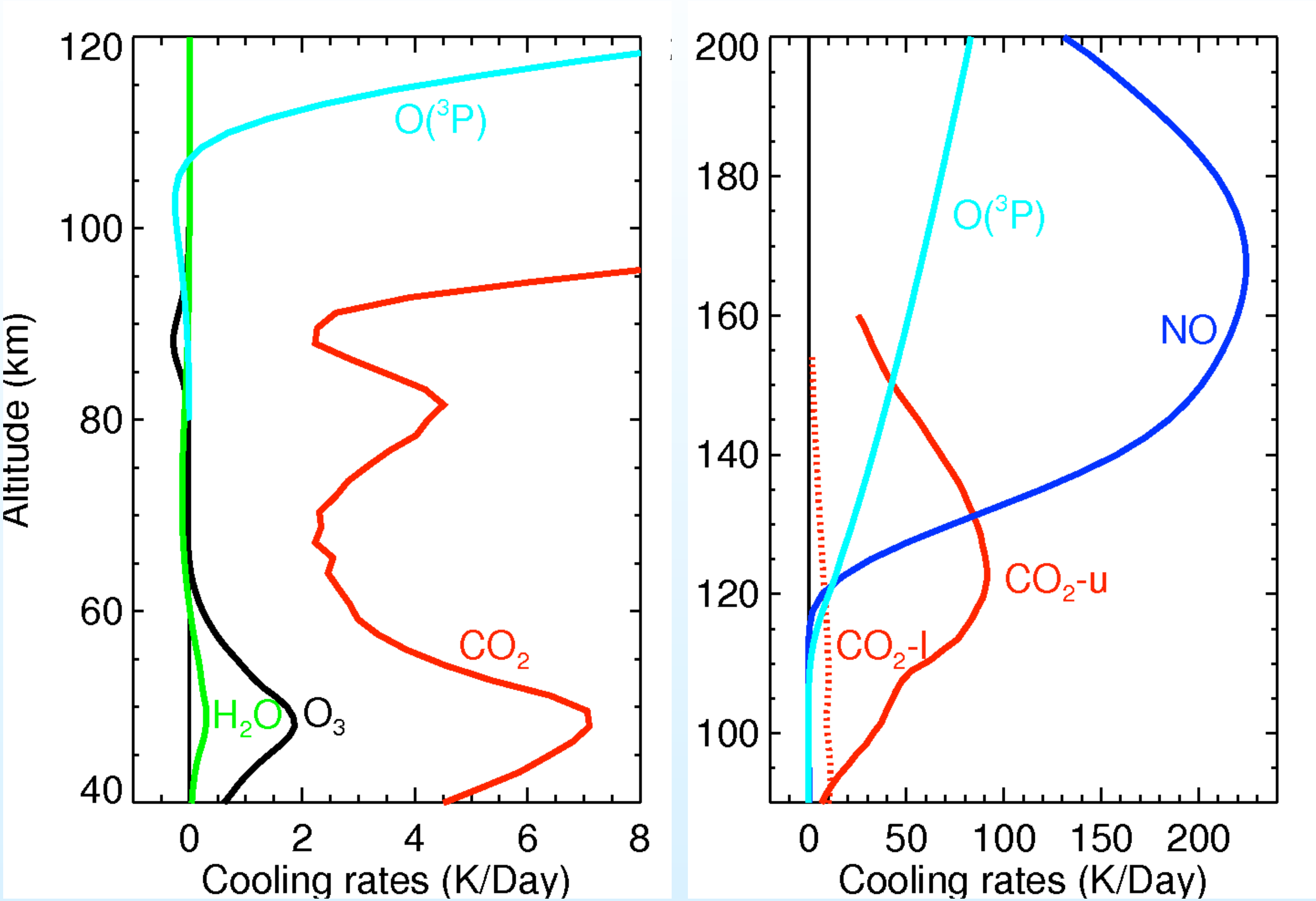
CO2 NIR Heating: Parameterizations for GCMs

- Ogibalov & Fomichev, AdvSR, 2003; Fomichev et al., 2004
- A simple approach.: h(p,SZA) = f(CO_2 vmr(p), CO_2 Column above p).
- Accurate (~10%) for current CO_2 but systematic underestimation (~0.1-0.2K/day) for 2xCO_2



Cooling rates

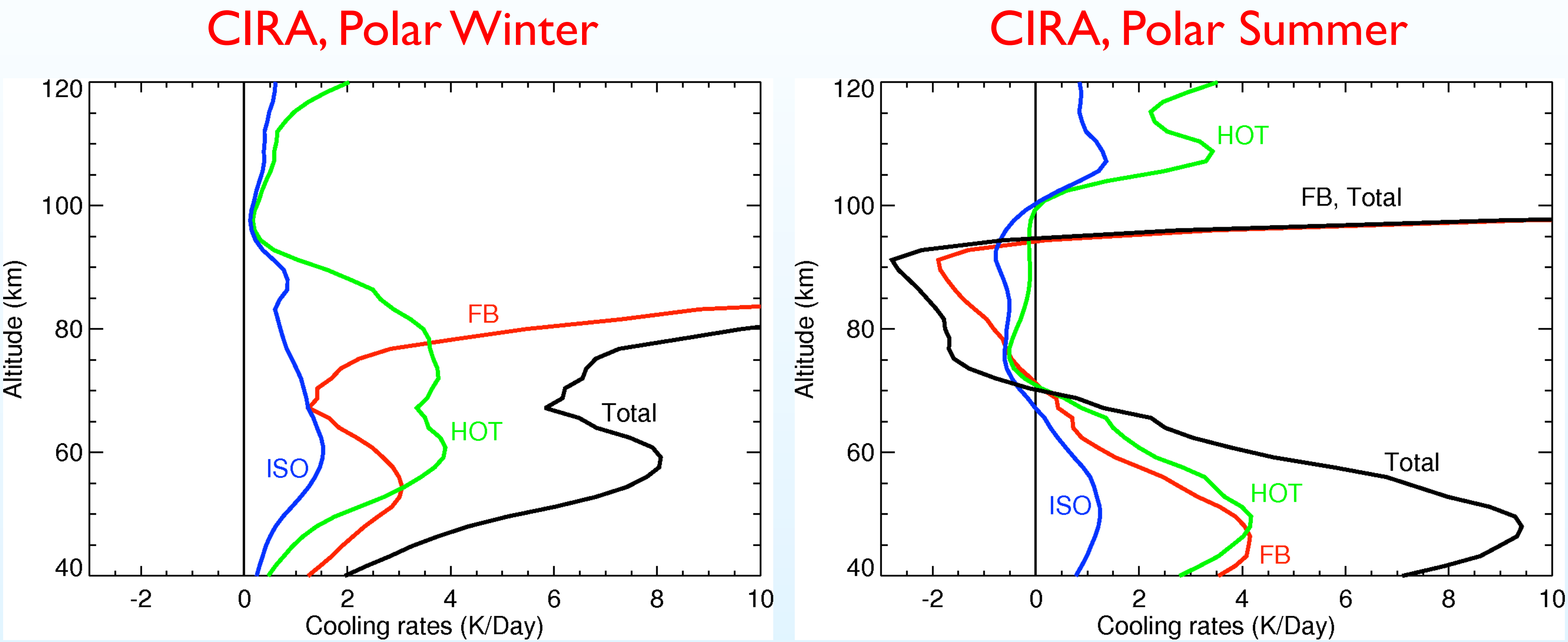
Cooling rates



López-Puertas & Taylor, 2001

CO_2 15 µm Cooling rates

CO2 15 µm cooling rates: Distributions

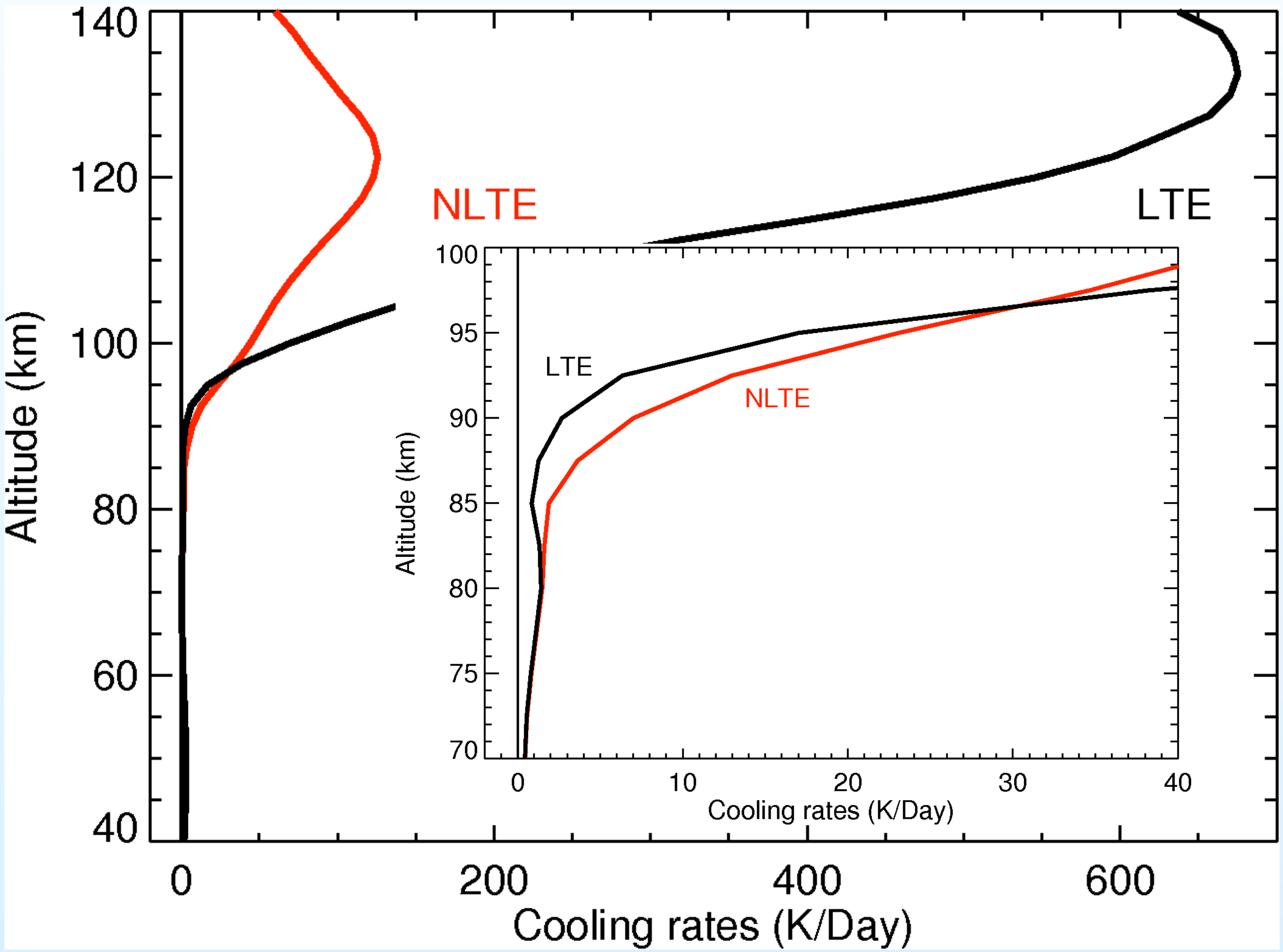


- FB: Fundamental band
- HOT: 10 bands
- ISO: 3 bands
- Depend very much on the Temp. structure

López-Puertas & Taylor, 2001

Non-LTE Cooling rates

- CO_2 15 µm cooling rates: Optically thin $\frac{q_{NLTE}}{q_{LTE}} = \frac{k_O[O]}{k_O[O] + A} \simeq \frac{k_O[O]}{A}$



López-Puertas & Taylor, 2001

CO2 15 µm CR: parameterizations

- Fomichev et al., JGR, 1998
- Explicit dependencies on T, composition, CO2 + col. rates
- 6 ref. p-T atmospheres

- NLTE: Fundamental band ONLY
- Cool-to-space + Contribution of the adjacent layer below

~93 km

- Only fundamental band. Rad. from upper layers included. Extended Recurrence formula

~85 km

- Several bands but in NLTE.
- Use of LTE method, corrected for NLTE

~70 km

- LTE: Curtis matrix par. Including Temp. dependence explicitly (no interpolation)
- Many bands included

$$h(z_0) = \sum_j [a_j(z_0) + b_j(z_0)\varphi_0]\varphi_j \quad \text{with} \quad \varphi_j = \exp(-\frac{h\nu}{kT_j})$$

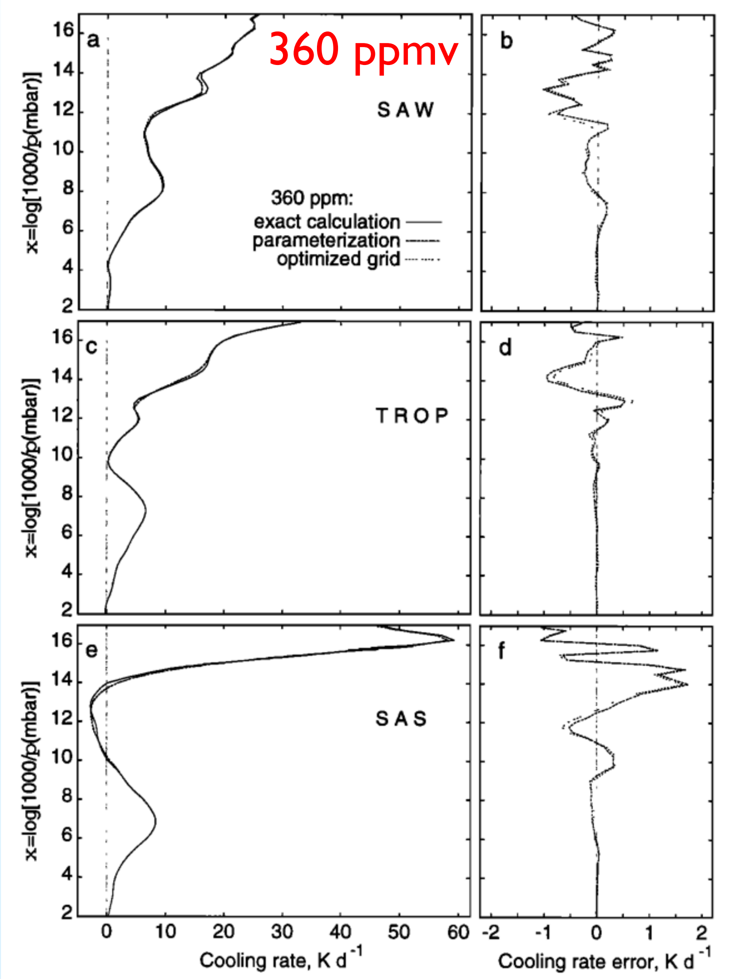
CO2 15 µm CR: parameterizations

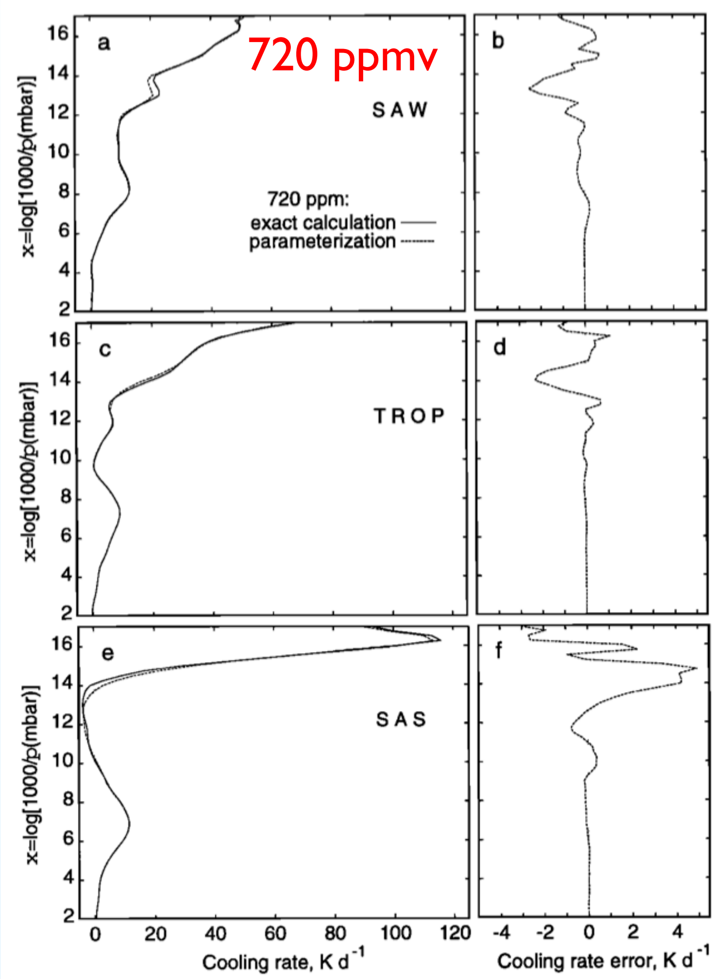
- Fomichev et al., 1998. Errors in the parameterization.

- Good overall accuracy
- Significant errors in the pol. summer mesopause
- Larger for 720 ppmv

Possible improvements:

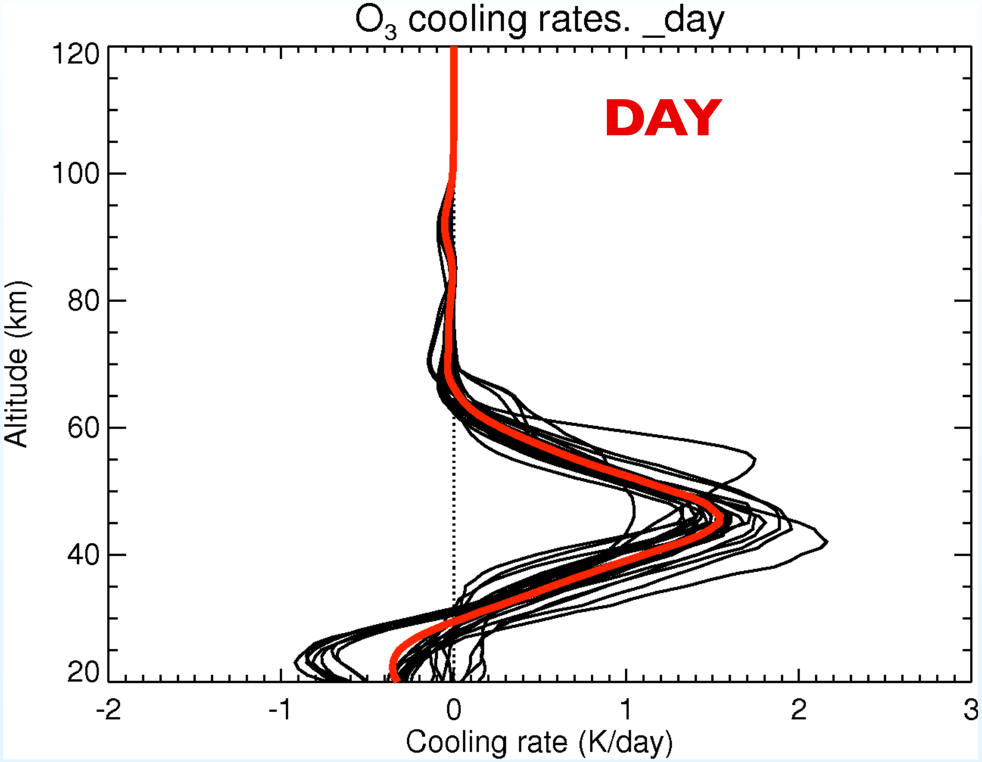
- Strat-warm T-profiles properly handled?
- Merging LTE/NLTE altitude is too high for strat-warm T-profiles?
- Need to be extended for 4xCO2

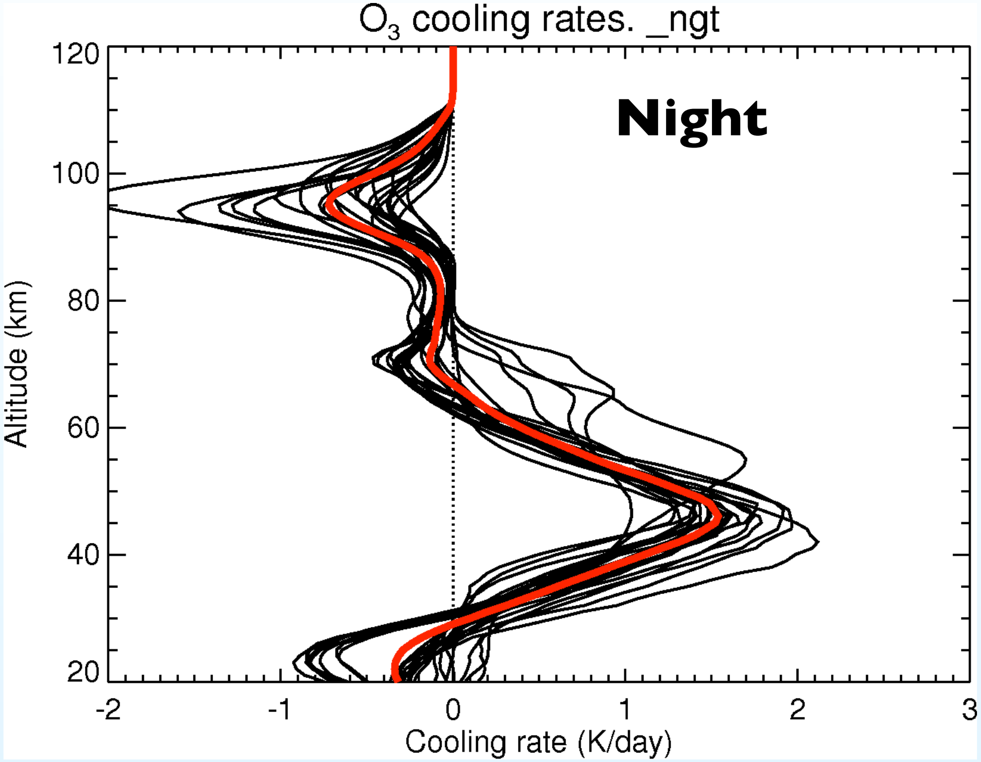




Other Cooling rates
(O_3, H_2O, NO, O)

O3 9.6 µm cooling rates



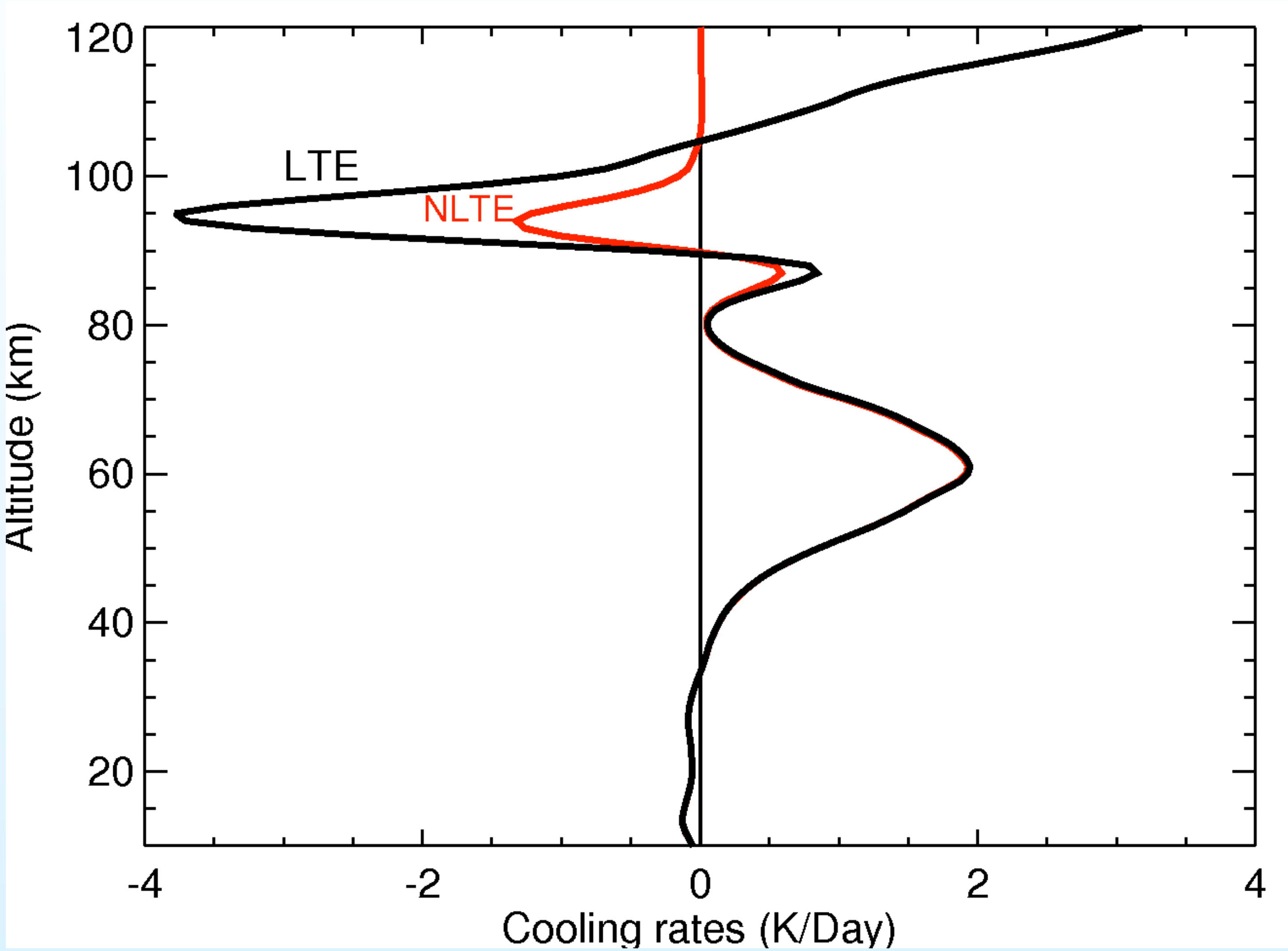


GRANADA NLTE model (Funke et al., JQSRT, 2012)

- Calculations for 48 ref. atmospheres
- O3 Heating important at night ~90-95 km

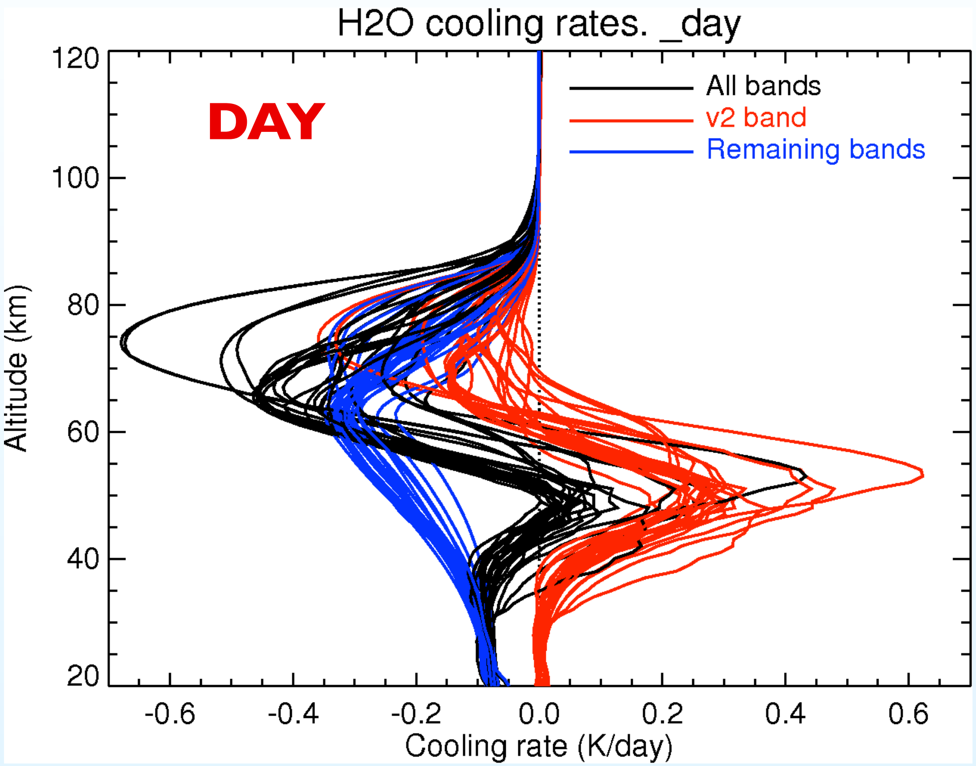
- Fomichev & Blanchet (1995) developed a parameterization for O3 9.6 µm (LTE)

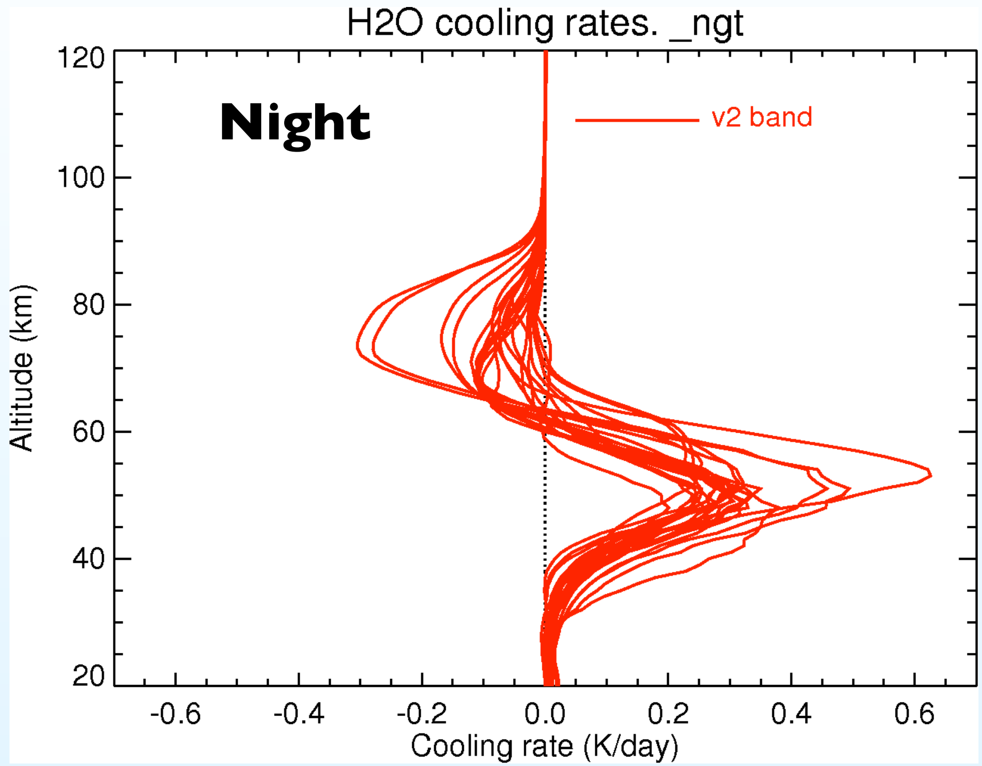
Non-ETL effects in O3 9.6µm cooling



López-Puertas & Taylor, 2001

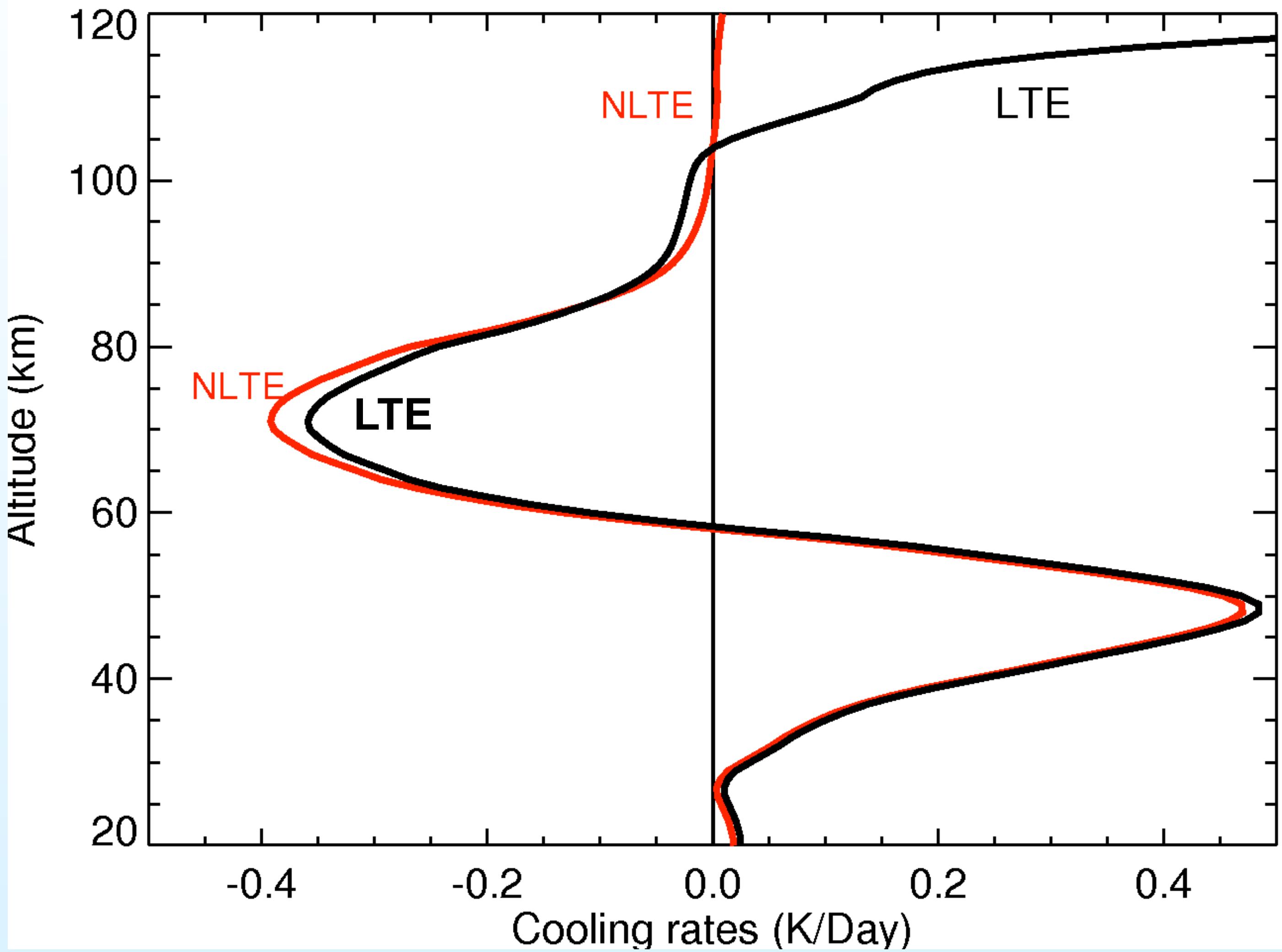
H2O 6.3 µm cooling rates





GRANADA NLTE model (Funke et al., JQSRT, 2012)

Non-ETL effects in H2O 6.3µm cooling



López-Puertas & Taylor, 2001

NO 5.3 μm cooling rates

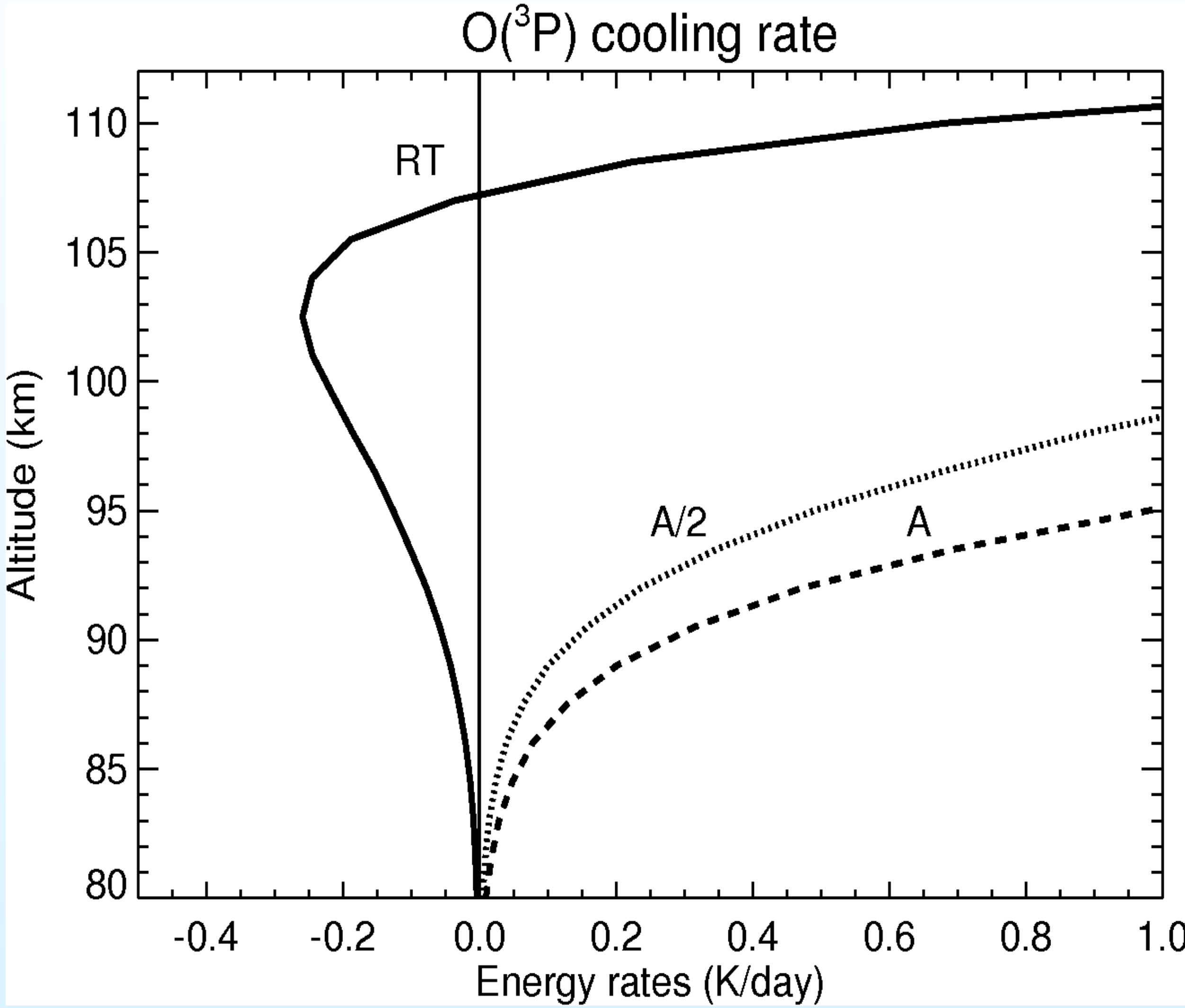
- Nitric oxide at 5.3 μm is the major cooling of the thermosphere.
- It is very variable, T, NO, O; Day/Night; Geomagnetic storms, Solar cycle
- Easy to compute

$$q = [\mathrm{NO}] \frac{k_{NO-O}\ [\mathrm{O}]}{A + k_{NO-O}\ [\mathrm{O}]} \exp(-\frac{h\nu_0}{kT})\ A\ h\nu_0$$

- $k_{NO\text{-}O} = 2.8 - 6.8\ 10^{-11}\ cm^3 s^{-1}$ (most recent accepted $4.2\ 10^{-11}\ cm^3\ s^{-1}$ *(Hwang et al., 2004)*)
- Very small contribution from the hot NO(2-1) band

O 63 µm cooling rate

- It produces a significant cooling in the upper thermosphere (~>200km)
- The increase with altitude is mainly due to increase in O vmr, not T
- Can be considered in LTE up to very high in the thermosphere but needs to be treated with rad. transfer



López-Puertas & Taylor, 2001

Summary (non-LTE retrieval) (1/3)

- MIPAS (& SABER) have substantially improved our knowledge of non-LTE
  - First detections of NLTE in CH4(v4), N2O(001), CO(2)
  - Improved NLTE in: H2O(020), NO2(v3=1, v3>1), O3(v_1,v_2,v_3), NO (spin & rot. temp., nascent vib. distributions),
  - New NLTE CO2-related collisional parameters, NO^+
- NLTE retrievals in the middle & upper atmosphere: A big step forward
  - Temperature (20-160 km) and CO_2 vmr (70 -140 km)
  - O_3, H_2O, CH_4, CO, NO, NO_2 (up to 100, 90, 75, 140, 170, 70 km)
- They have contributed to improve significantly our knowledge of the atmosphere:
  - Downward transport in polar regions, Thermosphere-Meso-Strat coupling, NOy budget, Solar storm composition changes, CO2 evolution
- Radiative transfer validation performed => Non-LTE models agree within 1K

Future prospects (non-LTE retrieval) (2/3)

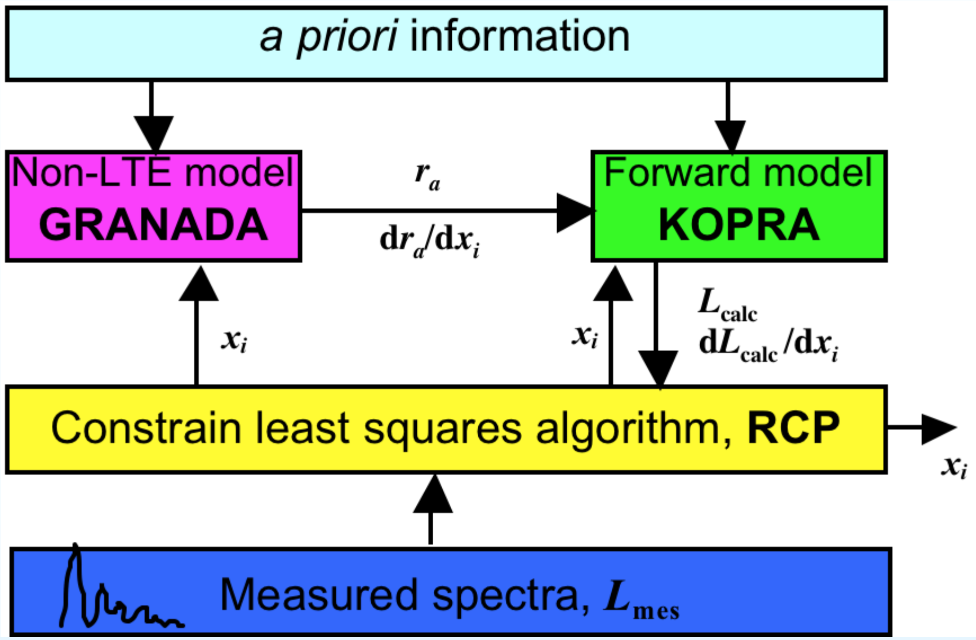
- To improve the accuracy of non-LTE retrievals:
  - To know more accurately the energy transfer (V-T) and V-V rates:
  - K_{CO2-O}: $CO_2(v_2) + O \Leftrightarrow CO_2 + O$ (**)
  - K_{vv}: $CO_2^i(v_2) + CO_2^j(v_2') \Leftrightarrow CO_2^i(v_2-1) + CO_2^j(v_2'+1)$
  - K_{vv}: $H_2O(v_2) + O_2 \Leftrightarrow H_2O(v_2-1) + O_2(1)$
  - K_{vt}: $O_2(1) + O \Leftrightarrow O_2 + O$
  - K_{V-T} & K_{V-V} rates at low (summer) temperatures (100-150 K)
  - To measure simultaneously atomic oxygen
- Understand CO2 4.3 µm daytime Nadir non-LTE emission (IASI) at winter (high SZAs) conditions

Summary & prospects (Cooling/Heating) (3/3)

- Non-LTE processes are required for the NIR and IR heating/cooling rates (energy budget) of the upper mesosphere and above.
- Improve the CO_2 NIR heating parameterization for $2xCO_2$ and extent it to larger (4x) CO_2.
- Parameterizations of CO_2 non-LTE cooling exist but need extensions to larger $4xCO_2$ vmrs and other temperature structures (polar summer, strat-warm)
- Large uncertainty in the K(CO_2-O) rate
- Lack of measurements of O
- Include O_3 NLTE cooling in the mesosphere

Thank you!

Non-LTE retrieval algorithm



Forward model: Karlsruhe Optimised and Precise Radiative transfer Algorithm (KOPRA)

- Line-by-line radiative transfer model
- Interface for generic NLTE-model GRANADA
- Supports vibrational and rotational non-LTE
- Computes spectra and Jacobians for LTE & NLTE

Retrieval Control Program (RCP)

- Global fit least squares algorithm + userdefined regularization

Non-LTE model: Generic RAdiative traNsfer AnD non-LTE population Algoritm (GRANADA)

- Calculation of rotational and vibrational populations and their derivitavies wrt the NLTE retrieval parameters
- Generalized scheme: used for populations of CO_2, O_3, CO, NO, NO_2, H_2O, CH_4, HCN,…
- User-defined (states and transitions, altitude range, iteration strategies, process definition, etc.)
- Rotational (and spin-orbit) non-LTE
- Line-by-line and line independent radiative transfer (KOPRA)
- Inversion of multilevel steady state equation with the Lambda iteration or Curtis matrix formalisms

Non-LTE effect: Radiances (emission)

- Radiance (emission) measurements: Effects on temperature and species abundances

Radiancia en ETL:

$$R(h) = \int_{LOS} B(x,\nu_0) \frac{d\tau^{LTE}(x)}{dx} dx$$

$$\tau^{LTE}(x) = \int_{\nu} F(\nu) \exp[-\textstyle\int_{x'} k^{LTE}(x',\nu) n_0(x') dx'] d\nu$$

Radiancia en no-ETL:

$$R(h) = \int_{LOS} J(x,\nu_0) \frac{d\tau(x)}{dx} dx; \qquad J(\nu_0) \simeq \frac{2h\nu^3}{c^2} \frac{g_0 n_1}{g_1 n_0} = \frac{2h\nu^3}{c^2} \exp\left(-\frac{h\nu}{kT_v}\right)$$

$$\frac{k(x,\nu)}{k^{LTE}(x,\nu)} = \frac{n_0}{n_0^{LTE}} \frac{[1-\exp(-h\nu/kT_v)]}{[1-\exp(-h\nu/kT)]}$$

(López-Puertas & Taylor, WSP, 2001)

The GRANADA model

- GRANADA: Generic RAdiative traNsfer AnD non-LTE population Algorithm
- Calculation of rotational and vibrational populations and their derivatives w.r.t. the NLTE retrieval parameters
- Generalized scheme: same algorithm used for populations of CO_2, O_3, CO, NO, NO_2, H_2O, CH_4, HCN,…
- User-defined (states and transitions, altitude range, iteration strategies, process definition, etc.)
- Rotational (and spin-orbit) non-LTE
- Line-by-line and line independent radiative transfer (KOPRA)
- Inversion of multilevel steady state equation with the Lambda-iteration or Curtis matrix formalisms
- Cooling/Heating rates

The GRANADA non-LTE model: Earth

- Produced a climatology (0-200 km) of non-LTE populations for:
  - 13 species (H_2O, CO_2, O_3, N_2O, CO, CH_4, O_2, NO, NO_2, HNO_3, OH, N_2 & HCN)
  - 425 vibrational or electronic energy levels
  - 48 ref. atmos. (Jan, Apr, Jul, Oct) x (75°S, 45°S, 10°S, 10°N, 45°N, 75°N) x (Day, Night)
  - http://w3.iaa.es/~puertas/granada.html.
- Major Heating/Cooling rates
- Includes the most updated collisional processes and rate coefficients for the Earth's atmospheric molecules
- Funke et al., JQSRT, 2012

Earth

- Vib. Temperatures calculated for:
  - **H_2O: 21 levels (1.1-6.3 μm)**
  - **CO_2: 129 levels (1.3-15 μm)**
  - **O_3: 104 levels (1-6-14.8 μm)**
  - **N_2O: 41 levels (2-15 μm)**
  - **CO: 4 levels (2.3-4.7 μm)**
  - **CH_4: 12 levels (1.6-7.6 μm)**
  - **O_2: 19 levels (0.63-6.4 μm)**
  - **NO: 10 levels (1.36-5.3 μm)**
  - **NO_2: 7 levels (1-6.3 μm)**
  - **HNO_3: 8 levels (5.8-20 μm)**
  - **OH: 18 levels (v=1,9, 1/2 and 3/2) (0.35-4 μm)**
  - **HCN: 25 energy levels (1.4-14 μm)**
- Nadir, Limb simulations and Inversion of species in the mid-IR

(López-Puertas et al., 2005a,b; Funke et al., 2005a,b; 2007, 2009; Gil-López et al., 2005, etc.)

KOPRA

Karlsruhe Optimised and Precise Radiative transfer Algorithm.
Line-by-line atmospheric radiative transfer code (Stiller et al., 2002)
(http://www.imk-asf.kit.edu/english/312.php)

- Spatial discretization / observational geometries
  - Limb/Nadir/Solar occultation
  - Treatment of horizontal inhomogeneities (3D rad. transfer)
  - Refraction
- Radiative transfer
  - Rotational and vibrational Non-LTE (population model GRANADA implicitly included) (Funke et al., 2007)
  - Single scattering, using provided scattering and extinction coefficients or using the internal Mie model (spherical particles) (Hoepfner et al., 2005)
  - Surface reflection
  - CO_2 line mixing (Funke et al., 1998)
  - Empirical solar spectral model (SO) (Hase et al., 1996)
  - Analytical calculations of Jacobians
- Instrumental modeling
  - Vertical FOV
  - ILS model input needed