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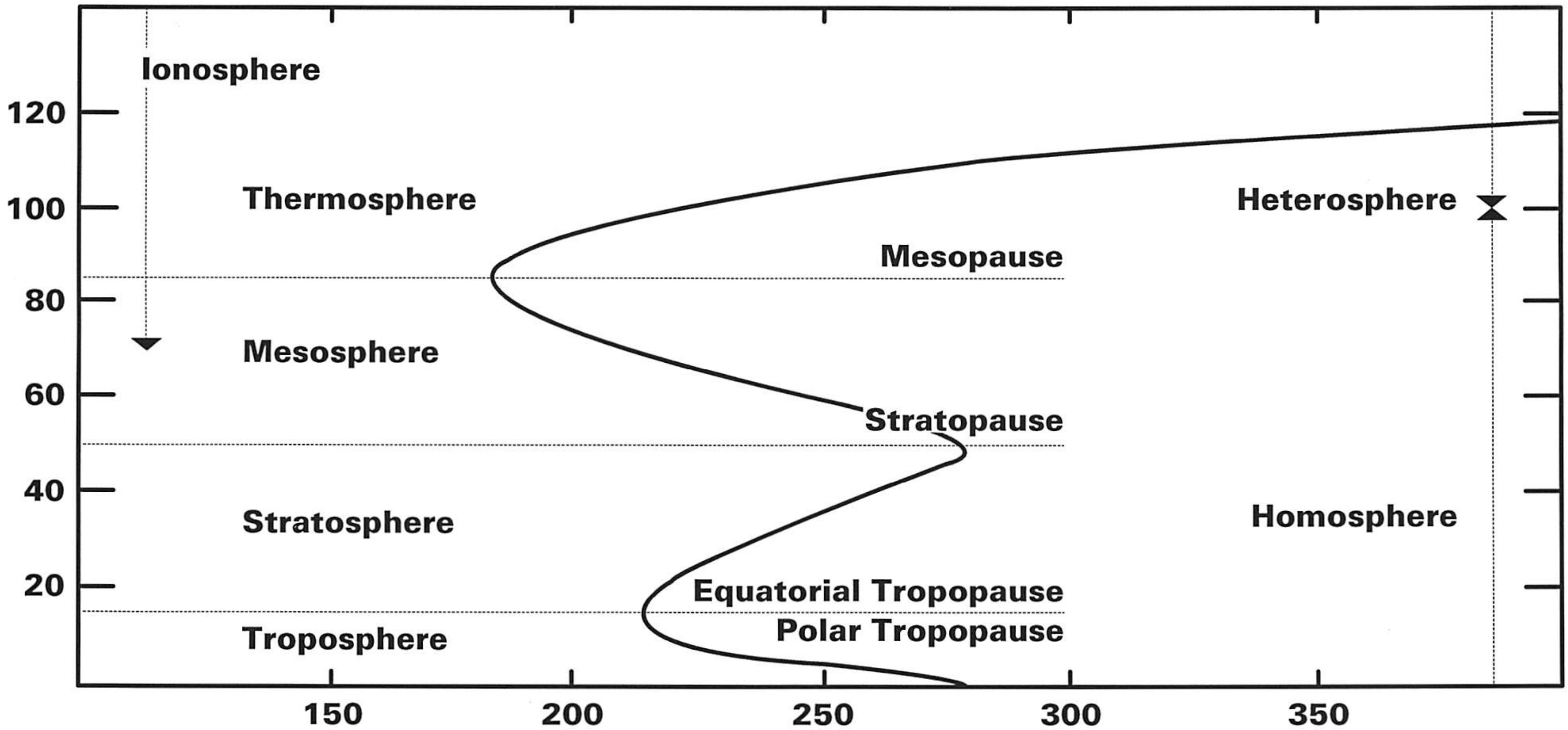
Coupled Energetics, Chemistry, and Dynamics in the Terrestrial Mesosphere and Lower Thermosphere



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Outline

- Review of interesting aspects of the mesosphere
- Model development and the thermodynamic equation
- Evidence for chemical heat sources
- Comparison of chemical, solar, and dynamical heating
- Status of knowledge of heat budget

Why study the mesosphere?

Some current areas of interest:

- The mesosphere couples space environment to lower atmosphere
  - Example 1 -- Thermospheric NO/Stratospheric NO_2
- The mesosphere is very sensitive to change
  - Example 2 -- Ozone changes over a solar cycle (Natural)
  - Example 3 -- Temperature response to increasing CO_2 (Anthropogenic)
- Mesospheric ozone photochemistry still not well understood
  - Example 4 -- Discrepancy between measured and modeled ozone
  - Are there unknown sources of ozone?

Why Study the Mesosphere?

- **Mesosphere is a "buffer" between the stratosphere and the space environment -- mesosphere couples stratosphere to space**

- **In the thermosphere N_2 photolysis yields $N(^4S)$ or $N(^2D)$**

$$N(^2D) + O_2 \rightarrow NO + O$$
$$N(^4S) + O_2 \rightarrow NO + O$$

- **NO is transported out of the thermosphere, especially during the winter, and into the mesophere and stratosphere**

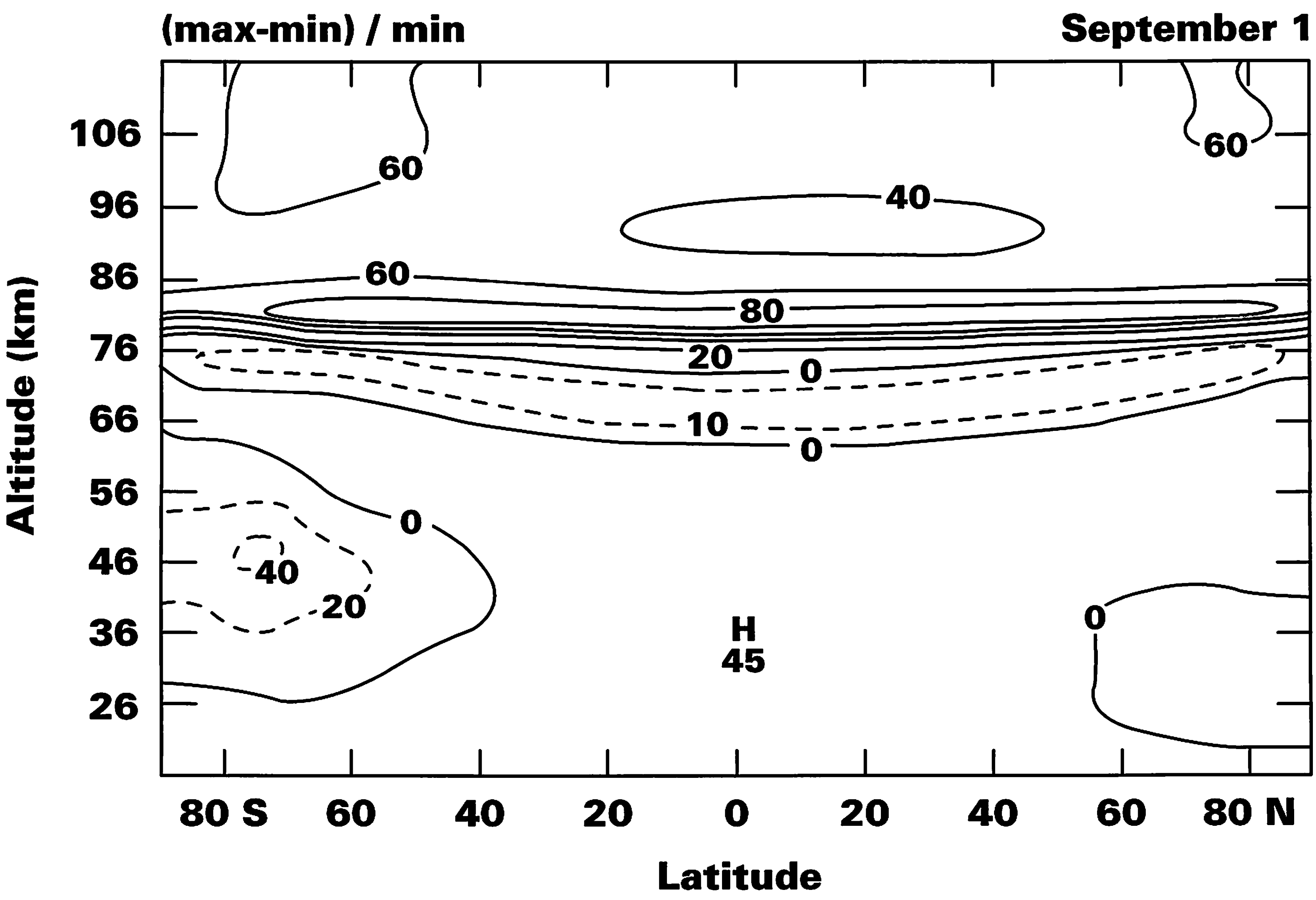
$$NO + O_3 \rightarrow NO_2 + O_2$$

- **NO_2 is greatly increased in the mesosphere and stratosphere as a result of this process and ozone is reduced.**

Why Study the Mesosphere?

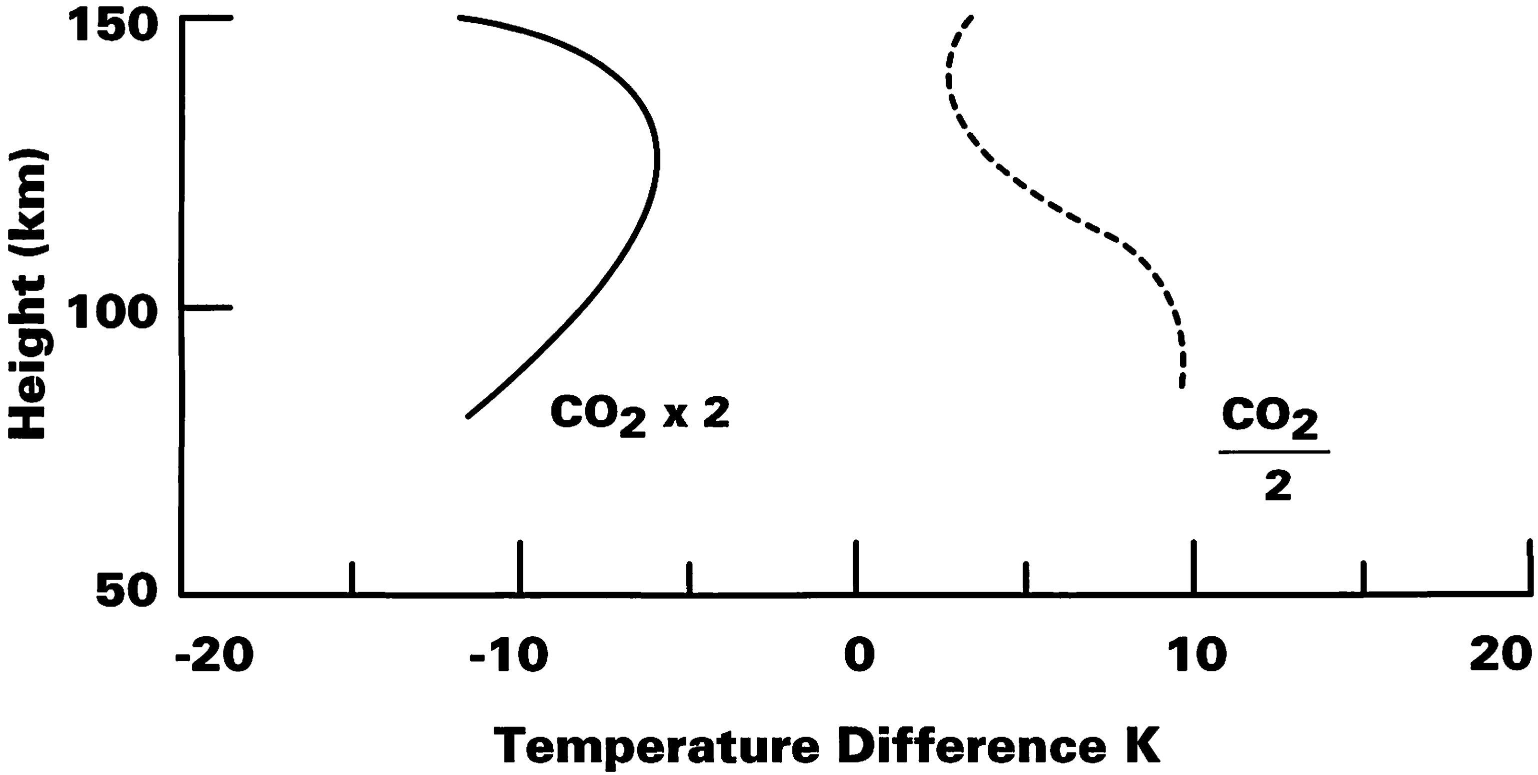
- The mesosphere is very sensitive to natural and possible anthropogenic changes, and on relatively short timescales
- Solar UV variability greatly alters chemistry
- Increased CO_2 concentrations may be responsible for "mesospheric cooling"

Percent difference in ozone over 1 solar cycle



(Garcia et al,.1984)

Calculated change in mesosphere/lower thermosphere temperatures



(Roble and Dickinson, 1987)

Why Study the Mesosphere?

Ozone Photochemistry

- **Mesosphere is a simpler environment than the stratosphere:**

  Mesosphere: HOx - O_3 interactions dominate

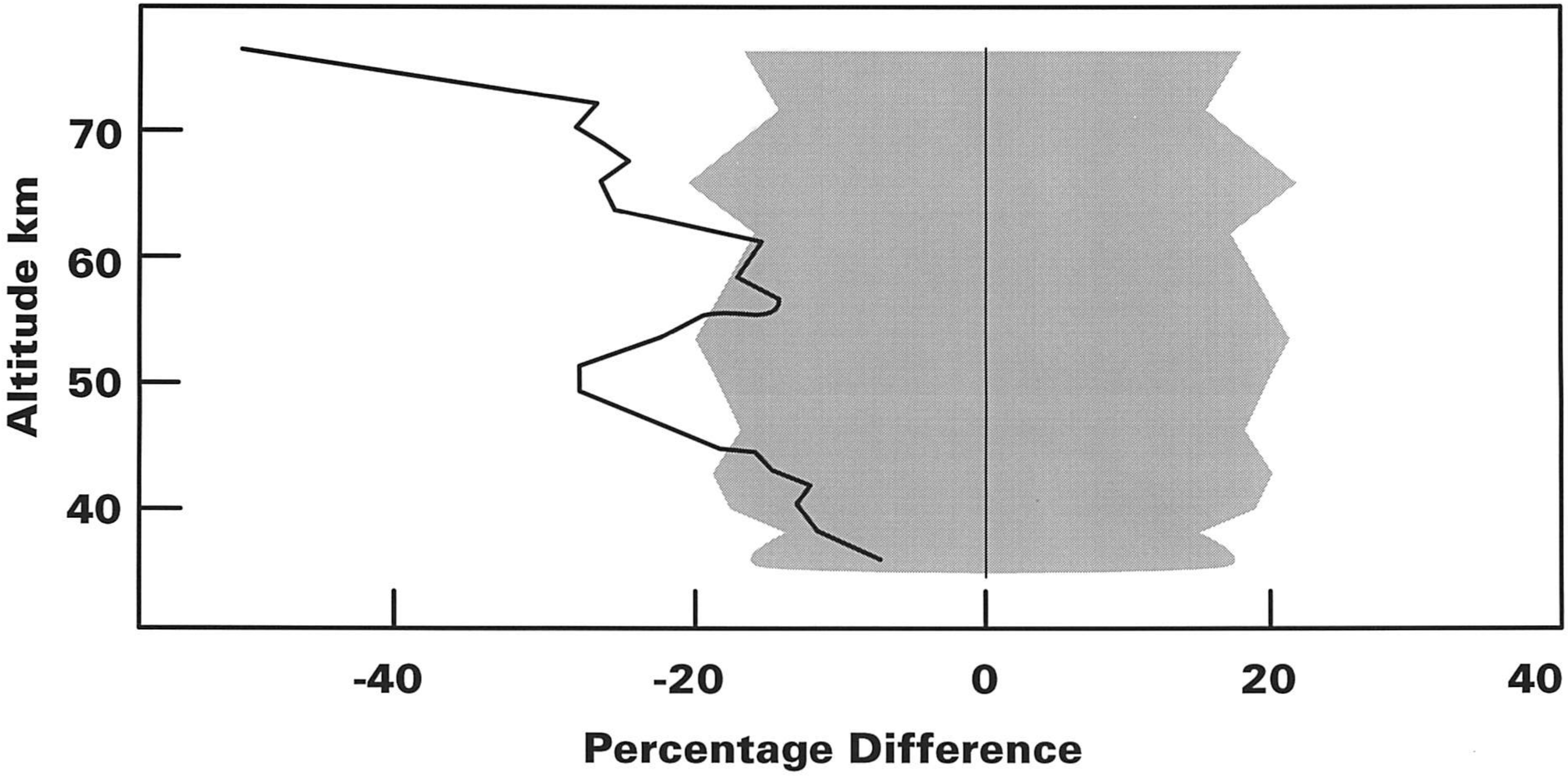
  Stratosphere: HOx, NOx, ClOx, BrOx, and Heterogeneous processes are all coupled

- **Discrepancy between measured and modeled ozone is largest in the mesosphere (e.g., Allen and DeLitsky, JGR, 1991)**

- **Implies that the fundamental chemistry is not understood**

- **New sources of ozone have been proposed**

Comparison of measured and modeled ozone in the mesosphere



(after Allen and Delitsky, 1991): $\frac{\text{(model-measured)}}{\text{model}}$

Why Study the Mesosphere?

- The discrepancy between measured and modeled ozone is such that more ozone is observed than modeled.

- Joens (JGR, 1986) proposed that significant portions of the ozone were in metastable electronic states not included in model calculations:

  $O + O_2 + M \rightarrow O_3^* + M \qquad \Delta E \sim 1.1$ eV

  O_3^* could be a long lived metastable state in significant populations.

- Arnold et al. (J. Chem. Phys., 1994, submitted) show that all electronic states lie above the dissociation limit -- inaccessible by recombination.

- The Joens mechanism is not an explanation for the measurement/model discrepancy in mesospheric ozone.

Why Study the Mesosphere?

- Slanger (Science, 1988) proposed a multi-step process

  O_3 + hυ --> O_2(v)+O; Ø=0.1

  O_2(v) + hν (visible) --> O + O

  O_2(v) + M --> O_2 + M

  Potential net gain of two ozone molecules per ozone dissociation

- The key is whether O_2(v) would be dissociated before being quenched
- Recent results indicate that quenching of O_2 (v) occurs much more rapidly than would photolysis, implying this mechanism is perhaps not a likely source of ozone
- Other suggestions include modifying rate coefficients or chemical abundances.
- The measurement/model discrepancy in upper stratospheric and mesospheric ozone remains unresolved.

Modeling the Mesospheric Environment

Continuity equation

$$\frac{\partial n_j}{\partial t} + \nabla \bullet (n_j v_j) = P_j - L_j$$

$$L_j = k_{ij}\, n_i\, n_j + J_j\, n_j + \ldots$$

Thermodynamic equation

$$n_j\, k \frac{DT_j}{Dt} = Q - L - n_j\, kT_j \nabla \bullet v_j - \nabla \bullet q_j$$

$$Q = k_{ij}\, n_i\, n_j\, E_{ij} + J_j\, n_j\, (h\nu - E_{ij}) + \ldots$$

$$\rho_j \frac{Dv_j}{Dt} + \nabla P_j = \Sigma\, n_j\, F_j$$

Momentum equation

- **Through chemistry, energetics, momentum, and continuity are coupled**
- **Investigate role of chemistry in heat budget**

new

Modeling the mesospheric environment

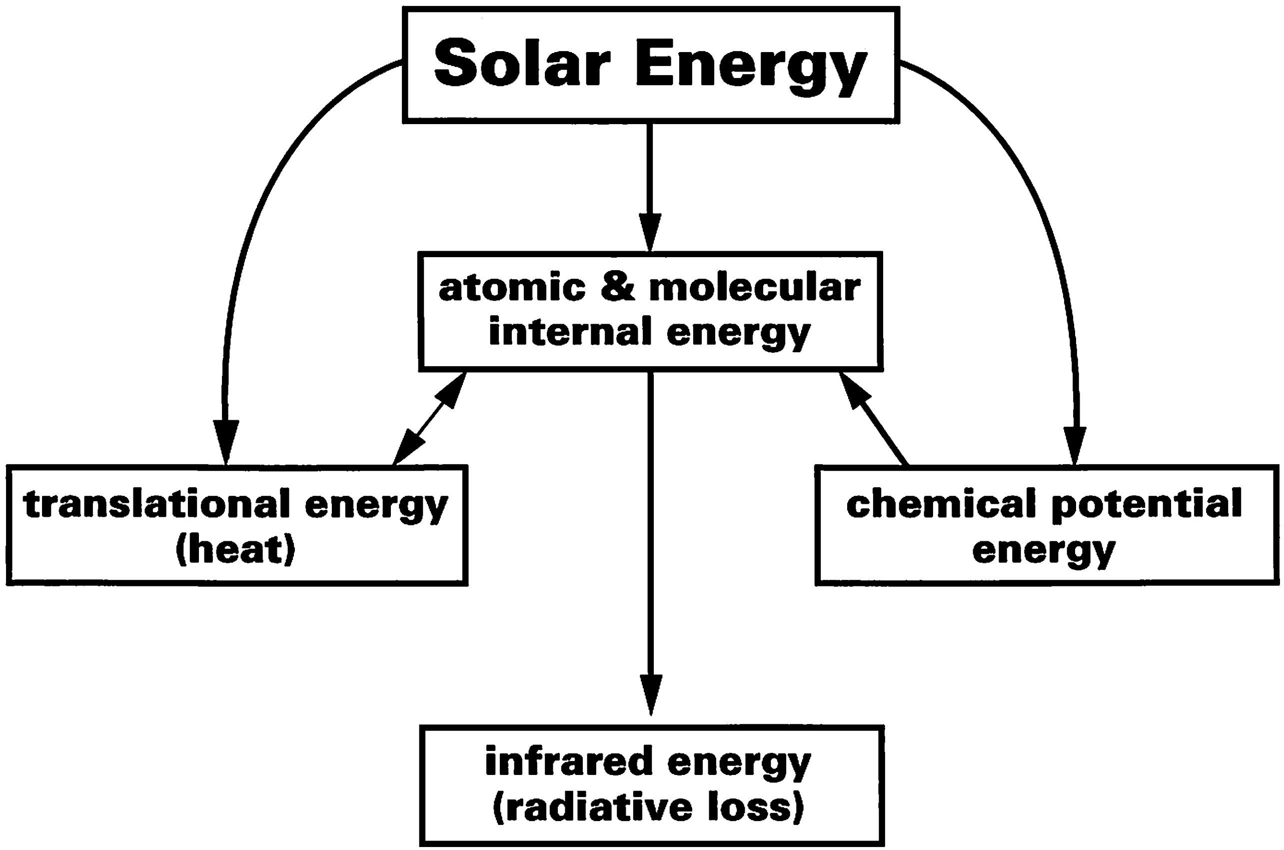
The Thermodynamic Equation

Key mechanisms of energy gain and less in the mesosphere:

- **Absorption of solar ultraviolet radiation**
- **Exothermic chemical reactions**
- **Radiative cooling**
- **Adiabatic expansion and compression**
- **Gravity wave breaking**
- **Airglow emission**
- **Chemiluminescent emission**

- **Joule heating**

Solar energy disposition in the middle atmosphere



The disposition of solar energy absorbed by O_3 and O_2

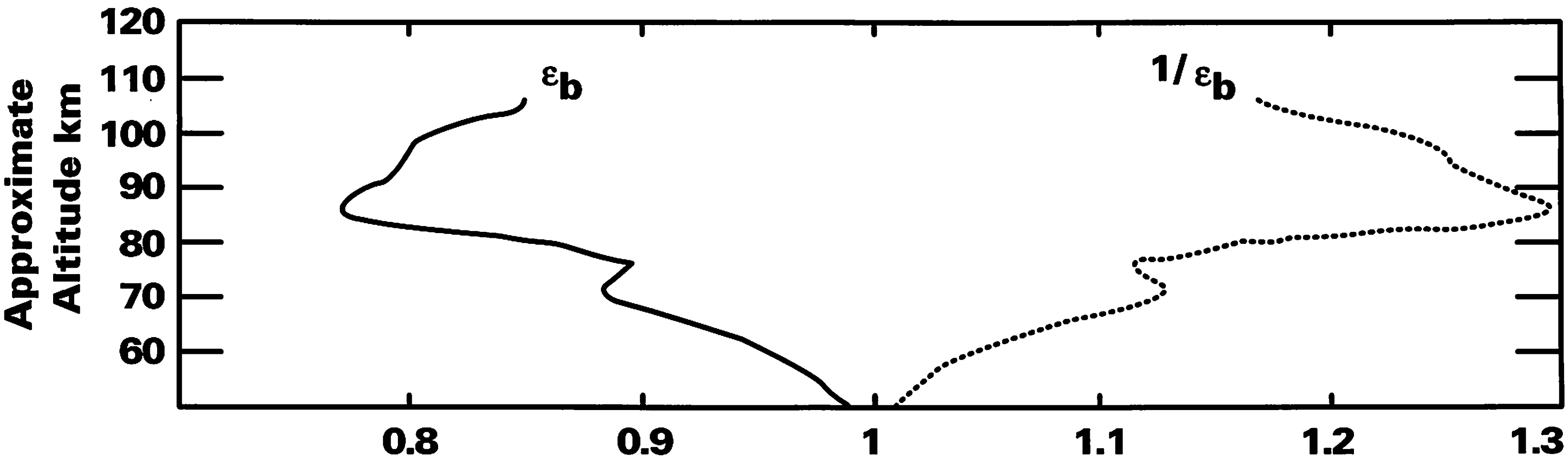
	Percent of incident photon energy		
	Directly to heat	Chemical	Internal
Ozone:			
Hartley	13%	24%	63%
Huggins Band	76%	24%	0%
Chappuis Band	76%	24%	0%
Molecular Oxygen:			
Schumann-Runge Band	24%	76%	0%
Schumann-Runge Continuum	1%	72%	27%
Lyman-Alpha Band	30%	51%	20%

- **Most of the absorbed solar energy is initially converted to chemical or internal form and not to heat**
- **The fate of the chemical and internal energy determines the heating rate and hence the heating efficiency. Not all absorbed energy is converted to heat.**

Disposition of internal energy

- **Significant internal energy pools created upon photolysis of O_2, O_3**
- **Much of this energy is radiated away, never being realized as heat**

$O_2(^1\Delta)$ at 1.27 um $O_2(^1\Sigma)$ at 762 nm $CO_2(001)$ at 4.3 um



Bulk Solar Heating Efficiency
(after Mlynczak and Solomon 1991, 1993)

- **Net effect is to reduce efficiency of solar heating**

Mechanism of heat generation by exothermic reactions

- **Specific example: $H + O_3 \rightarrow OH + O_2$ • ΔE = 76.9 kcal/mole**

  Released energy ΔE initially resides in internal energy of OH and/or O_2

  Internal energy realized as heat through collisional removal

  $$OH(\vartheta) + M(N_2, O_2, O) \rightarrow OH(\vartheta'') + M$$

  Internal energy may also be radiated before being converted to heat

  $$OH(\vartheta) \rightarrow OH(\vartheta'') + h\nu$$

  Absolute heating will depend on competition between collisional quenching and spontaneous emission.

Role of chemical heating in the mesosphere

- If two species [A], [B] react, the rate of heat deposition is:

$$Q = k_r [A] [B] \Delta E$$

- The associated rate of change of kinetic temperature is:

$$Q = \rho \ C_p \ \frac{\delta T}{\delta t} \Rightarrow \frac{\delta T}{\delta t} = \frac{2}{7} \ \frac{k_r [A] [B] \Delta E}{M}$$

- For a termolecular reaction,

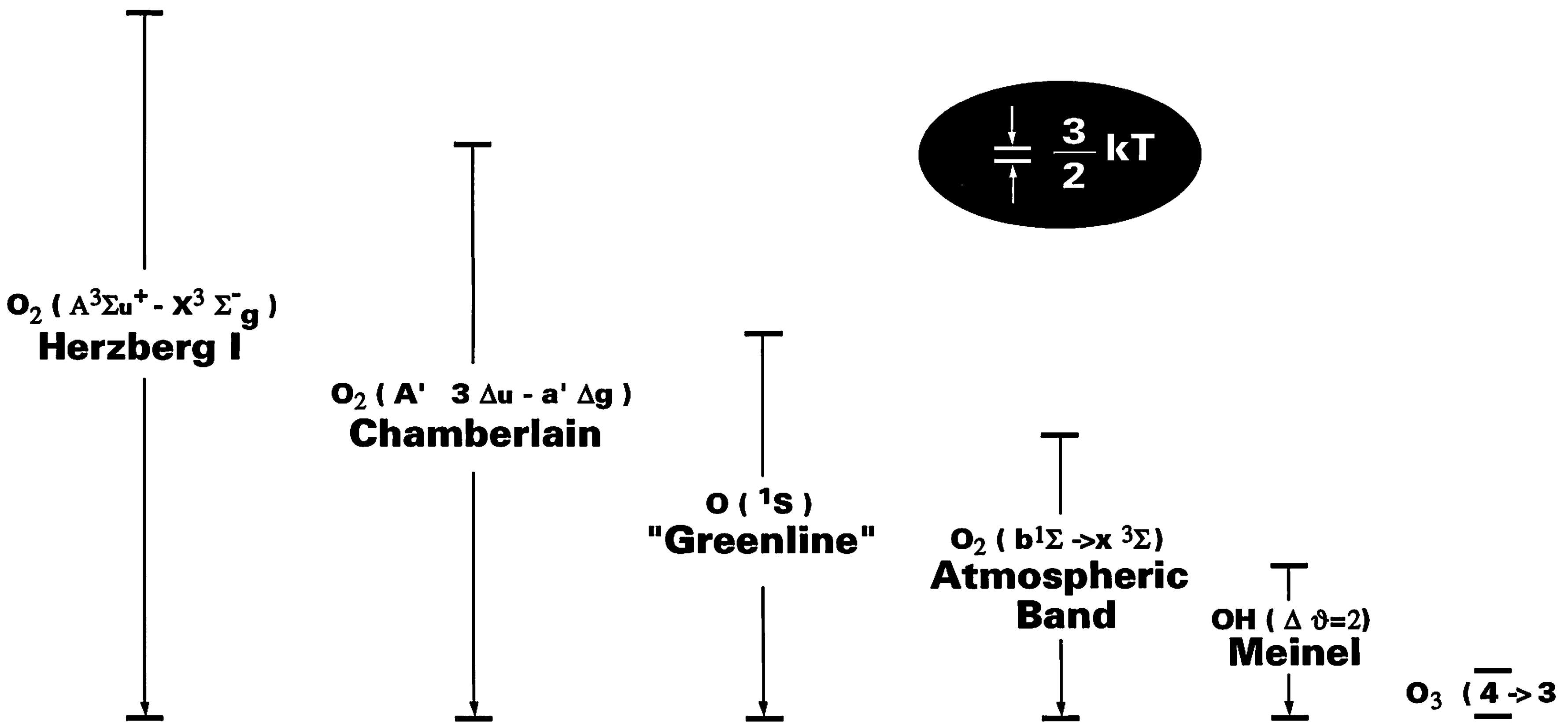
$$\frac{\delta T}{\delta t} = \frac{2}{7} \ k_r [A] [B] \Delta E$$

- Three factors influence heating rate:

  Reactant abundance
  Exothermicity and reaction rate
  Chemiluminescence rate

- What evidence is there of chemical reactions/heating?

Evidence for chemical heating in the mesosphere. Observed UV, visible, and infrared nightglows:



Evidence for chemical heating

- The high energies (some>100 kT) imply non-thermal excitation sources;

Within allowed chemistry,

O_2 (UV) emissions imply:	$O + O + M \rightarrow O_2^* + M$
OH (υ) emissions imply:	$H + O_3 \rightarrow OH(\upsilon) + O_2$
O_3 (high υ) emissions imply:	$O + O_2 + M \rightarrow O_3(\upsilon) + M$

By the law of mass action, the following must also be occurring:

$$O + OH \rightarrow H + O_2$$
$$O + O_3 \rightarrow O_2 + O_2$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$O + HO_2 \rightarrow OH + O_2$$

- At least 7 exothermic reactions are taking place.

Evidence for chemical heating

- **Night airglow provides evidence that reactions are occurring.**

  Are there sufficient reactants to influence heating?

  Is the airglow/chemiluminescence a significant sink?

- **Consider the following:**

  Calculations of chemical heating based on photochemical model abundances.

  Calculations of chemical heating from observed constituent abundances.

  Calculations of airglow losses from models and observations.

  Role of "odd-hydrogen" reactions 80-100 km.

  Evidence for chemical heating in observed thermal structure.

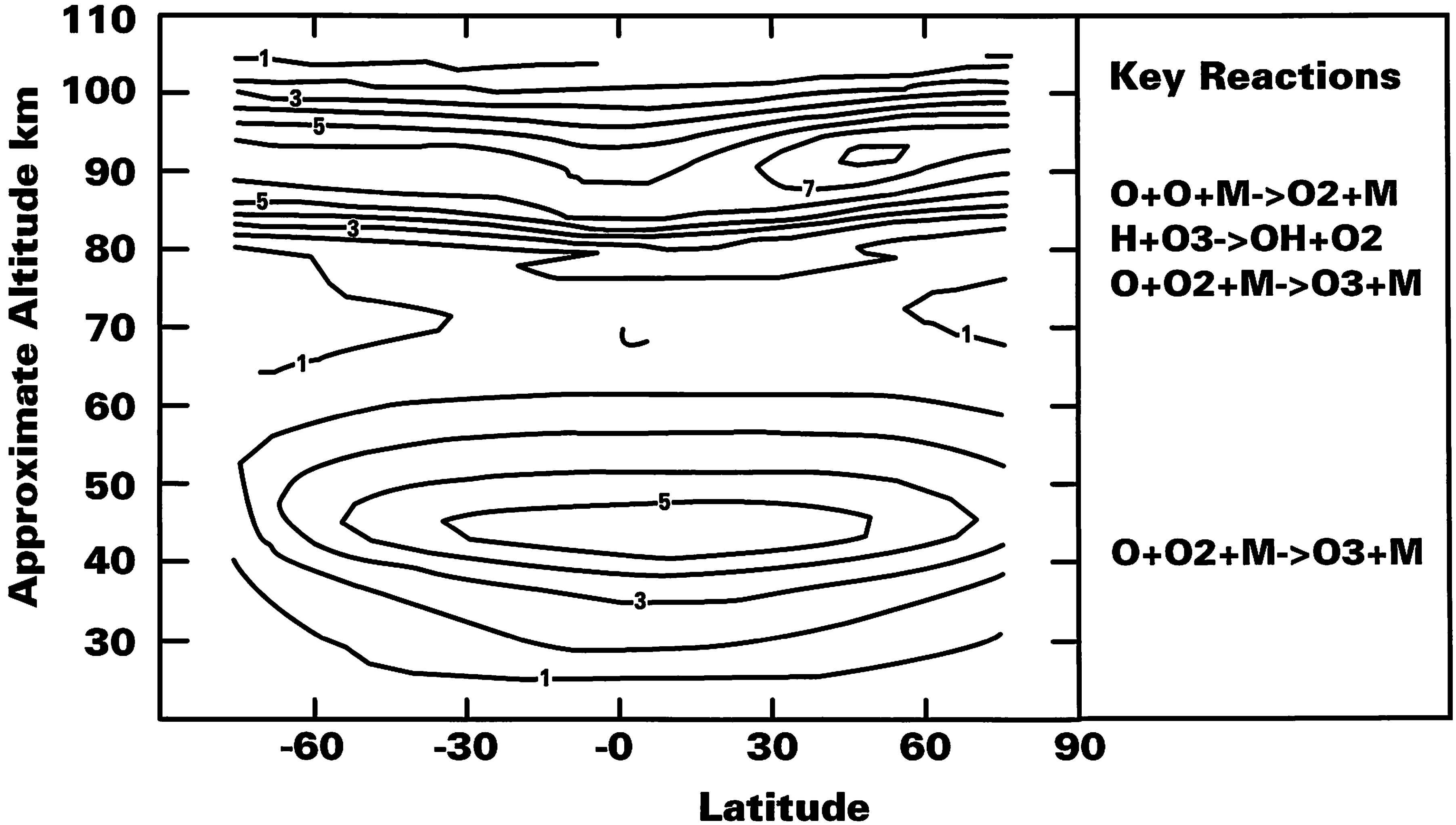
The reactions of exothermic heating

- **A total of seven reactions deposit significant amounts of heat in the atmosphere from the tropopause to the turbopause (15-110 km)**

"Odd-Oxygen" Reactions:	Altitude Range
$O + O + M \rightarrow O_2 + M$	80-110 km
$O + O_2 + M \rightarrow O_3 + M$	15-110 km
$O + O_3 \rightarrow O_2 + O_2$	90-110 km
"Odd-Hydrogen" Reactions:	
$H + O_3 \rightarrow OH + O_2$	75-100 km
$O + OH \rightarrow H + O_2$	70-100 km
$O + HO_2 \rightarrow OH + O_2$	60-95 km
$H + O_2 + M \rightarrow HO_2 + M$	80-100 km

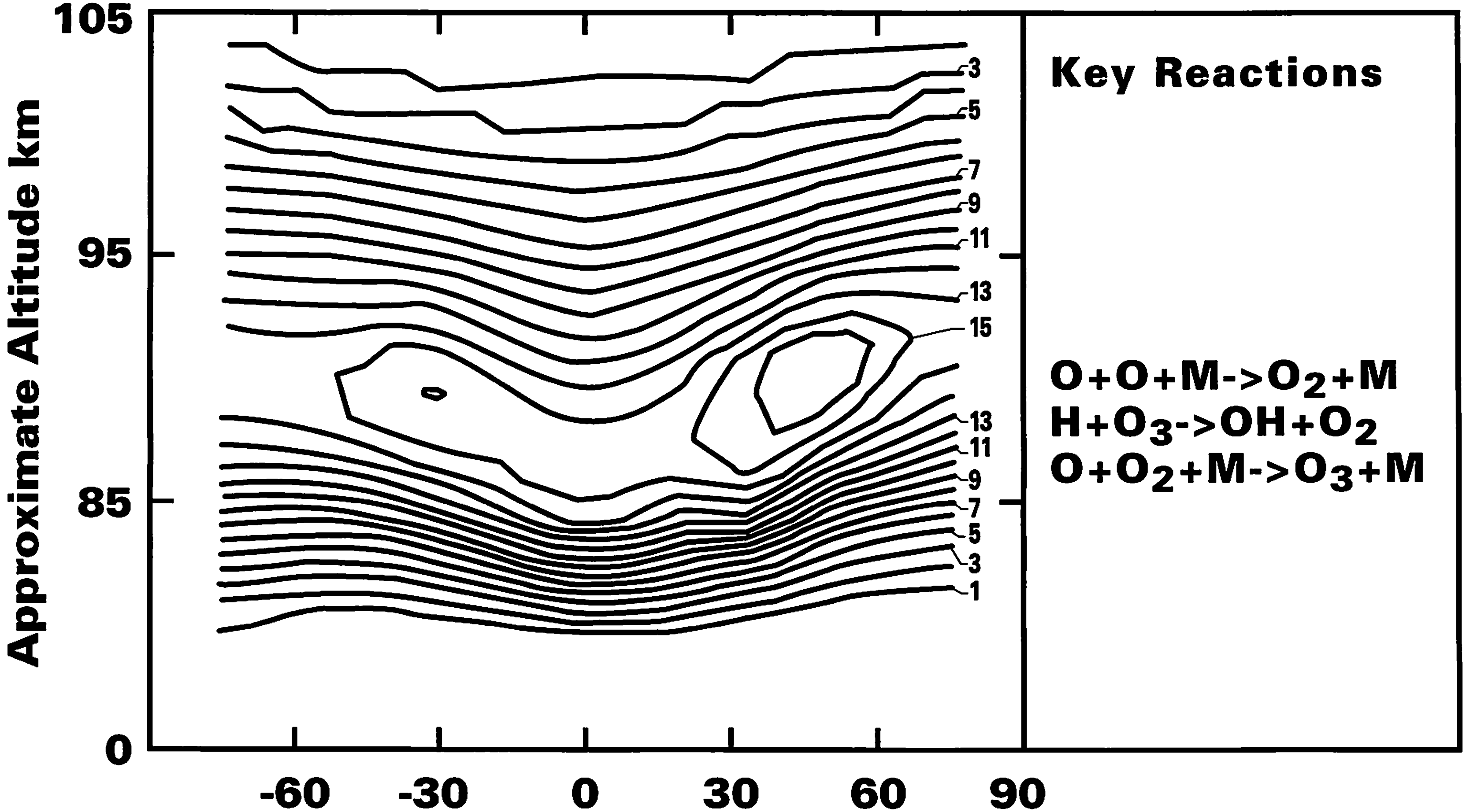
- **Use abundances from the Garcia and Solomon 2-D model to calculate heat release from these reactions**

Instantaneous chemical reaction heating rate, Day



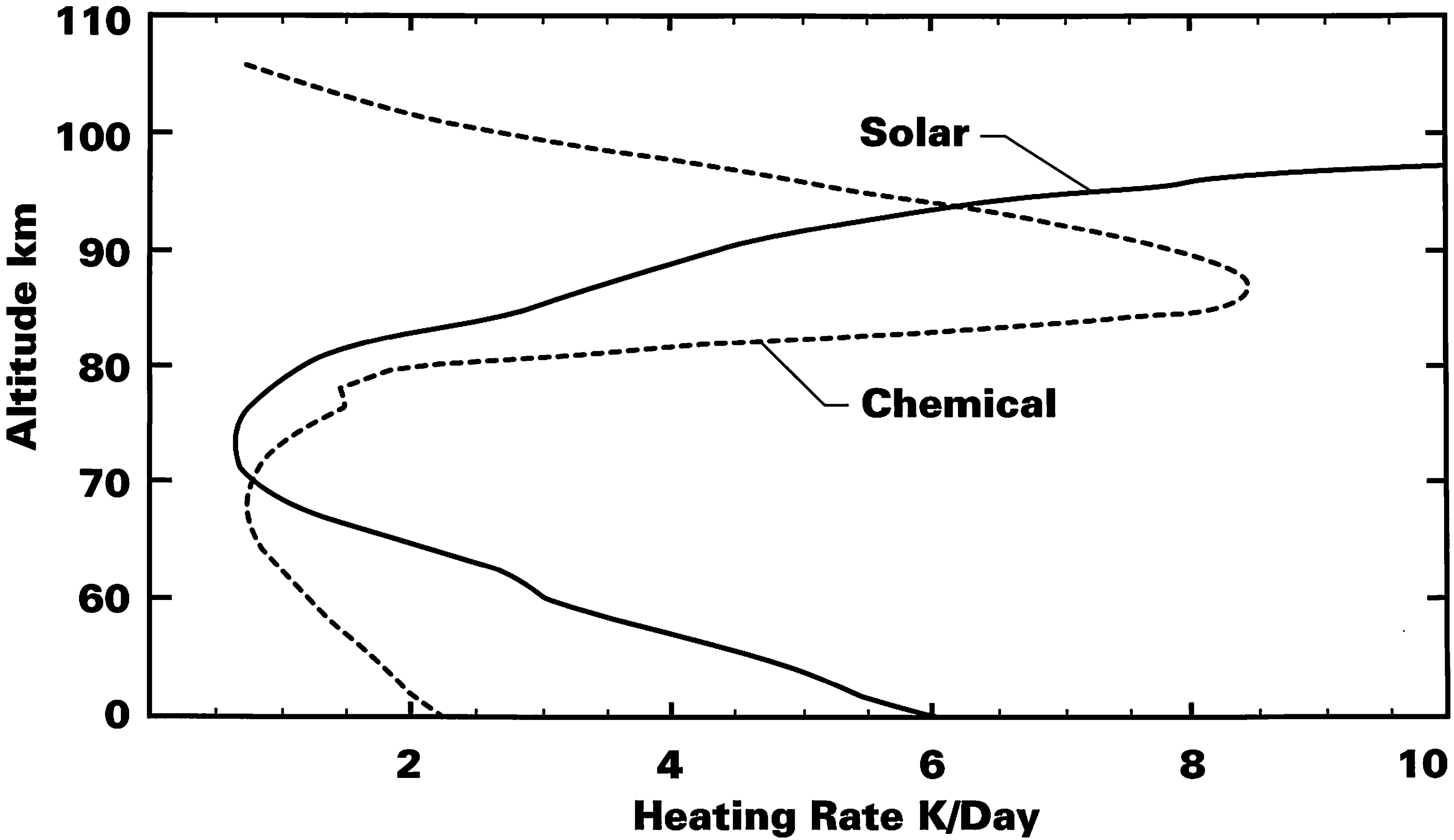
(after Mlynczak and Solomon, 1993)

Instantaneous chemical reaction heating rate, Night



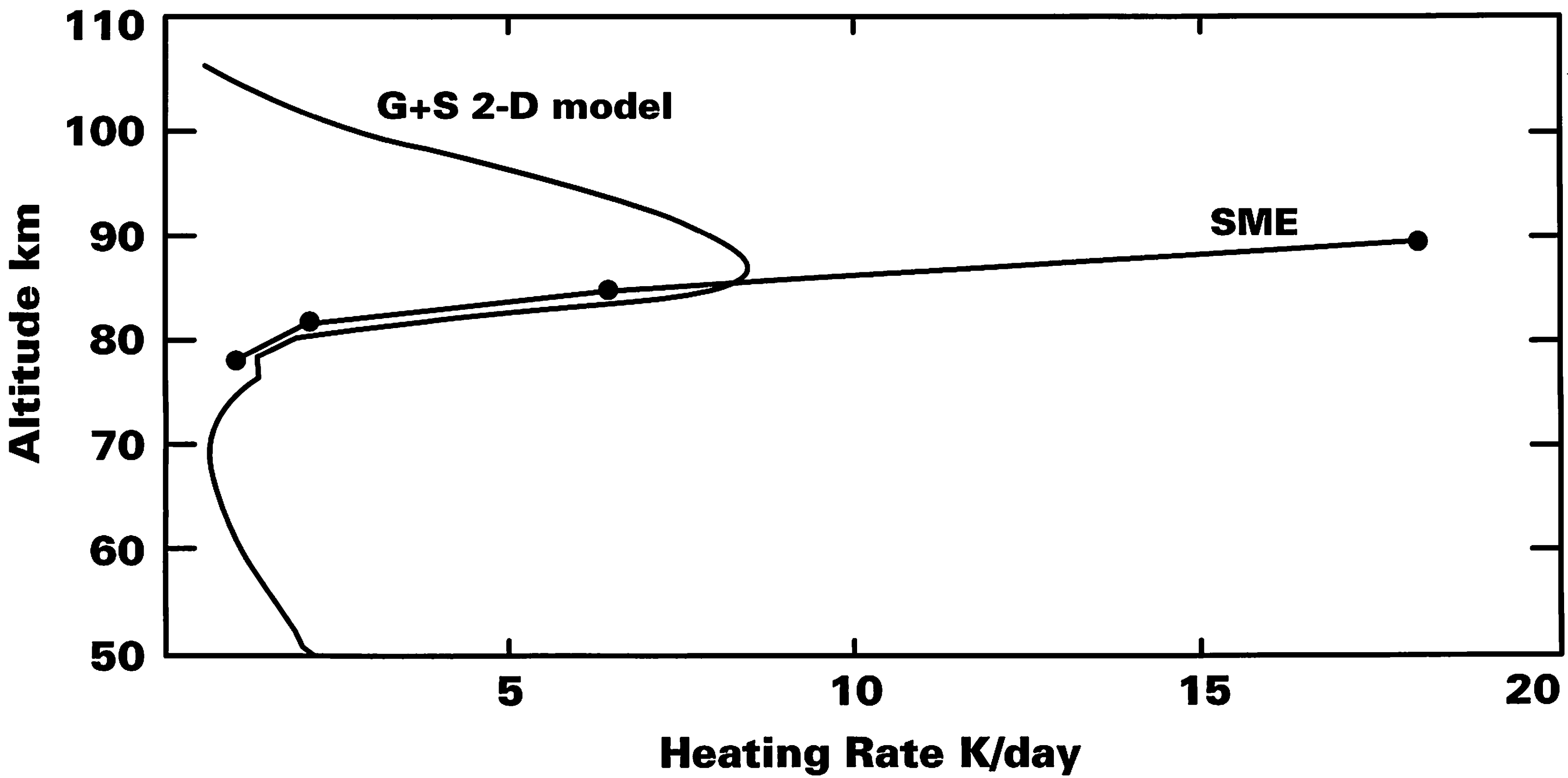
(after Mlynczak and Solomon, 1993)

Daily average heating



(after Mlynczak and Solomon, 1993)

Chemical heating: Model and observations



(after Mlynczak and Solomon,1991;1993, and Riese al., 1992)

Heating by exothermic reactions

- Exothermic chemical reactions and direct deposition of solar UV, are prime sources of heat in the mososphere

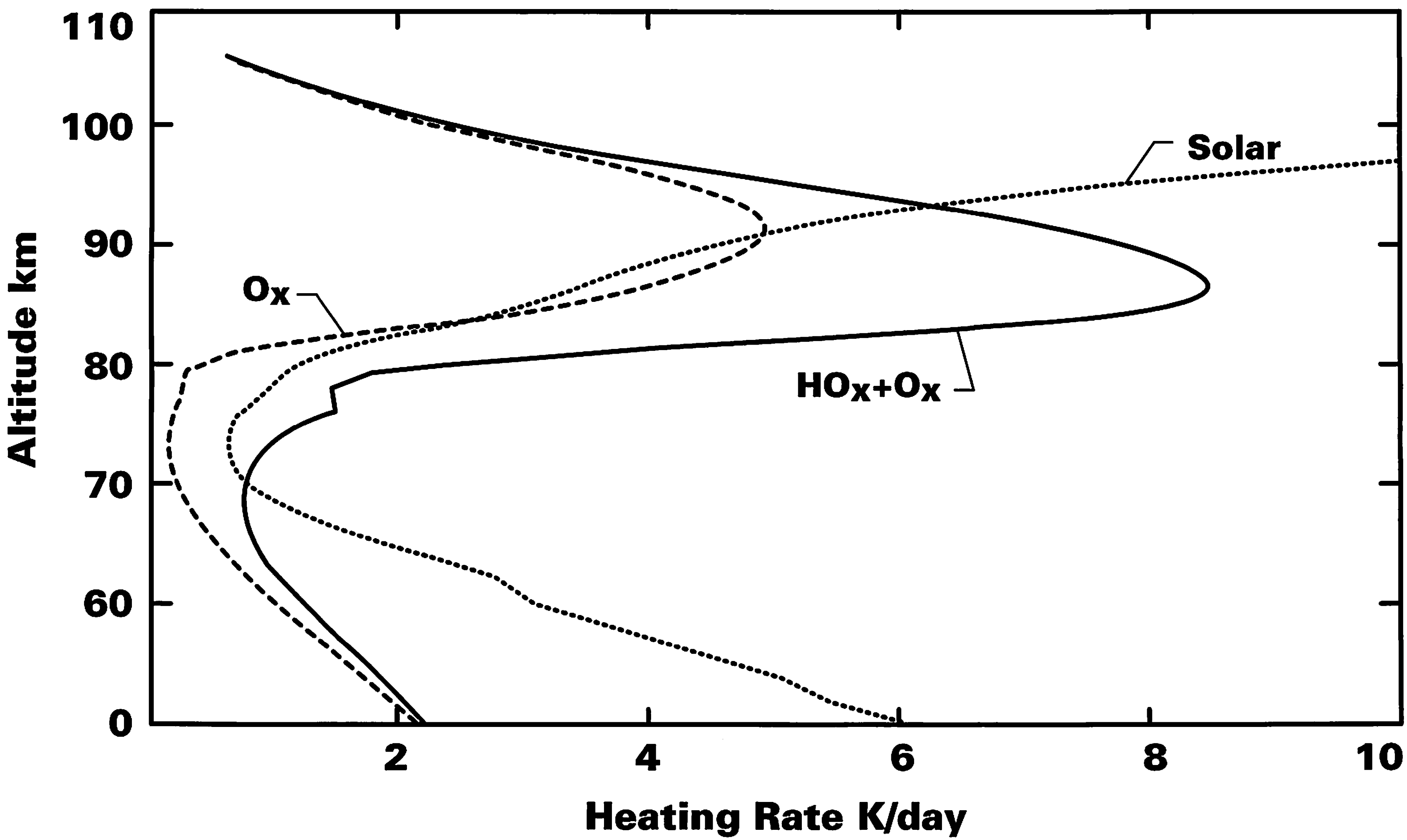
- Between 70 and 95 km, heating by exothermic reactions competes with and exceeds the heating by solar UV.

- Primary chemical heat source is heating by the odd hydrogen reactions:

$$H + O_3 \rightarrow OH + O_2$$
$$O + OH \rightarrow H + O_2$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$O + HO_2 \rightarrow OH + O_2$$

- These key reactions had been greatly over looked in heat budget calculations until recently.

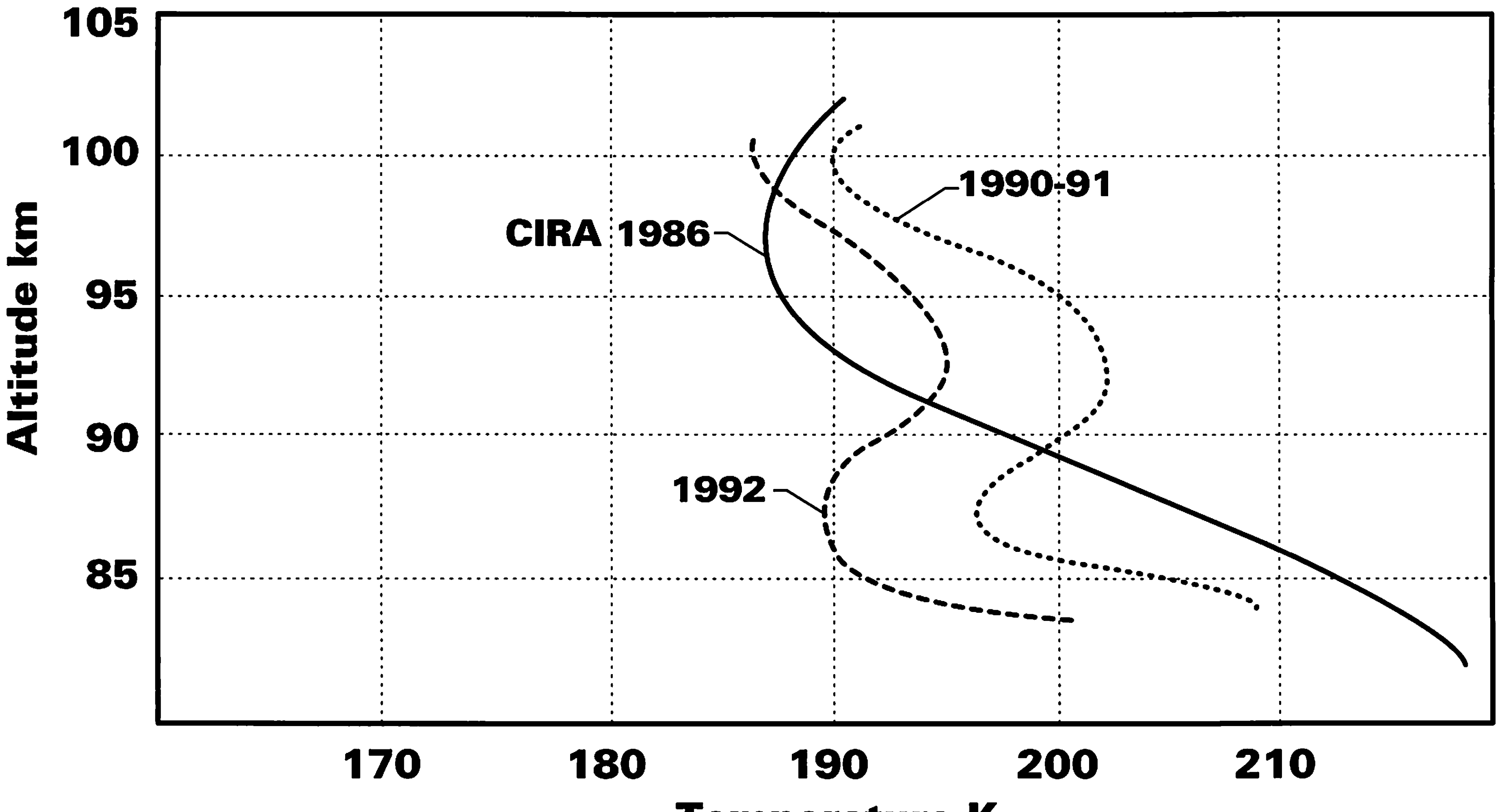
HO_x, O_x chemical heating and solar heating



(after Mlynczak and Solomon, 1991,1993)

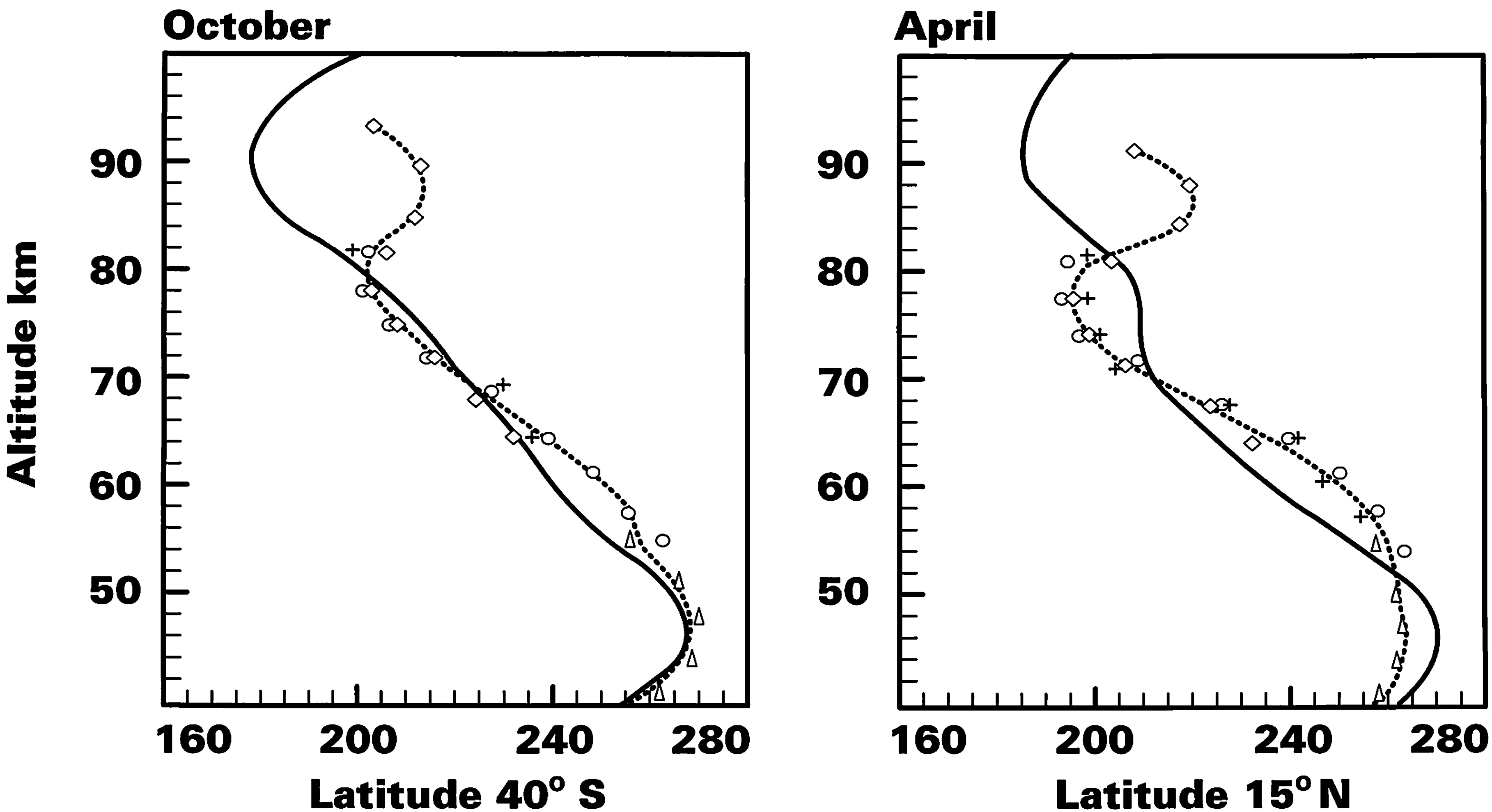
Evidence for chemical heating in observed thermal structure?

Spring



(from She et al., GRL, 1993)

Evidence for chemical heating in observed thermal structure?



SME data from Clancy et al., 1994

Chemical reactions and associated chemiluminescence

Energetically accessible emissions and states in product species

- O_2 Herzberg (I, II, III), Chamberlain, Atmospheric, IR-Atmospheric, and Noxon bands
- $O(^1S)$ green line
- O_3 vibration-rotation bands in ground electronic state
- OH Meinel bands and pure rotational emission
- HO_2 (electronically or vibrationally excited)
- CO_2(4.3 μm), O_2 IR atmospheric; both from OH(υ) transfer

- From a combination of atmospheric measurements (e.g., ETON, CIRRIS), laboratory data, and kinetic modeling heating due to the following reactions may be significantly reduced by chemiluminescent emission:

$H + O_3 \rightarrow OH + O_2$	(Meinel bands)
$O + O_2 + M \rightarrow O_3 + M$	(Vibration-rotation bands)
$H + O_2 + M \rightarrow HO_2 + M$	(Vib-rot, electronic bands)

- Chemiluminescence reduces energy available for heat by 20-30%.

Additional heat sources

- **Gravity wave breaking:**

  ↓ **breaking gravity wave**

  ↓ **turbulence**

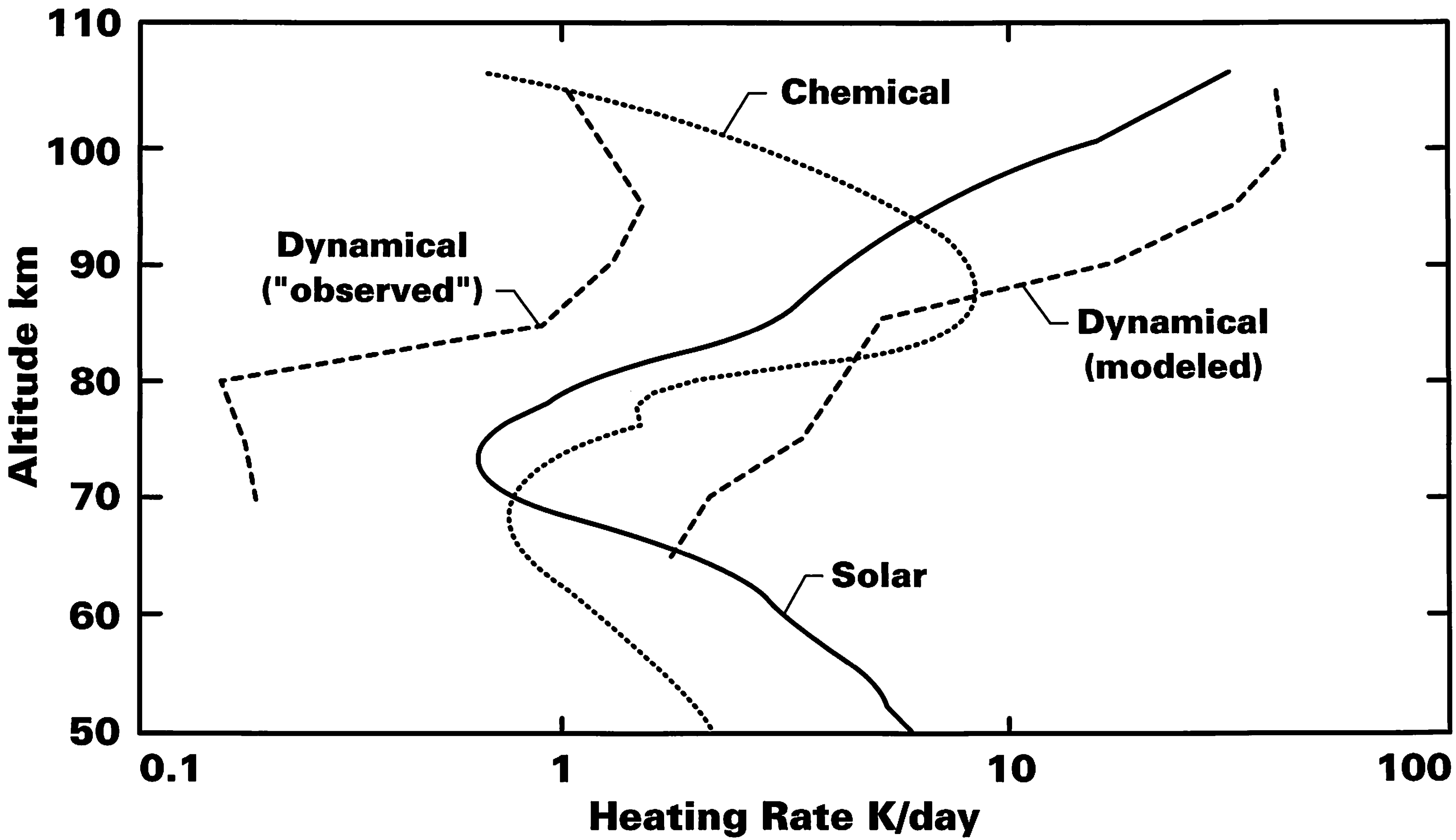
  ↓ **viscous dissipation**

  ↓ **heat**

- **Compare heating rates from models compared with those derived from observation and solar and chemical sources.**

  Model: (Fritts and Lu, JAS, 1993)
  Observed: (Lubken et al, JGR, 1993)

Comparison of heat sources



Radiative Cooling

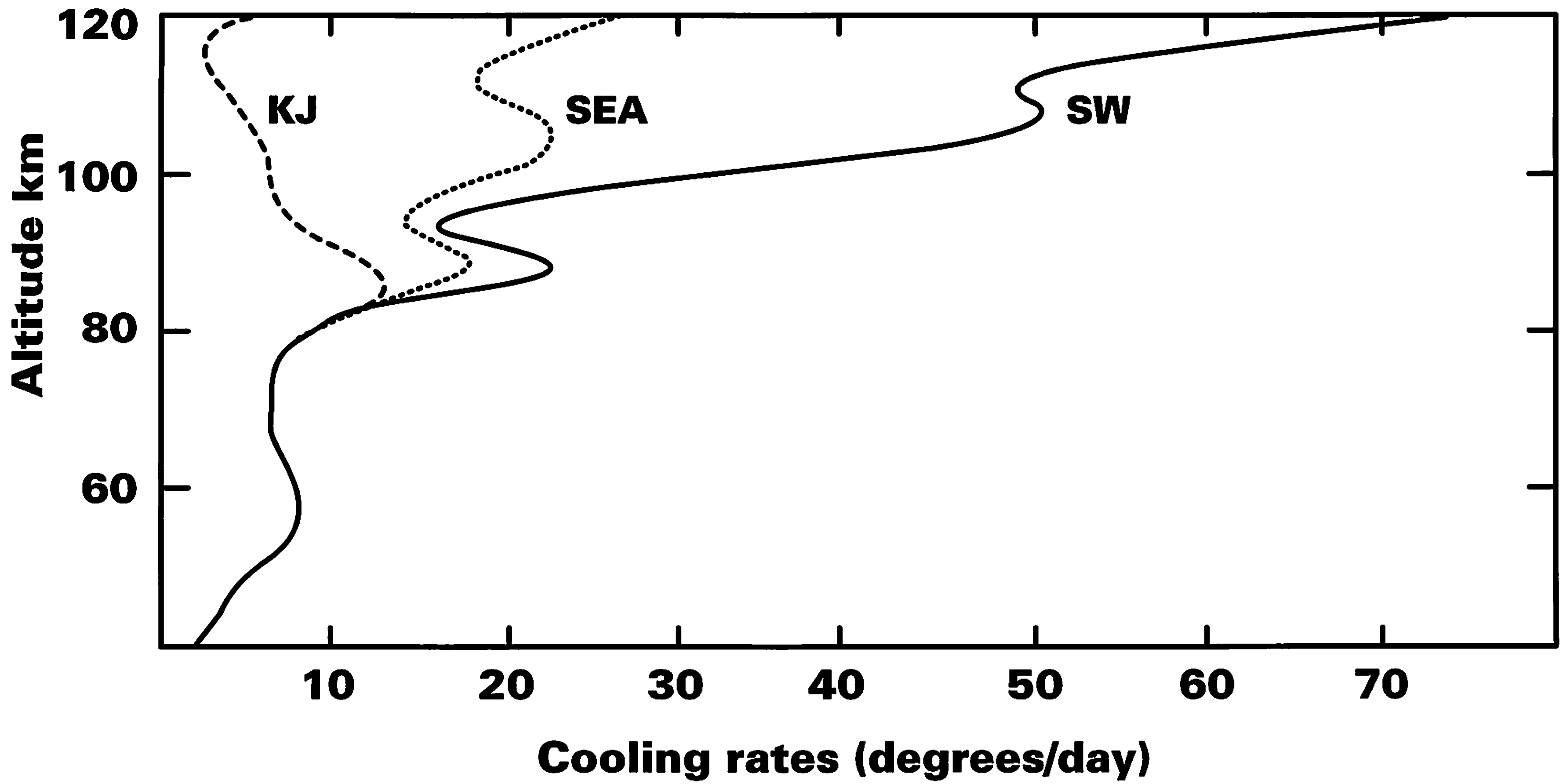
- Radiative cooling occurs when thermal kinetic energy is converted to internal energy of some species (eg, CO_2 primarily), and then is radiated to space:

$$CO_2 + M \rightarrow CO_2(\upsilon) + M$$
$$CO_2(\upsilon) \rightarrow CO_2(\upsilon'') + h\nu$$

- A key process is the efficiency at which collission between CO_2 and atomic oxygen result in the excitation of CO_2.

- This process $O + CO_2 \rightarrow CO_2(\upsilon) + O$ has recently been found to be much more efficient than previously thought => much larger cooling.

Cooling by CO_2 15 um emission



after Lopez-Puertas et al (QJRMS, 1992)

Summary

- The mesosphere remains a frontier of atmospheric science research
- The energy budget of the mesosphere is not well quantified
- Progress in numerous recent results
- Solar heating efficiency significantly less than 1.0 in mesosphere
- Chemical heating is quite large, competing with and exceeding direct solar heating between 70 and 110 km
- Observed thermal structure suggests that chemical heating effects are important
- Dynamical heating from breaking gravity waves is not yet well known. Recent results suggest it may be much smaller than model calculations have indicated.
- Radiative cooling larger than previously calculated

Summary

- **Continued progress through observation and modeling**

Global observations of:

- **Thermal structure**
- **Chemical abundances (O_3, O, H, H_2O, NO, NO_2)**
- **Airglows ($O_2(^1\Delta)$, $O_2(^1\Sigma)$, CO_2(4.3 μm), OH(υ))**
- **Cooling rates (CO_2(15 μm), NO(5.3 μm), O_3(9.6 μm))**
- **Winds:**
  Horizonatal by direct measurement
  Vertical by observations of long-lived chemical tracers (e.g., CO, H_2O)

- **Wave structures**