

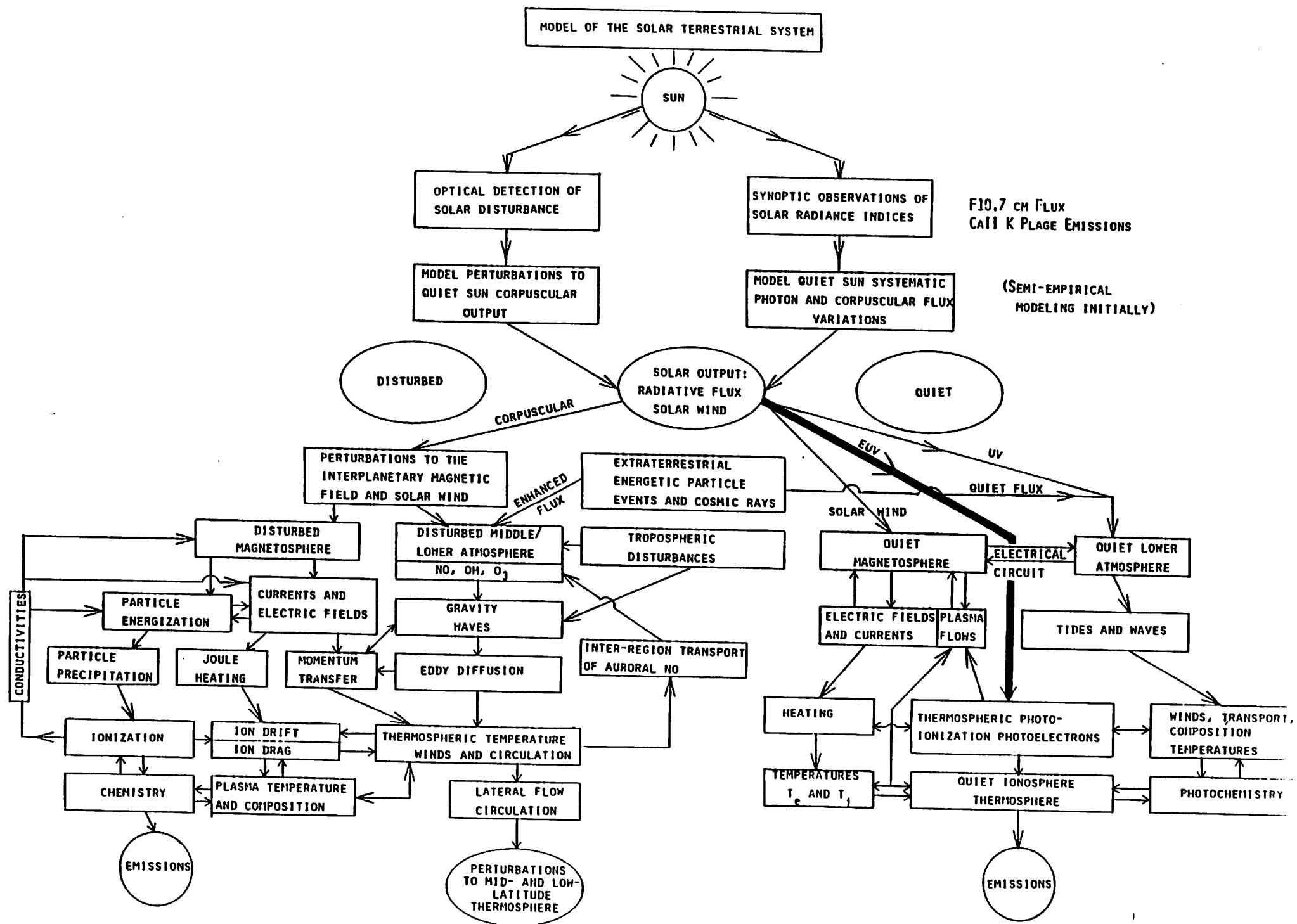
PHOTOCHEMISTRY OF THE LOWER THERMOSPHERE AND MESOSPHERE

PRESENTED AT THE 1993 ANNUAL CEDAR MEETING

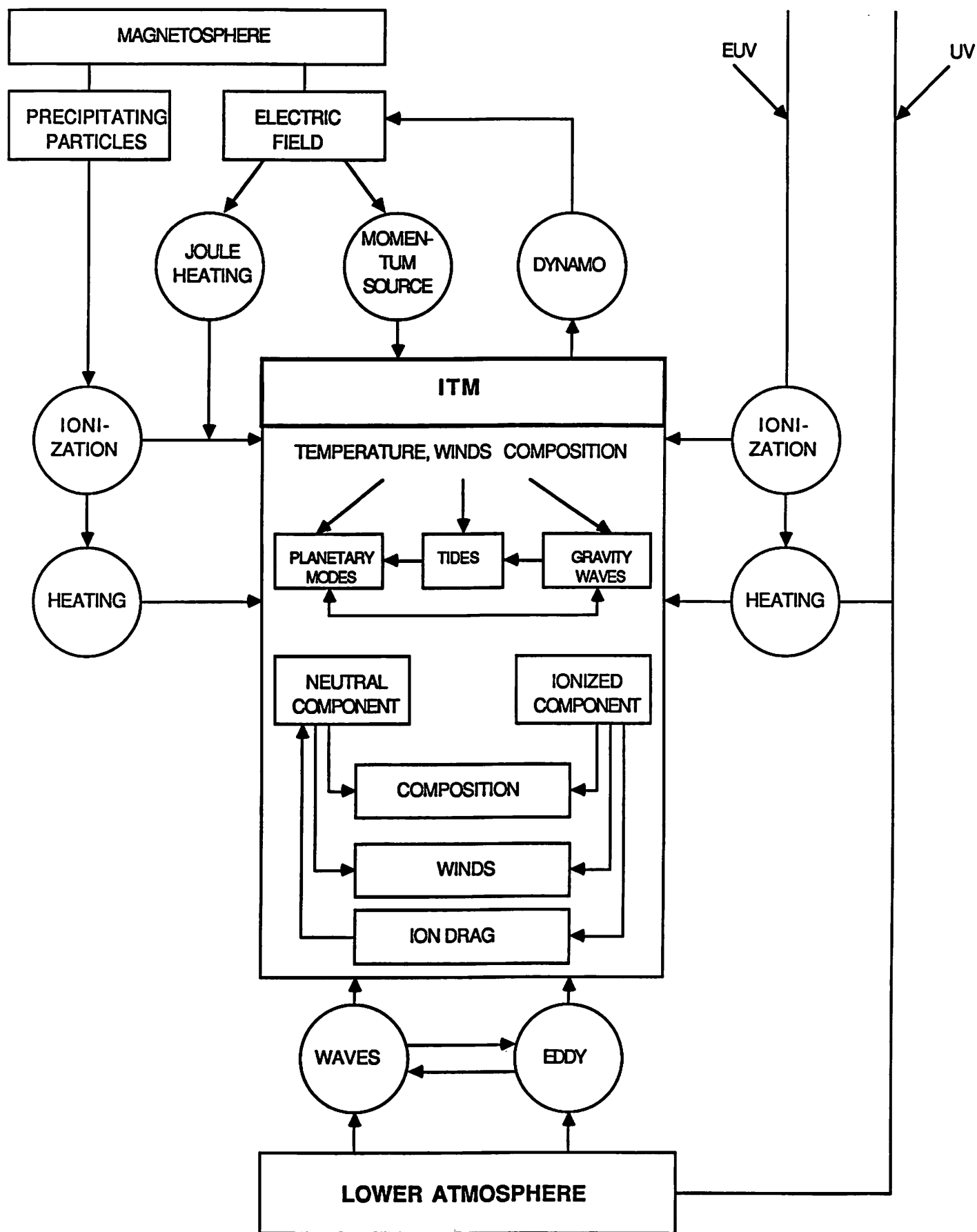
by

D .G. TORR

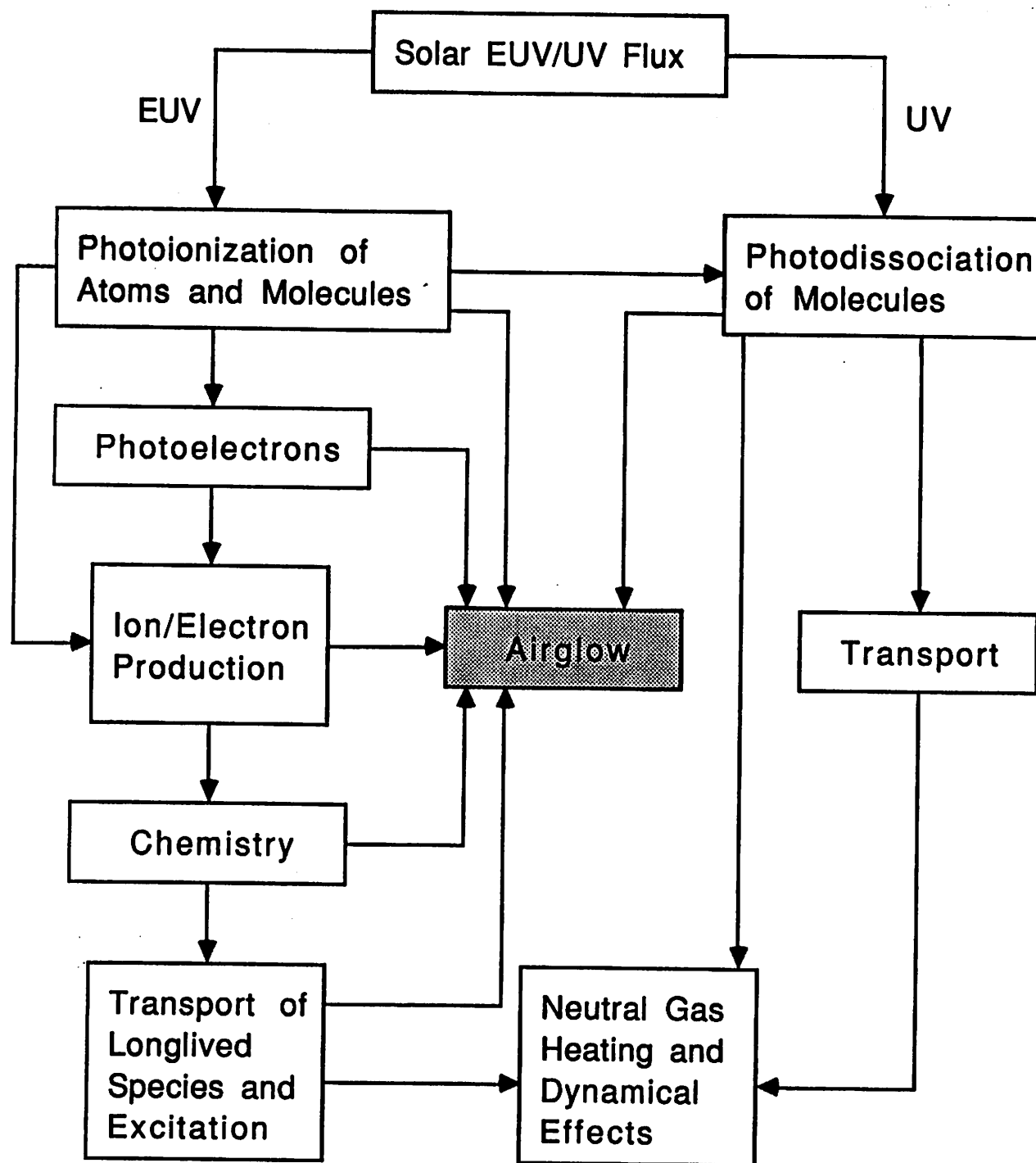
**OPTICAL AERONOMY LABORATORY
CENTER FOR SPACE PLASMA AND AERONOMIC RESEARCH
UNIVERSITY OF ALABAMA IN HUNTSVILLE**



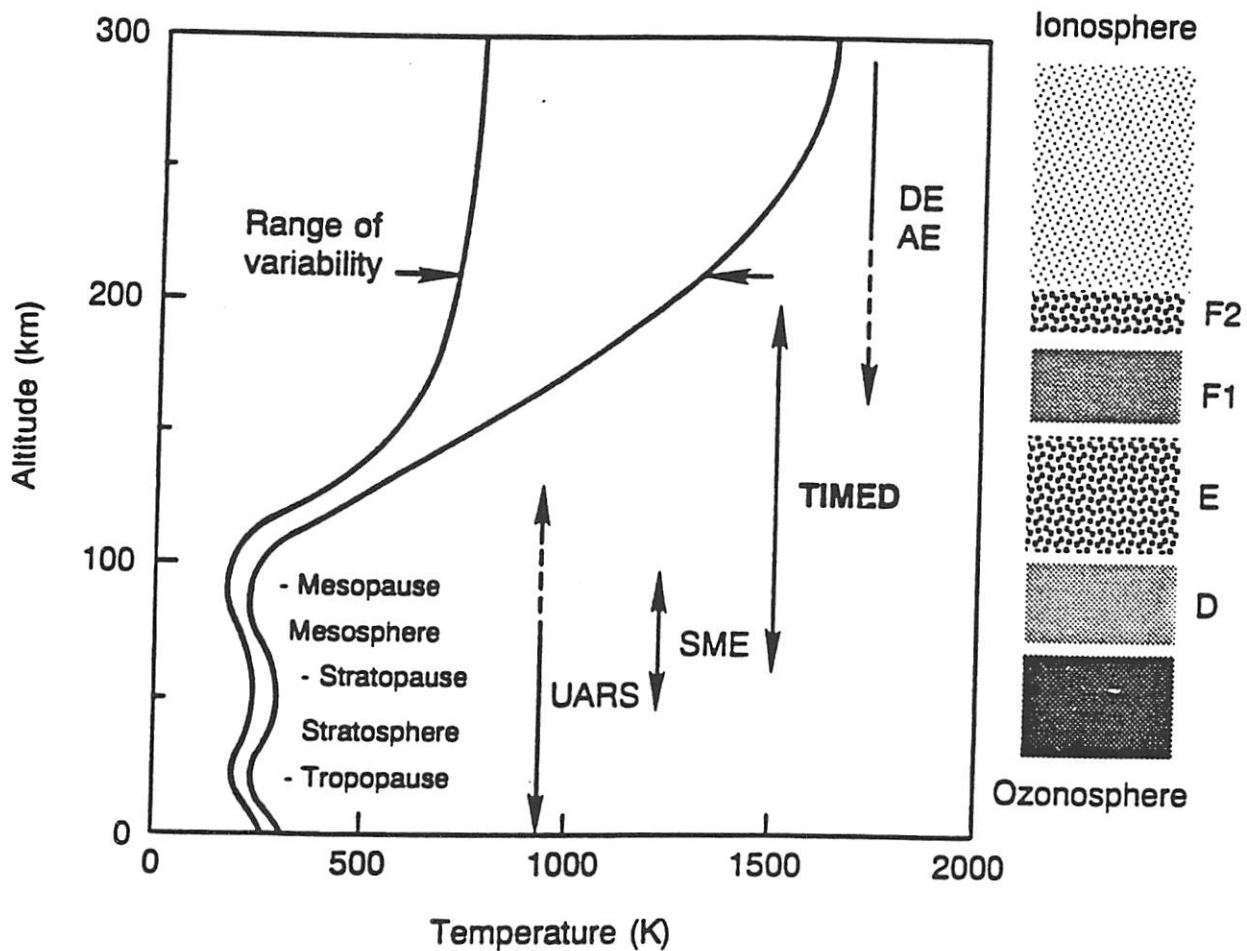
SCIENCE OBJECTIVES: THE COUPLED IONOSPHERE THERMOSPHERE MESOSPHERE SYSTEM



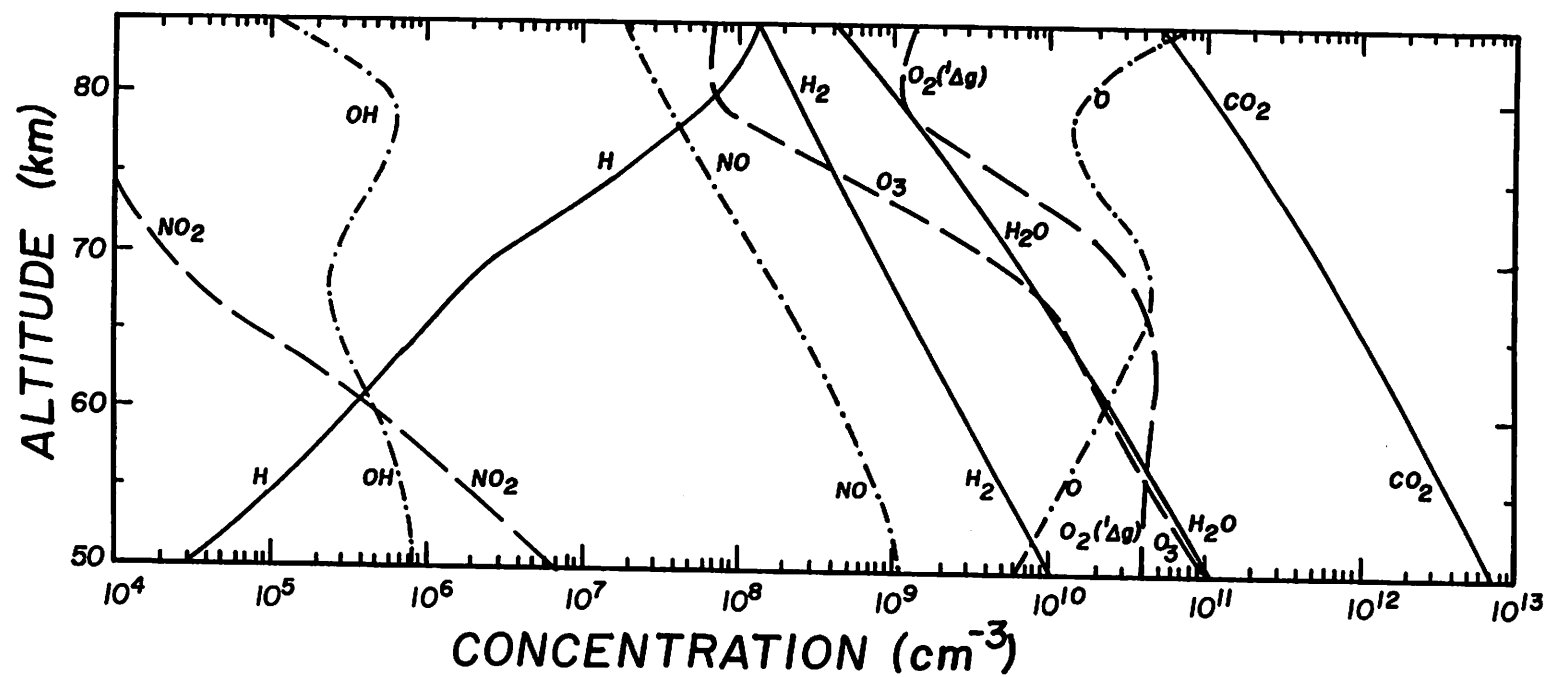
BASIC THERMOSPHERIC PHOTOCHEMISTRY



Temperature Structure of the Atmosphere



Temperature structure of the atmosphere and nomenclature for those regions defined by the temperature structure. The TIMED Mission will provide the first comprehensive experimental investigation of the critical transition region characterized by the most rapidly changing lapse rates in the Earth's atmosphere. Regions mentioned by other NASA missions are indicated.



Mesospheric Constituents (Wisemburg and Kockarts, 1980)

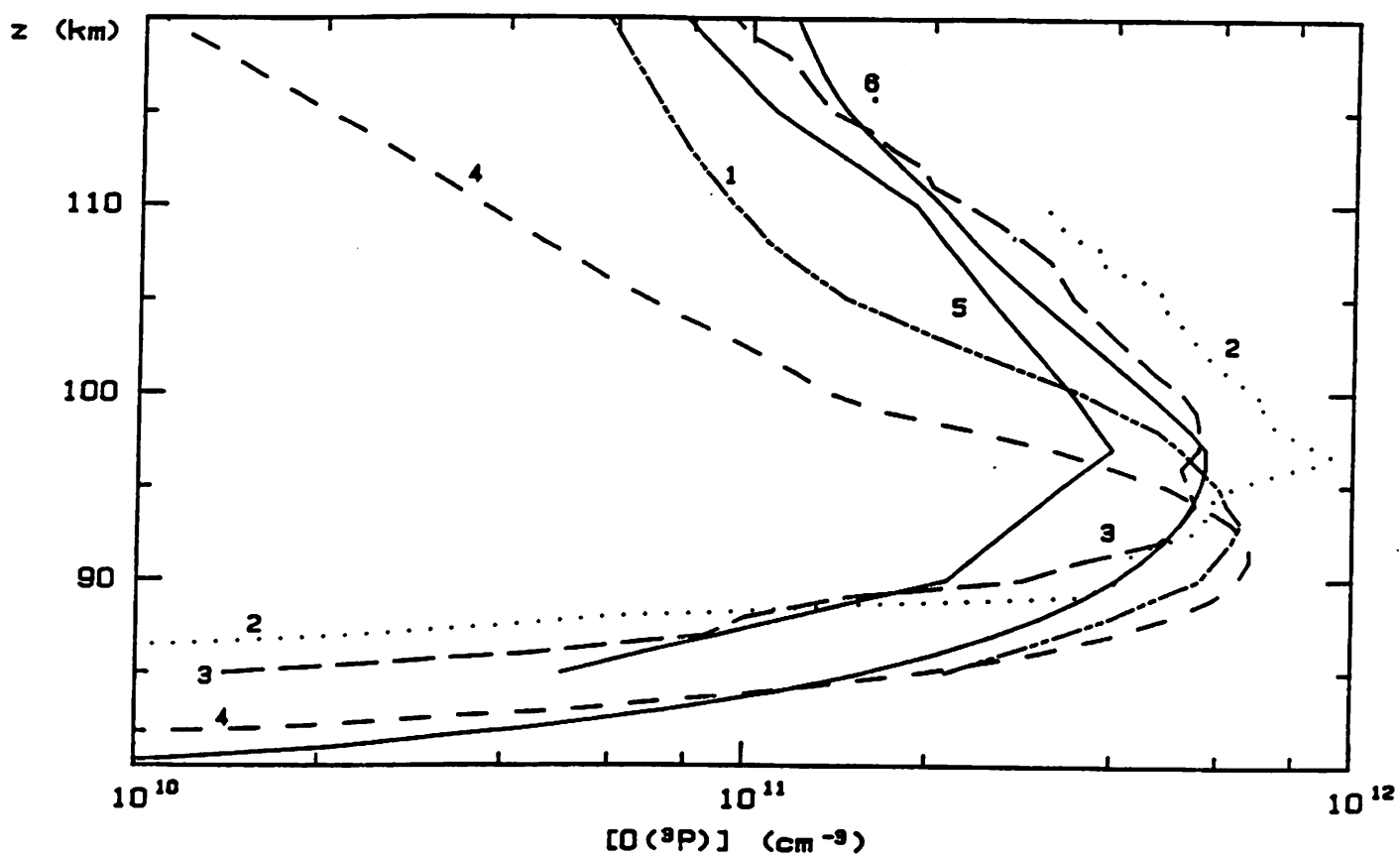
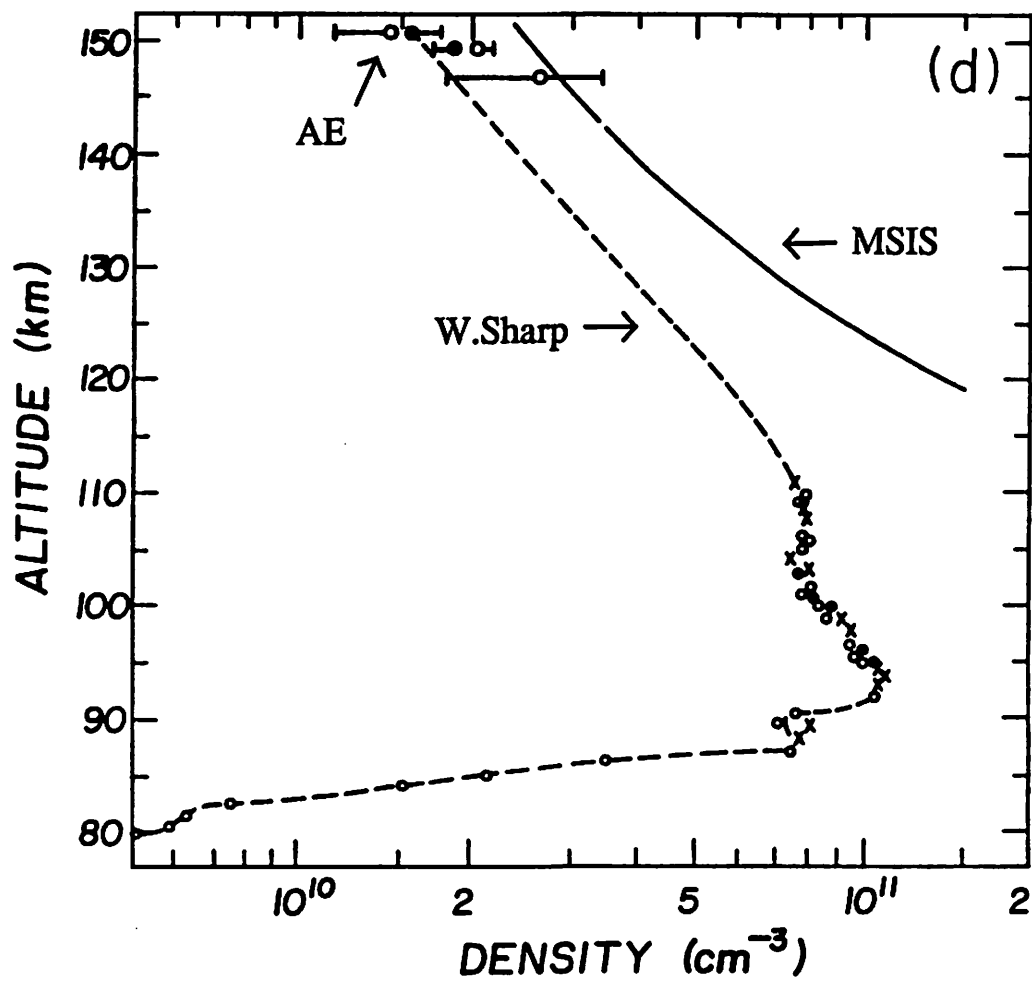
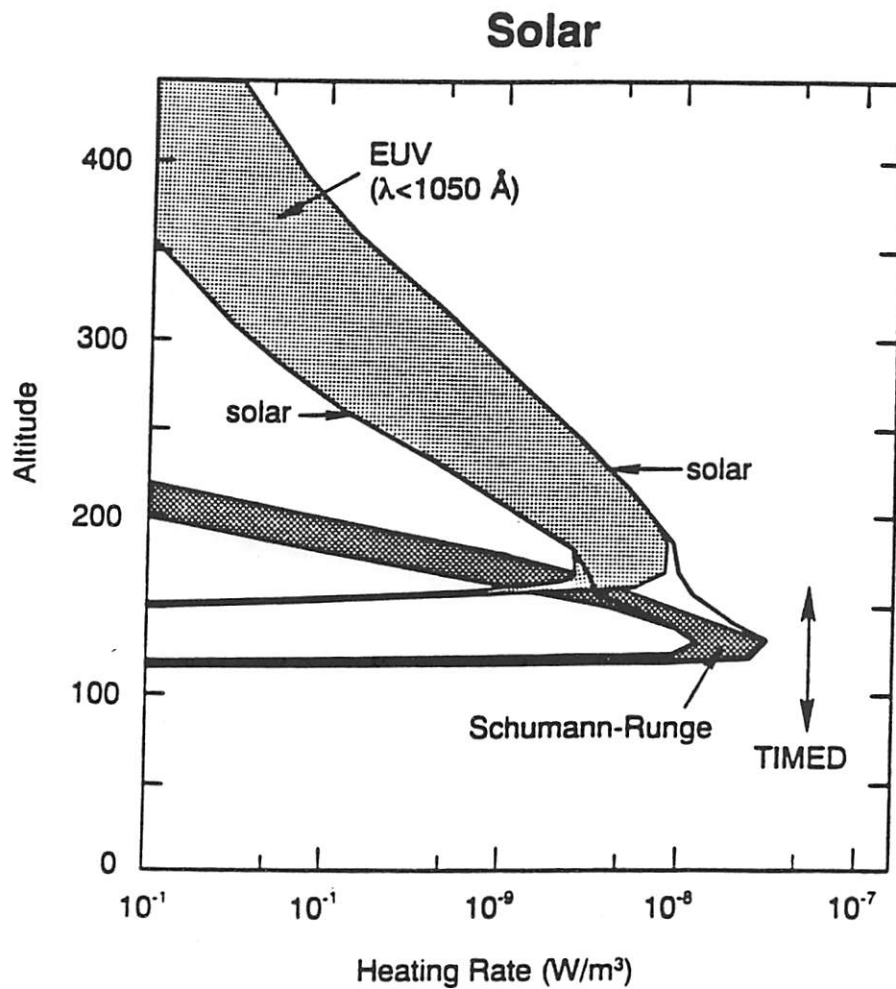


FIG. 10. NIGHTTIME ATOMIC OXYGEN PROFILE.

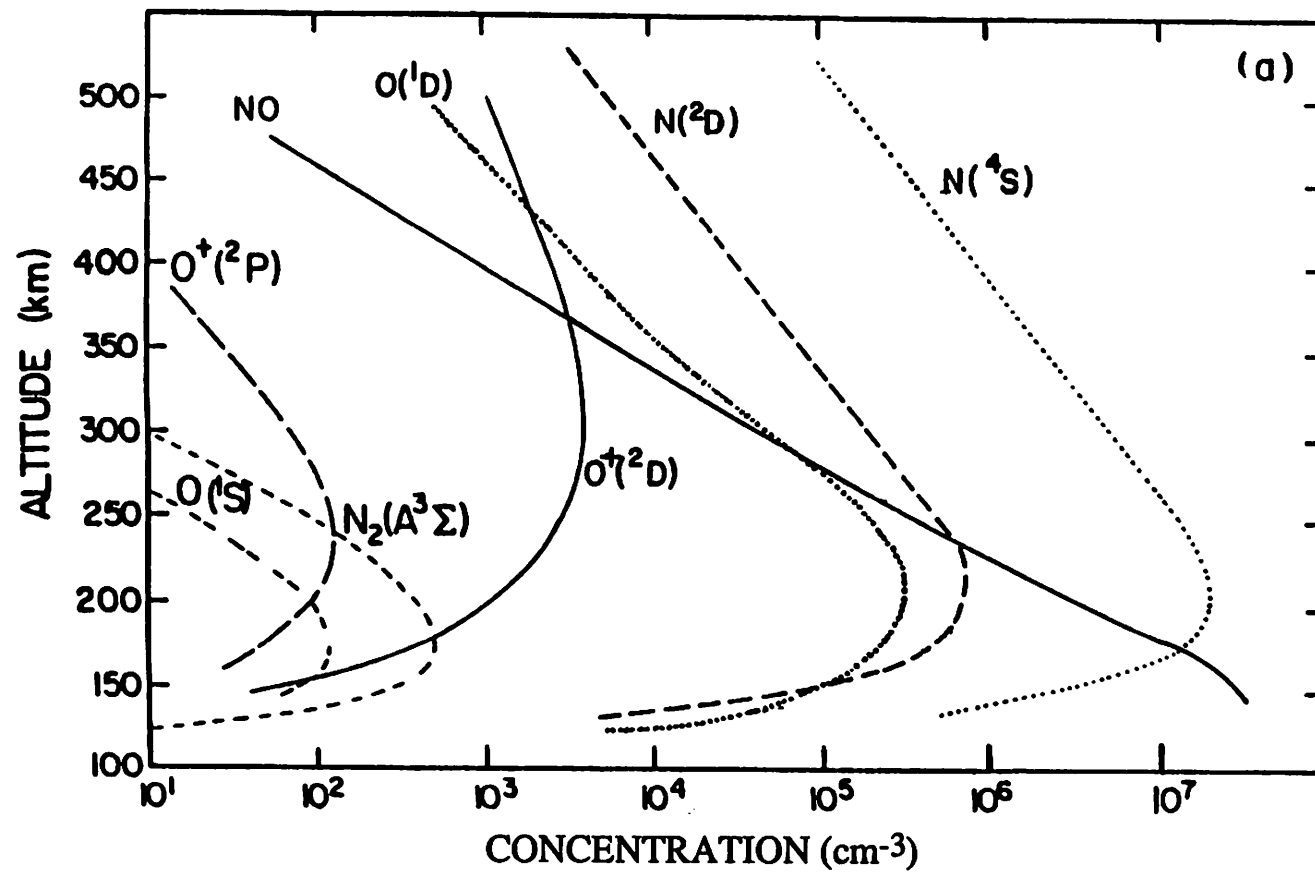
Curve 1: Trinks *et al.* (1978). Curve 2: Thomas *et al.* (1979). Curve 3: Thomas (1981). Curve 4: Rodrigo *et al.* (1981). Curve 5: Hedin (1983). Curve 6: This model.

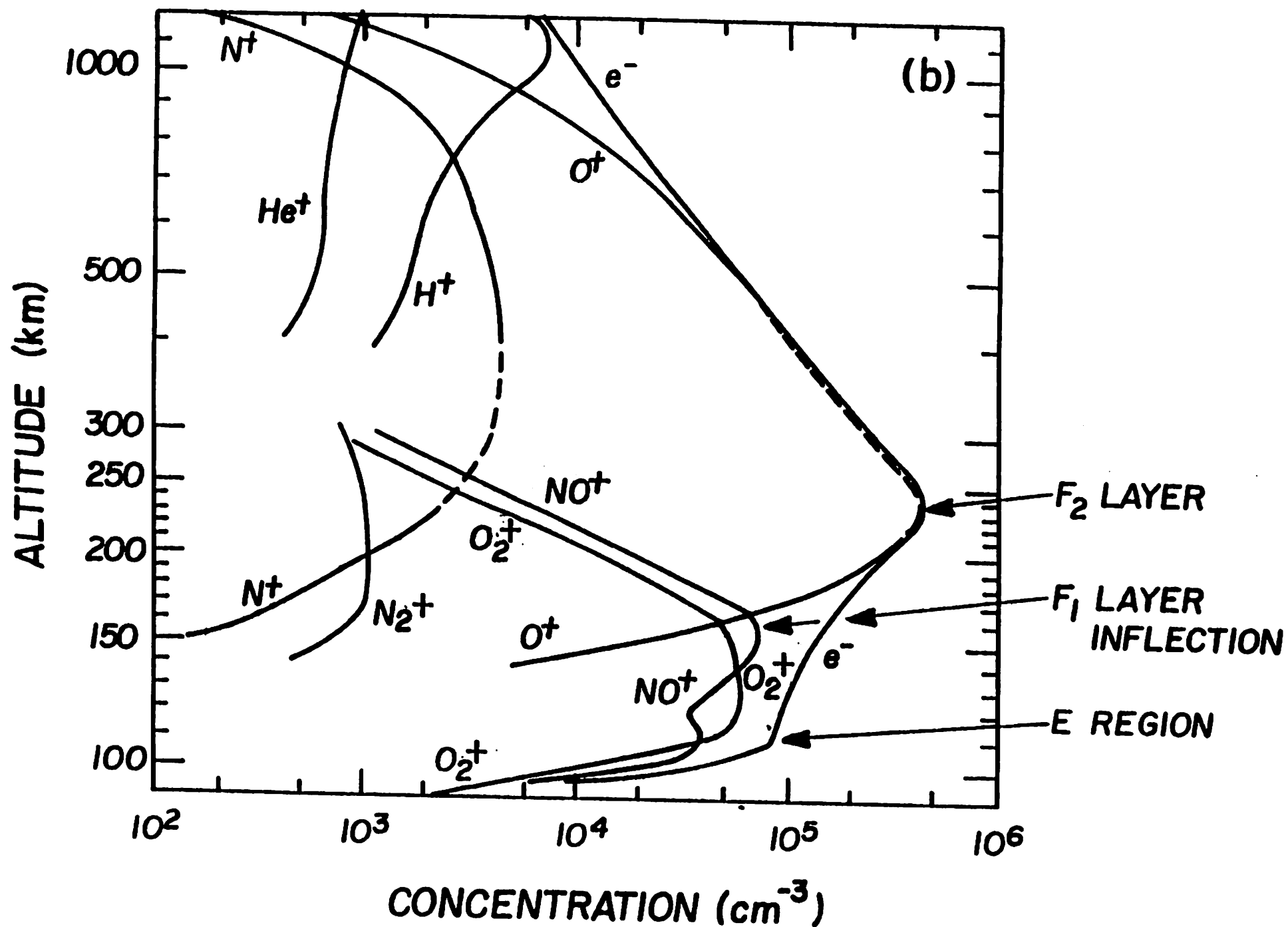


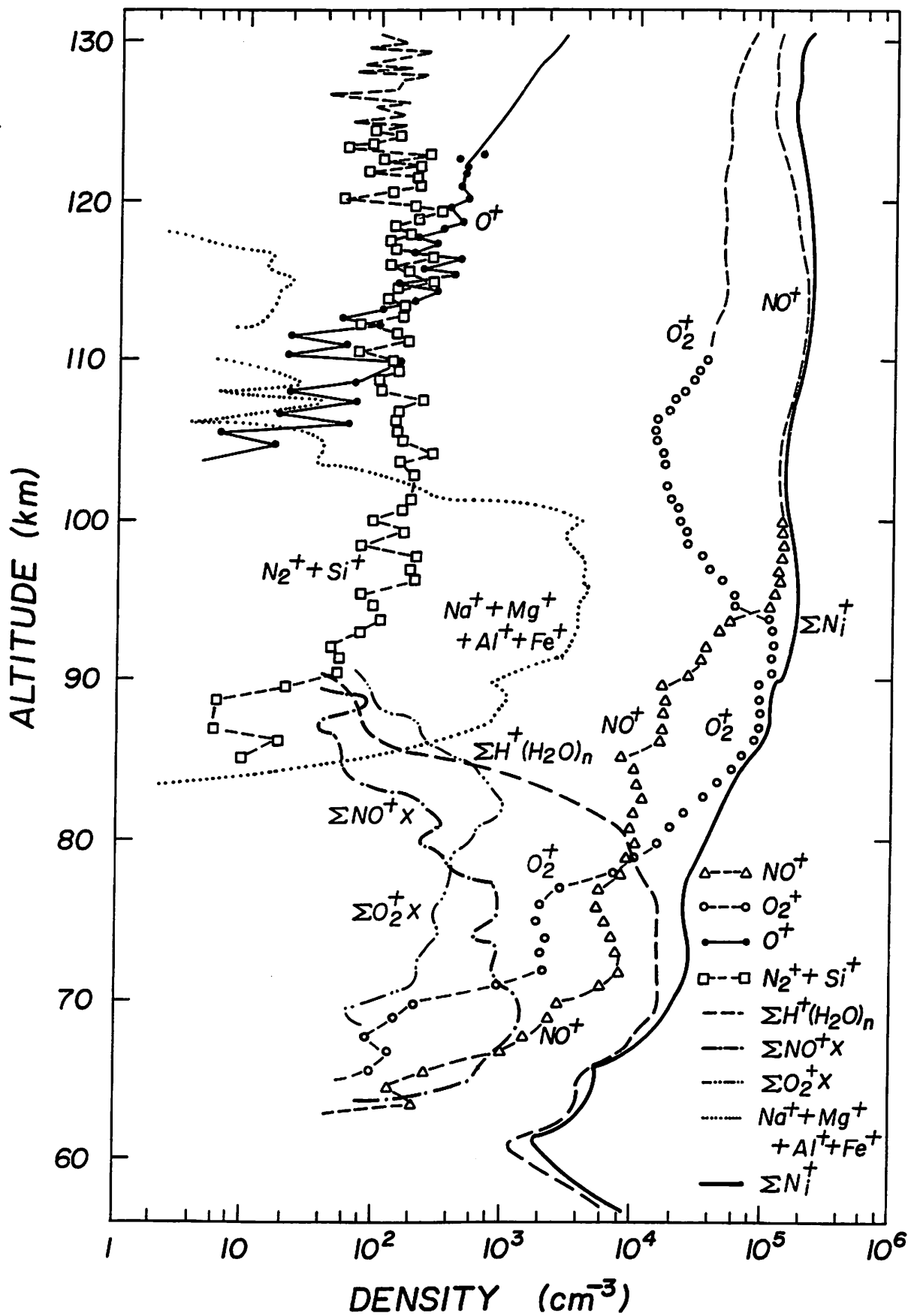
ATOMIC OXYGEN



Altitudinal profiles of heating rates due to solar EUV and UV absorption. The shaded regions indicate the range of variations with solar activity. The TIMED Mission investigates the region of maximum energy deposition.







Kopp and Hermann (1982)

WHY IS PHOTOCHEMISTRY IMPORTANT?

COMPOSITION AND TEMPERATURE:

PHOTOCHEMISTRY PLAYS A FUNDAMENTAL ROLE IN CONTROLLING SPECIES ABUNDANCE AND THERMAL STRUCTURE, (ENERGETICS) AND IS AN IMPORTANT ENERGY SOURCE THAT DRIVES DYNAMICS.

PHOTOCHEMICAL - DYNAMICAL COUPLING:

VARIATIONS IN CHEMICAL COMPOSITION RAPIDLY INFLUENCE THE THERMAL STRUCTURE AND DYNAMICS OF THE MESOSPHERE AND LOWER THERMOSPHERE, AND VICE-VERSA

ENERGETICS:

PHOTOCHEMICALLY PRODUCED MINOR CONSTITUENTS PLAY IMPORTANT ROLES IN CONTROLLING ENERGETICS

CONSTITUENTS ABSORB SOLAR AND CORPUSCULAR ENERGY, RESULTING IN EXCITATION, DISSOCIATION OR IONIZATION WHICH CAN BE COLLISIONALLY TRANSFERRED EITHER LOCALLY OR NON LOCALLY TO THE SURROUNDING ATMOSPHERE RESULTING IN HEATING.

PHOTOCHEMISTRY PLAYS A CRITICAL ROLE IN DETERMINING THE PARTITIONING AND REDISTRIBUTION OF THE ABSORBED ENERGY, AND HENCE THE EFFICIENCY OF CONVERSION TO HEAT.

RADIATIVE LOSS IS THE PRIMARY COOLING PROCESS AND THIS TOO IS CONTROLLED BY PHOTOCHEMICAL INTERACTIONS.

WHY IS PHOTOCHEMISTRY IMPORTANT?

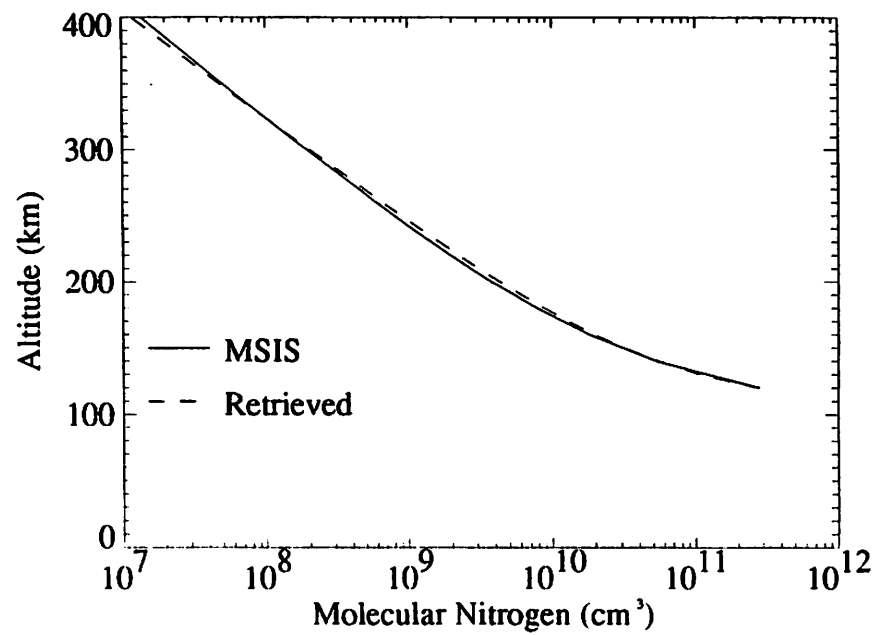
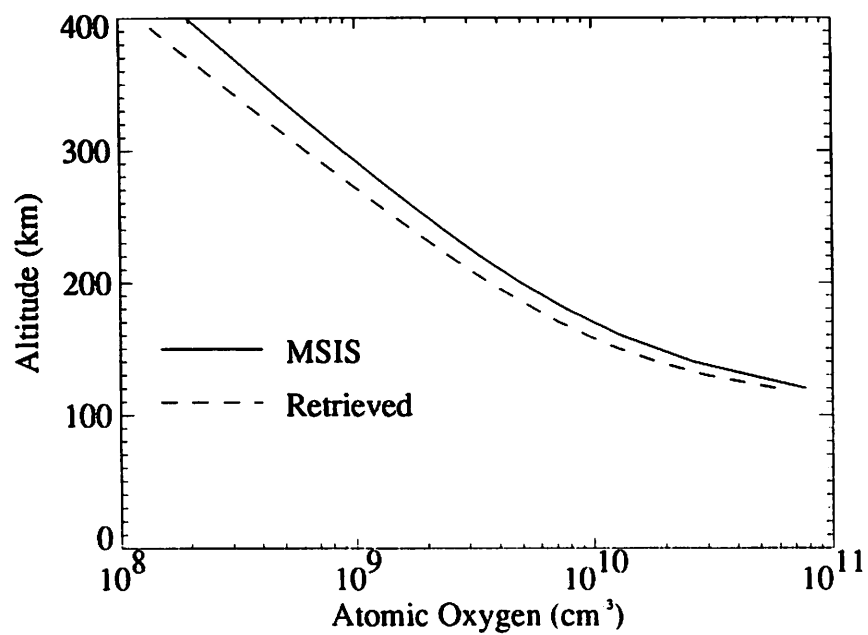
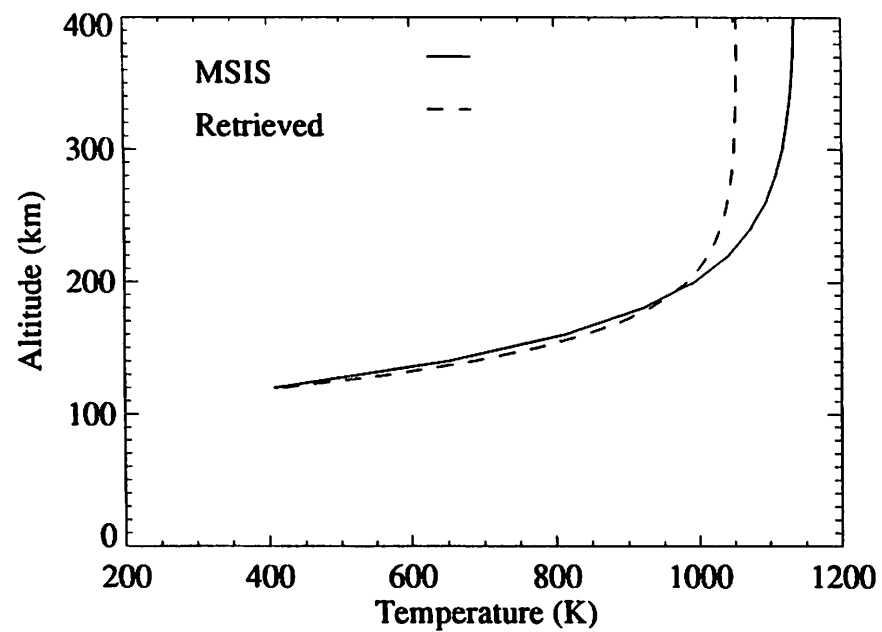
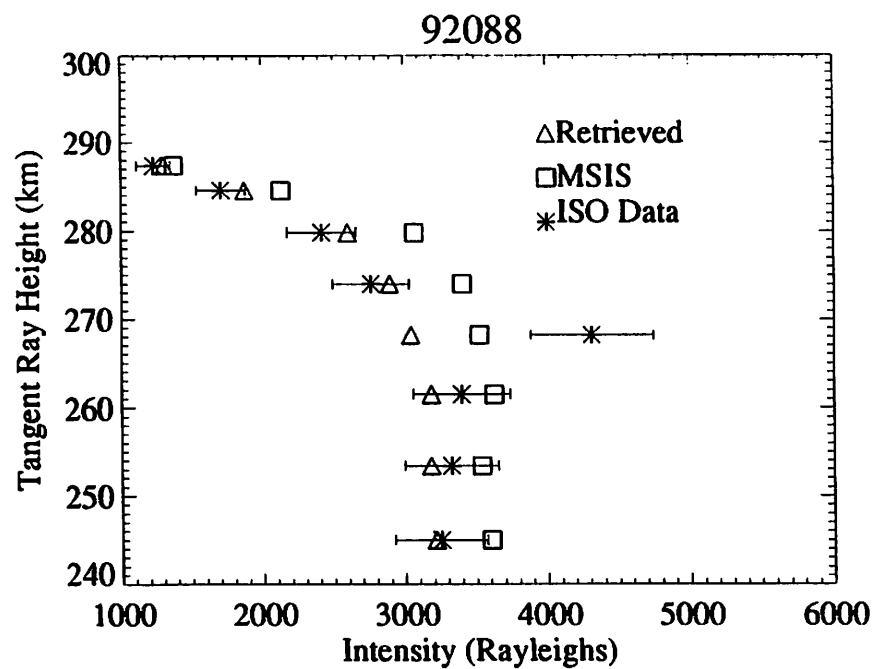
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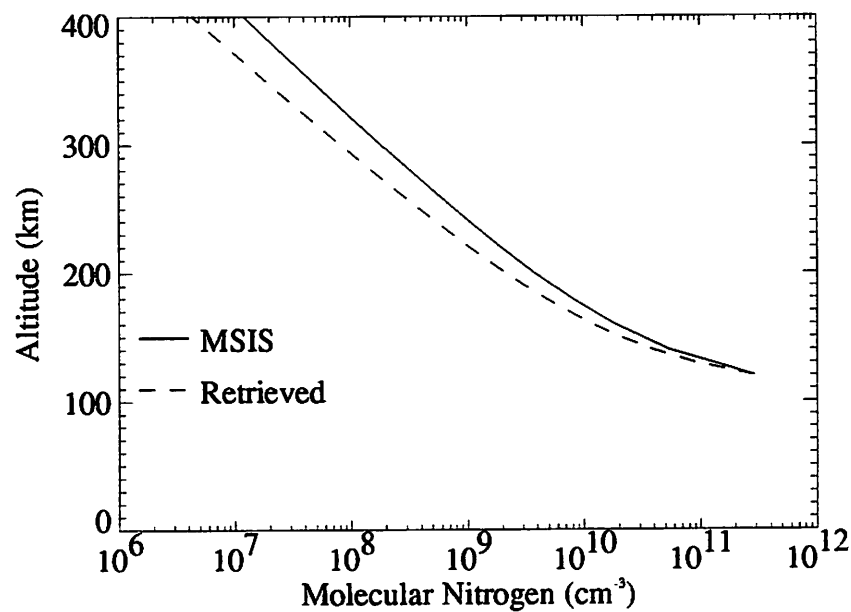
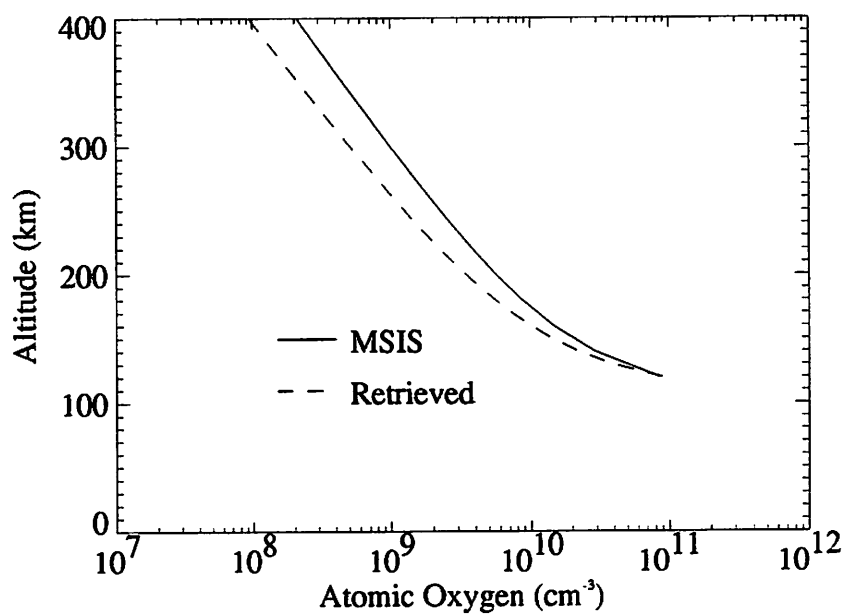
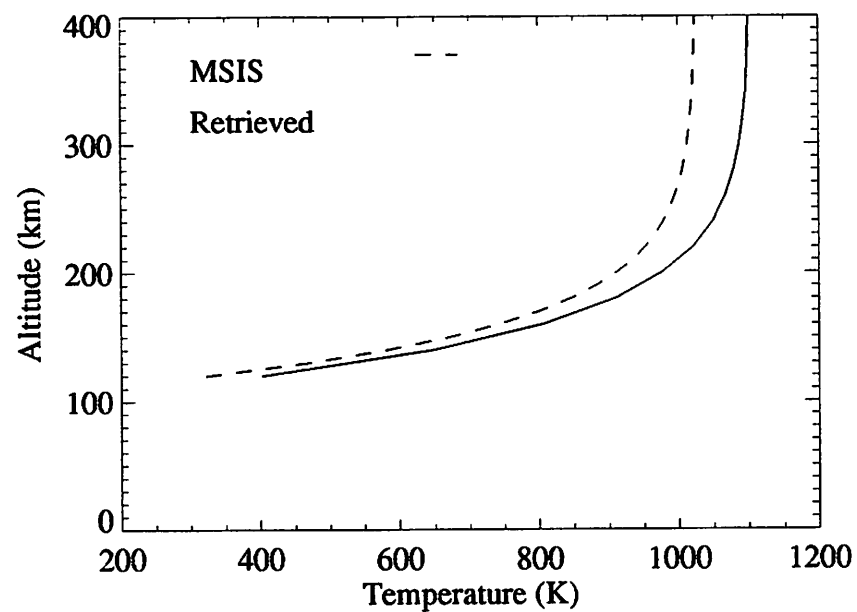
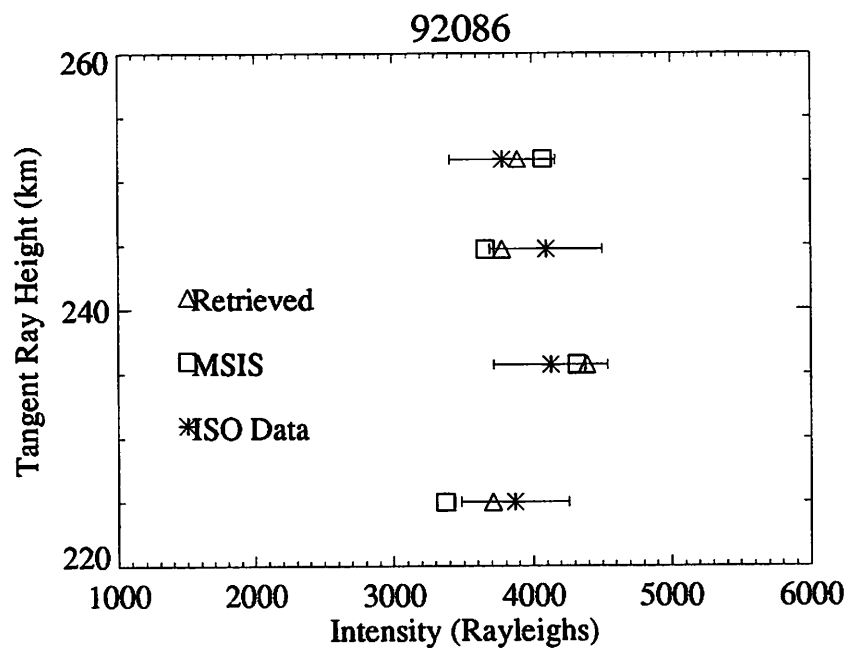
GENERATES OBSERVABLES:

INVERSE PHOTOCHEMICAL MODELING OF MEASURED AIRGLOW, AURORAL EMISSIONS AND ELECTRON DENSITY PROVIDES A POWERFUL APPROACH FOR DETERMINING MANY GEOPHYSICAL PARAMETERS *E.G.* COMPOSITION, TEMPERATURE AND ENERGY INPUTS.

ADVANTAGES OF A QUANTITATIVE UNDERSTANDING OF PHOTOCHEMISTRY

- **PHOTOCHEMISTRY IS FUNDAMENTAL TO ALL MULTI-MODELING.**
- **PROVIDES A POWERFUL MEANS FOR RETRIEVING KEY PARAMETERS FROM BOTH ORBITAL AND GROUND-BASED MEASUREMENTS OF PLASMA DENSITIES AND RADIATION FIELDS.**
- **KNOWLEDGE OF NEUTRAL (AND ION) COMPOSITION, TEMPERATURE AND INPUT ENERGY FLUXES WILL PROVIDE CRITICAL TESTS OF GLOBAL MODELS.**
 - *E.G.* THE TIE-GCM REQUIRES ENERGY INPUTS AND PROVIDES COMPOSITION AND TEMPERATURE AS OUTPUT.





STATUS OF PHOTOCHEMICAL UNDERSTANDING

UPPER THERMOSPHERE:

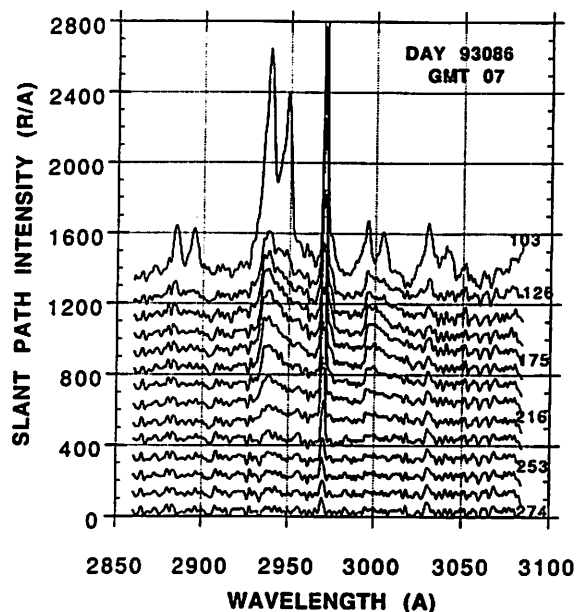
- GOOD QUANTITATIVE UNDERSTANDING.

LOWER THERMOSPHERE:

- MUCH IN COMMON WITH UPPER THERMOSPHERE - BUT UNPROVEN UNDERSTANDING.

MESOSPHERE:

- RELATIVELY GOOD CONCEPTUAL UNDERSTANDING.
- POOR QUANTITATIVE UNDERSTANDING.



Conclusions

The ISO has obtained the first broadband spectra of the thermospheric dayglow emissions, providing a database with considerable potential for constraining photochemical models. The agreement between measurement and model for the 12 major dayglow features shown in Figures 3 and 4 is surprisingly good (better than a factor of 2). There are, of course, many details and subtleties that must be studied, and for which this multiparameter database can provide substantial constraints. We conclude that the basic thermospheric photochemistry established on the basis of the Atmosphere Explorer database explains a large number of thermospheric

Fig. 2. Example of the spectra obtained at different tangent ray heights in the course of the roll maneuver. While the absolute scale is the same for each, the various spectra have offsets added in order to display the data.

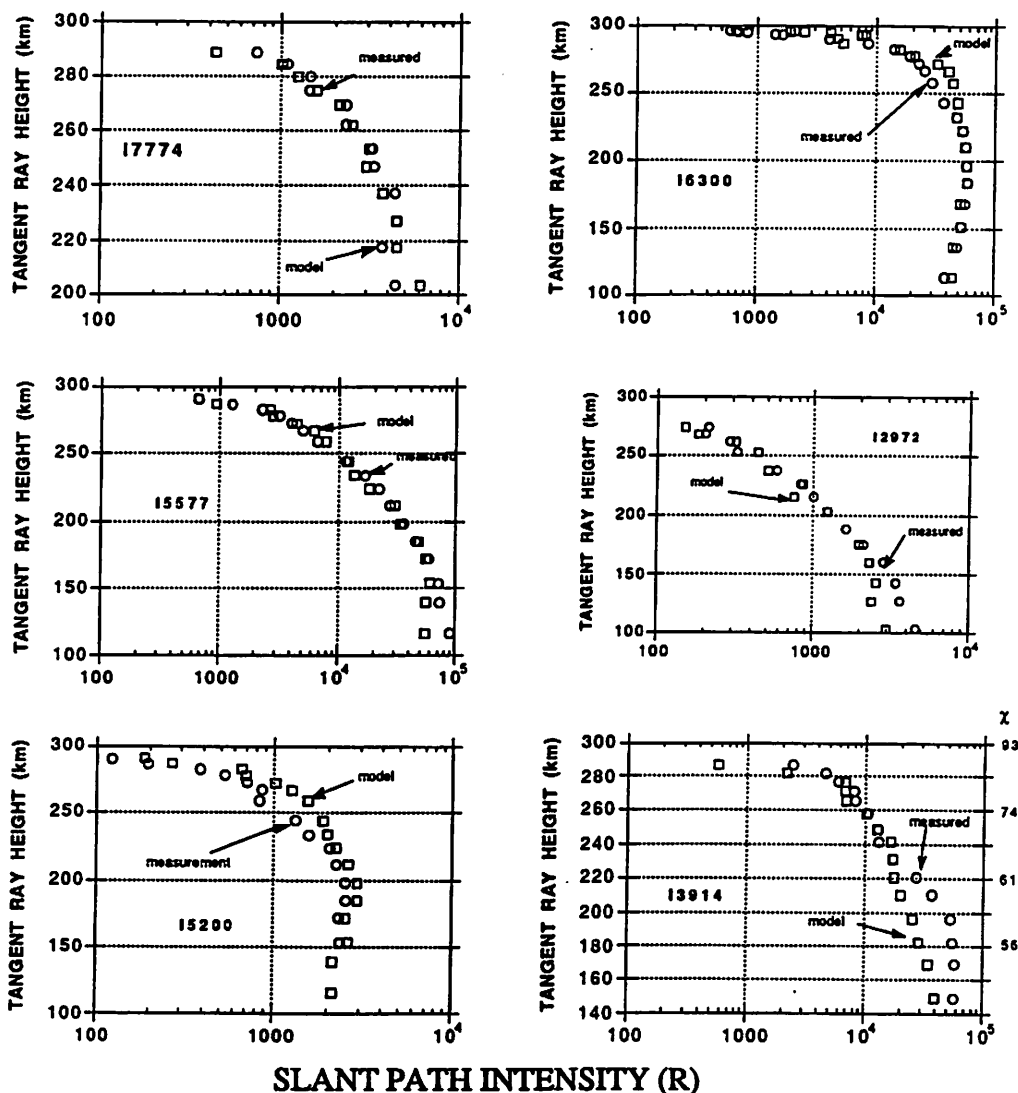


Fig. 3. Comparison of measured and modeled slant path intensity for: OI 7774 Å, OI 6300 Å, OI 5577 Å, OI 2972 Å, NI 5200 Å, and N_2^+ 1N 3914 Å. The variation of solar zenith angle is shown on the right-hand axis of the 3914 Å panel.

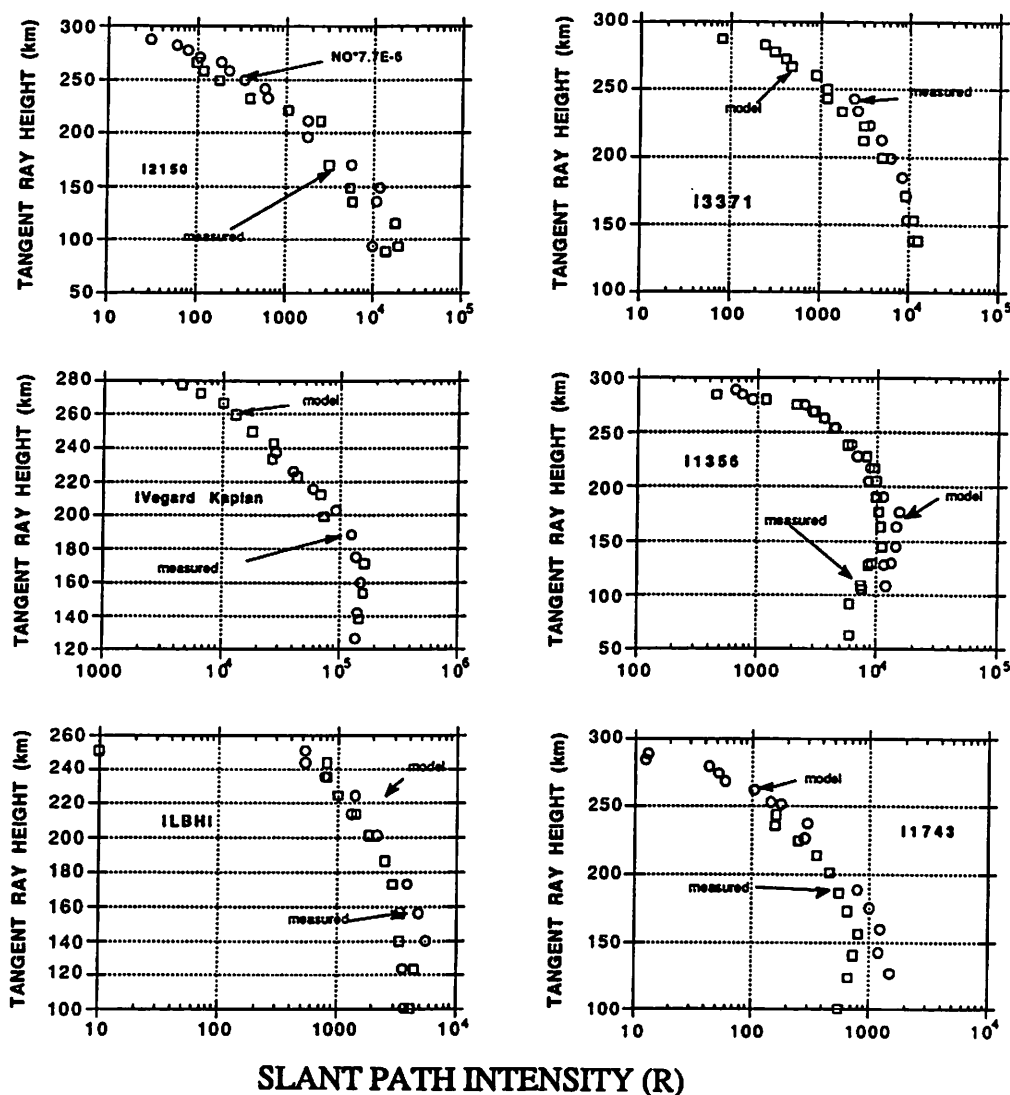


Fig. 4. Comparison of measured and modeled slant path intensity for: NO γ 2150 Å, N₂ 2P 3371 Å, N₂ V-K (0-6, 0-7), OI 1356 Å, N₂ LBH 1670-1850 Å, NI 1743 Å.

emissions measured with an entirely different type of instrument almost 20 years later. This means that we are now in a good position to similarly establish the photochemistry of the lower thermosphere and mesosphere.

Acknowledgements. We thank the crew of the ATLAS-1 mission; Charles Bolden, Brian Duffy, and David Leestma, for their care in executing the maneuvers necessary to acquire these data; Kathy Sullivan, Michael Foale, Byron Lichtenberg, and Dirk Frimont for their assistance during the operations. This work was supported by contract NAS8-37106 to the University of Alabama in Huntsville.

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- P. G. Richards and D. G. Torr, Center for Space Plasma and Aeronomic Research, University of Alabama in Huntsville, Huntsville, AL 35899.
- M. R. Torr, Space Science Laboratory, NASA Marshall Space Flight Center, Huntsville, AL 35812.

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PHOTOCHEMICAL SYSTEMS

MAJOR SPECIES (O, O₂, N₂)

RESERVOIR MOLECULES (*eg.* H₂O, H₂)

METASTABLE NEUTRALS

PERMITTED EXCITED STATES

ODD HYDROGEN FAMILY

ODD OXYGEN FAMILY

ODD NITROGEN FAMILY

METALLIC NEUTRALS AND IONS

MAJOR AND MINOR IONIC SPECIES

METASTABLE IONS

CLUSTER IONS

TRACER SPECIES

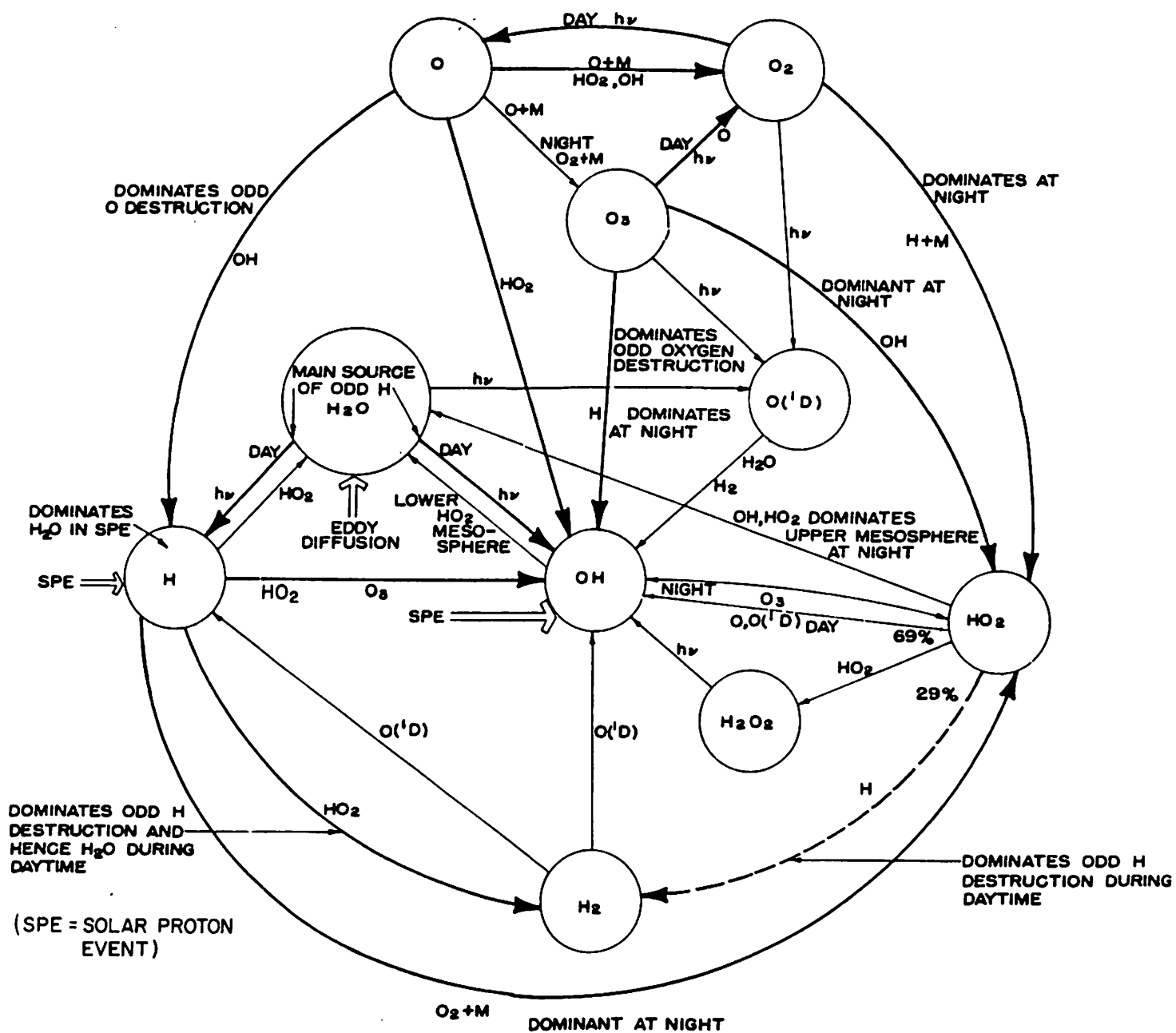
MESOSPHERE LOWER THERMOSPHERE PHOTOCHEMICAL SYSTEMS

SYSTEM	MEMBERS	REGION	ROLE
MAJOR SPECIES	O, O ₂ , N ₂	MLTI	ENERGY ABSORBERS, REACTANTS START OF PHOTOCHEMICAL CHAIN
METASTABLE NEUTRALS	O(¹ D), O(¹ S), N(² D), N(² P)	MLT	ENERGY STORAGE/TRANSFER
	N(² P), N ₂ [*] (V), O ₂ [*] (V), N(² A)		KINETICS MODERATORS
	O ₂ (A, A', C1, a, b), OH [*]		RADIATORS/HEAT LOSS
	CO ₂ (VIB)		OBSERVABLES
EXCITED STATES	O, O ₂ , N ₂ , N, OH, NO		RADIATORS/HEAT LOSS
			METASTABLE SOURCES
ODD OXYGEN (O _x)	O	M	SINGLE SOURCE OF O ₃
			KEY REACTANT
			RADIATOR/HEAT SINK
			CHEMICAL HEAT SOURCE
	O ₃	M, STRAT	UV ENERGY ABSORBER, RADIATOR, REACTANT
			CLIMATOLOGY CONTROL
			D REGION ION CHEMISTRY
ODD HYDROGEN	H, OH, HO ₂ , (HO _x)	M	CATALYTIC O _x DESTRUCTION
			CHEMICAL HEAT SOURCES
HO _x RESERVOIRS	H ₂ O, H ₂		HO _x PHOTOCHEMICAL SOURCES
ODD NITROGEN	N, N(² D), N(⁴ S), NO, NO ₂	LT	HEAT SOURCES AND TRANSFER, REACTANTS
	N(² D)	LT	OBSERVABLE FOR NO ⁺
	NO	LT	SOURCE OF NO ⁺
		MLT	RADIATOR/HEAT SINK
		MLT	SOURCE OF STRAT NO
		STRAT	O ₃ CATALYTIC DESTRUCTION
METALLIC NEUTRALS	Na, Ca, K, Fe	M	OBSERVABLES/TRACERS
MAJOR IONS	O ⁺ , O ₂ ⁺ , NO ⁺ , N ₂ ⁺	MLTI	REACTANTS/HEAT SOURCES
MINOR IONS	N ⁺	LT	MINOR REACTANT
METASTABLE IONS	O ⁺ (² D)	LT	CHEMICAL ENERGY TRANSFER
	O ⁺ (² P)	T	LT COMPOSITION MONITOR
METALLIC IONS	Ca ⁺ , Mg ⁺ , Fe ⁺	MLTI	DYNAMICS TRACERS

THE HYDROGEN-OXYGEN SYSTEM

Odd Oxygen Photochemistry (Chapman, 1930)

Hydrogen-Oxygen (Bates and Nicolet, 1950)



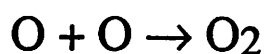
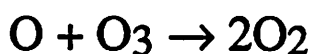
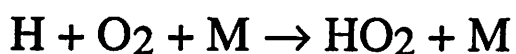
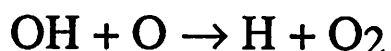
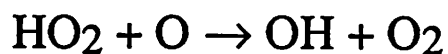
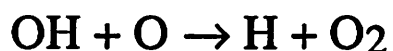
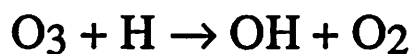
MESOSPHERIC OXYGEN-HYDROGEN CHEMISTRY

ROLE OF KEY OXYGEN-HYDROGEN CONSTITUENTS IN THE MLTI

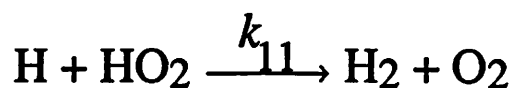
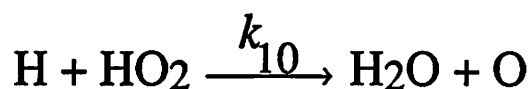
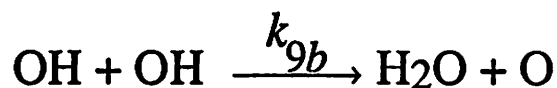
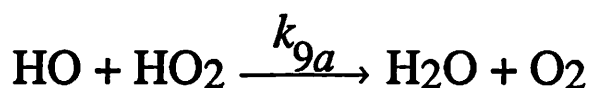
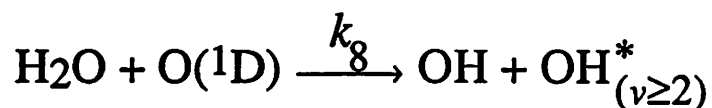
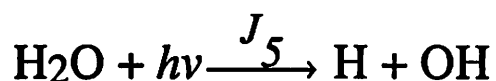
ID	KEY PROCESSES	REGION	KEY ROLES
O	$O + h\nu$	LTI	Ion Chemistry; Photoionization $\rightarrow O^+(^4S, ^2D, ^2P)$
	$O + N_2^+$	LTI	Ion Atom interchange Conversion of N_2^+ to NO^+
	$O + e \rightarrow O^* + e$	LTI	Source of Excited Metastable $O(^1D)$, $O(^1S)$ and Permitted States
	$O^* \rightarrow O + h\nu$	LT	Radiative Sink
	$O + X^* \rightarrow X + O$	LTI	Quenches $N_2(A)$, $O(^1D, ^1S)$, $N(^2D, ^2P)$, $O(^2D, ^2P)$, N_2^* , O_2^*
			LT Heat Source
	$O + O + M \rightarrow O_2$	MLT	Heat Reservoir; Source of $O_2(C^1, A, A') \rightarrow$ Precursors to Several emissions
	$O + O_2^* \rightarrow O_2'$	MLT	Quenches $O_2(A, A', C^1, a, b)$
	$O + O_2 + M \rightarrow O_3$	MLT	Only Source of Ozone $\rightarrow$ Primary Mesospheric Heat Source
	$O + O_3 \rightarrow O_2 + O_2$	MLT	Destruction of Ox
	$O + OH \rightarrow H + O_2$	MLT	Step in Catalytic Destruction of Ozone and Ox Loss Cycle
			MLT Heat Source
	$O + M \rightarrow O^* + M$	MLTI	Fine Structure Excitation
	$O^* \rightarrow O (63 \mu m)$	MLTI	Fine Structure Cooling
	$O + CO_2^* \rightarrow CO_2 + O$	MLT	Energy Transfer to $CO_2 \rightarrow$ Radiative Loss
O ₃	$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$	M	Absorption of UV Energy; Mesospheric Heat Source + Excitation
			Radiative Loss $\rightarrow$ Heat Sink and Observable Emissions
			UV Absorption $\rightarrow$ Observable Signature for O ₃ Measurement
H ₂ O	$H_2O + h\nu \rightarrow OH + O$	MLT	Source of Mesospheric HO _x ; Drives Hydrogen-Oxygen Chemistry
	$H_2O + O(^1D) \rightarrow$	MLT	Minor Source of Mesospheric OH
	$H_2O + O_2^+ + e \rightarrow$	MLT	$O_2 + H + OH$; Storm Time Enhancement of HO _x Through Ion Clusters
H	$H + O_3 \rightarrow OH^* + O_2$	MLT	First Step in Catalytic Destruction of O ₃ ; Heat Source
			Source of Meinel Bands $\rightarrow$ O ₃ Destruction Rate or H Density
	$H + HO_2 \rightarrow H_2O + O$	M	HO _x Destruction
	$H + O_2 + M \rightarrow HO_2$	M	HO _x Partitioning
OH	$OH + O \rightarrow H + O_2$	MLT	2nd Step in Catalytic Destruction of O ₃ ; Heat Source *****
			OH Moderates the NO and Cl Anthropogenic Cycles in the Strat.
	$OH + OH \rightarrow H_2O + O$	M	HO _x Destruction
	$OH + HO_2 \rightarrow H_2O + O_2$	M	HO _x Destruction.

MLT MEASUREMENTS OF H, OH, O AND H₂O ARE SPARSE.

CATALYTIC DESTRUCTION OF ODD OXYGEN BY ODD-HYDROGEN

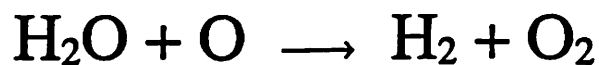
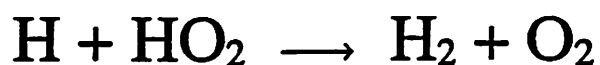
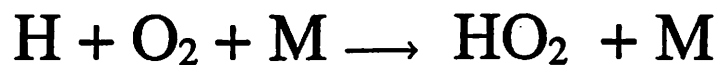
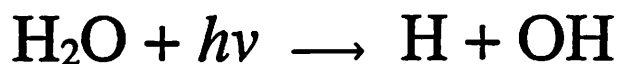


PRODUCTION AND DESTRUCTION OF ODD-HYDROGEN RADICALS

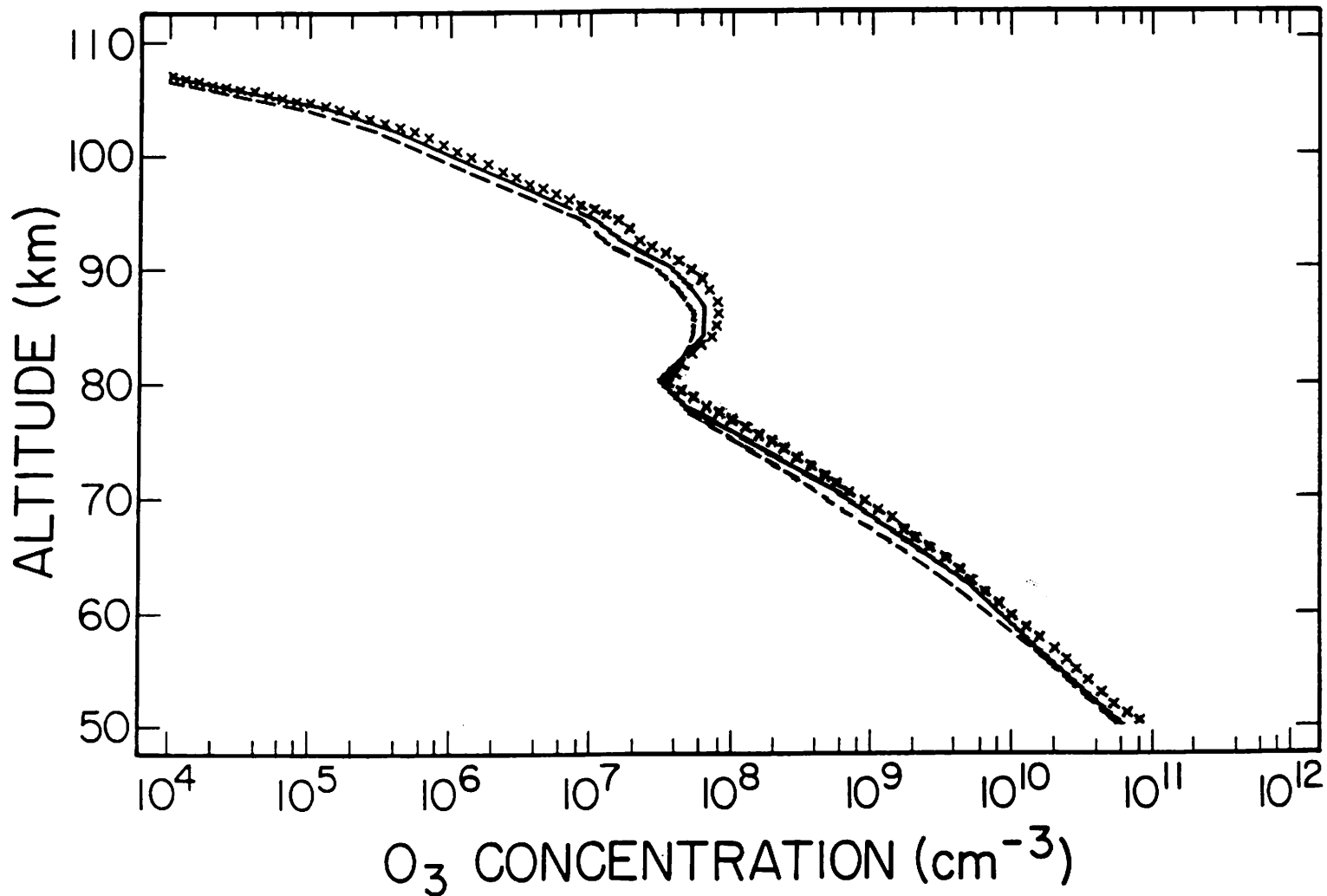


WATER VAPOR

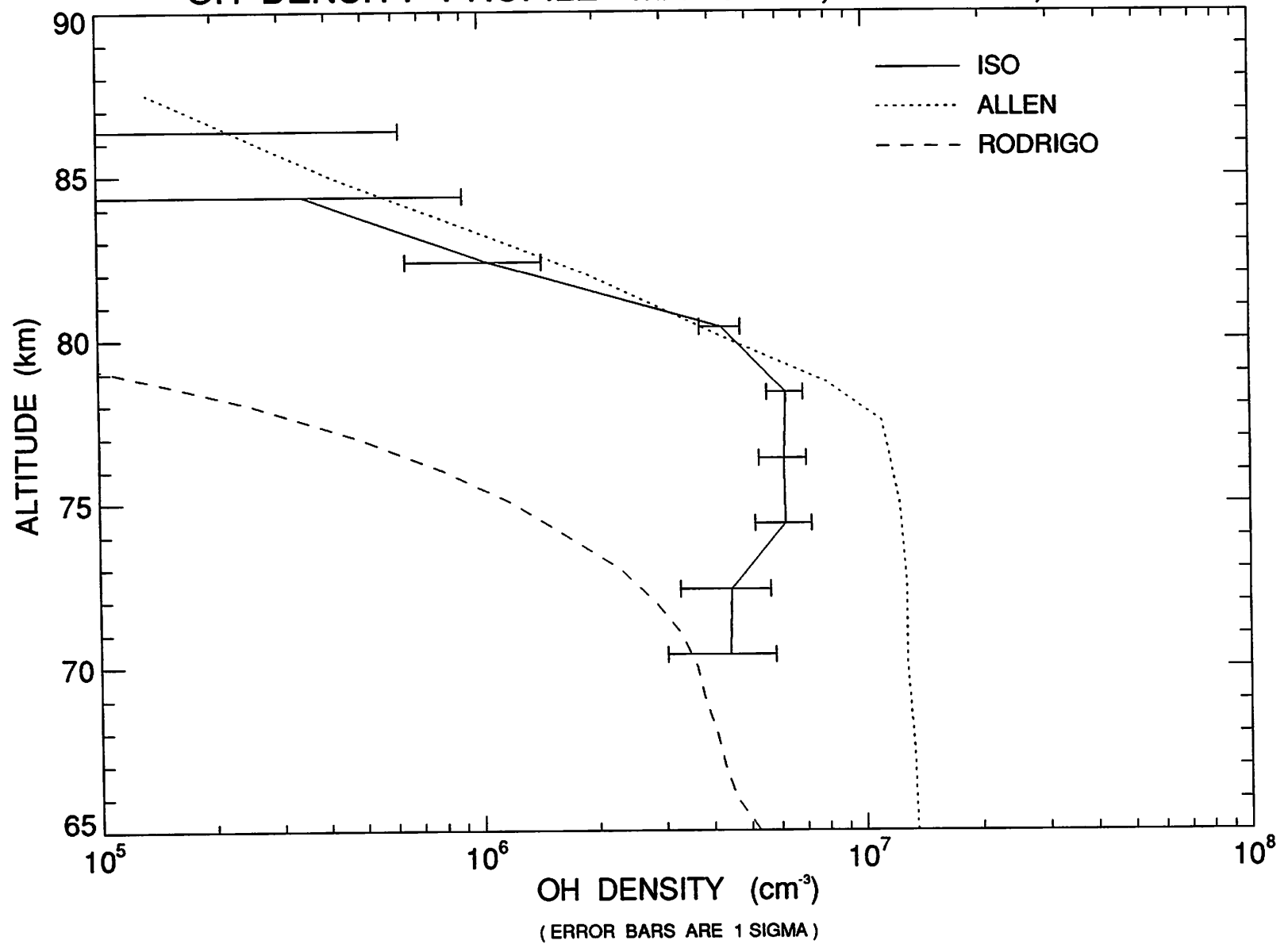
The upward transport of H₂O is balanced by photochemical conversion to H and H₂ via



In the paper "The Vertical Distribution of Ozone in the Mesosphere and Lower Thermosphere" by M. Allen, J. I. Lunine, and Y. L. Yung (*Journal of Geophysical Research*, 89(D3), 4841–4872, 1984) the shading in Figures 11 and 12 was not reproduced. Both figures are reproduced in better detail below. See the original article for captions.



OH DENSITY PROFILE - MARCH 30, LST 15:20, 39°N



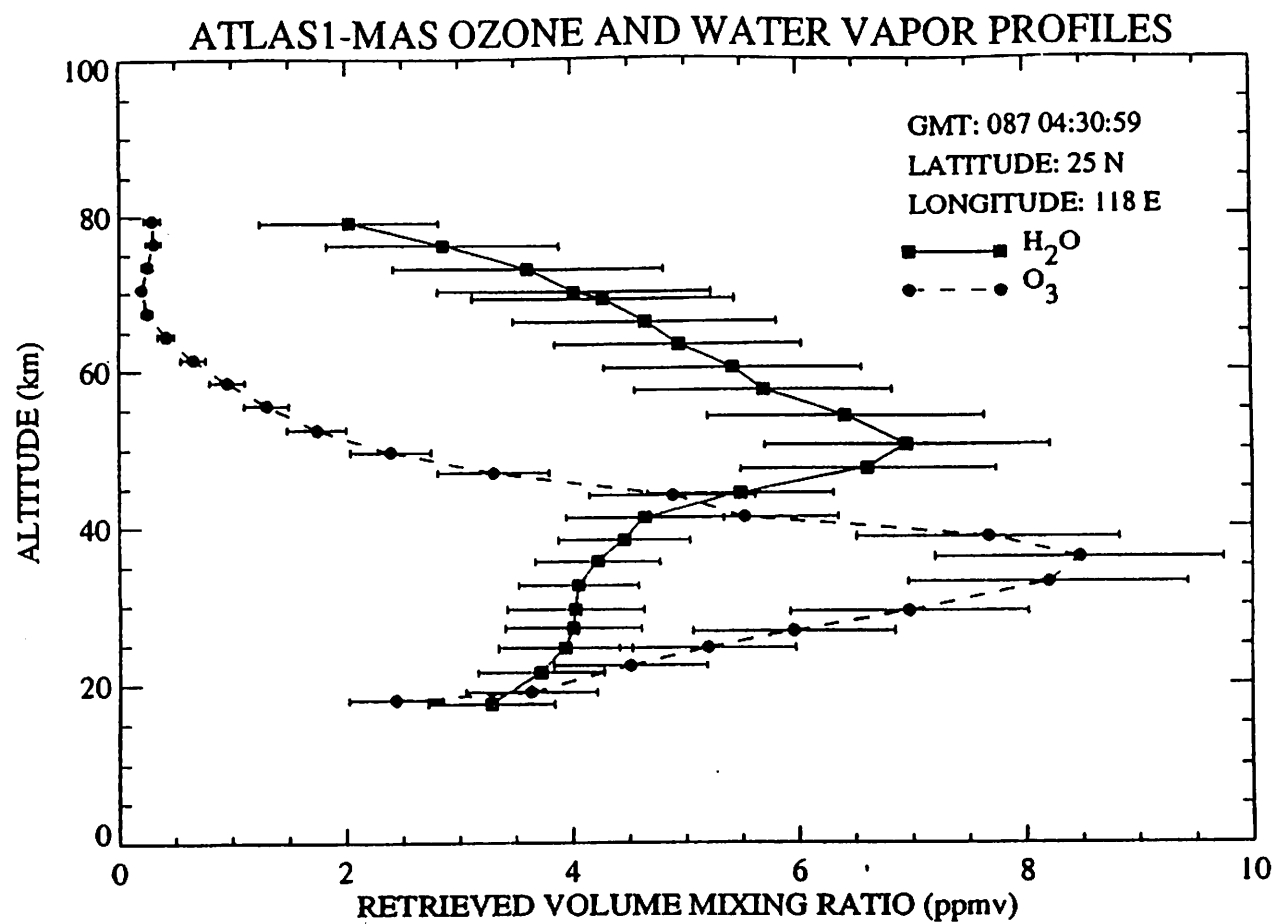
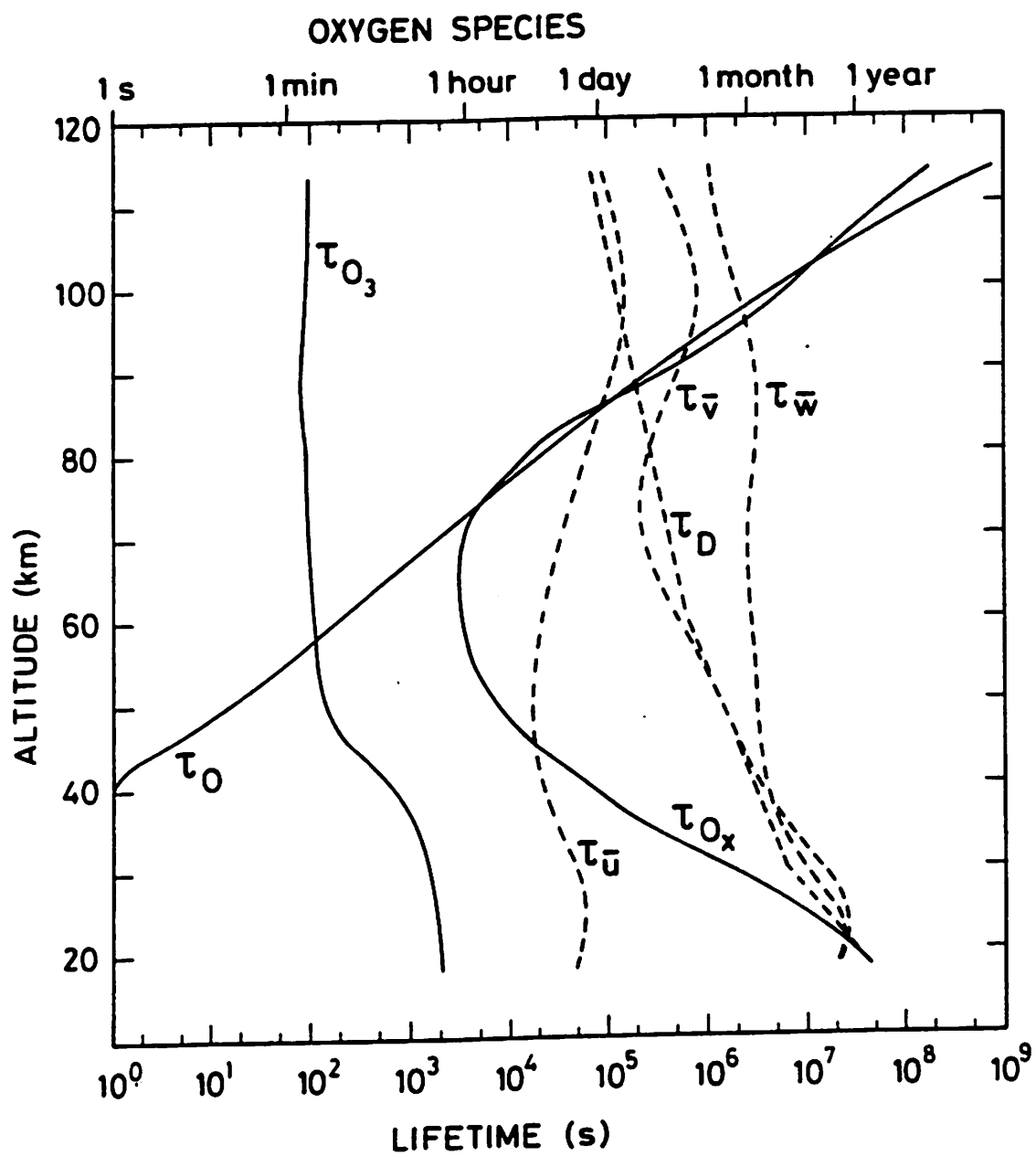
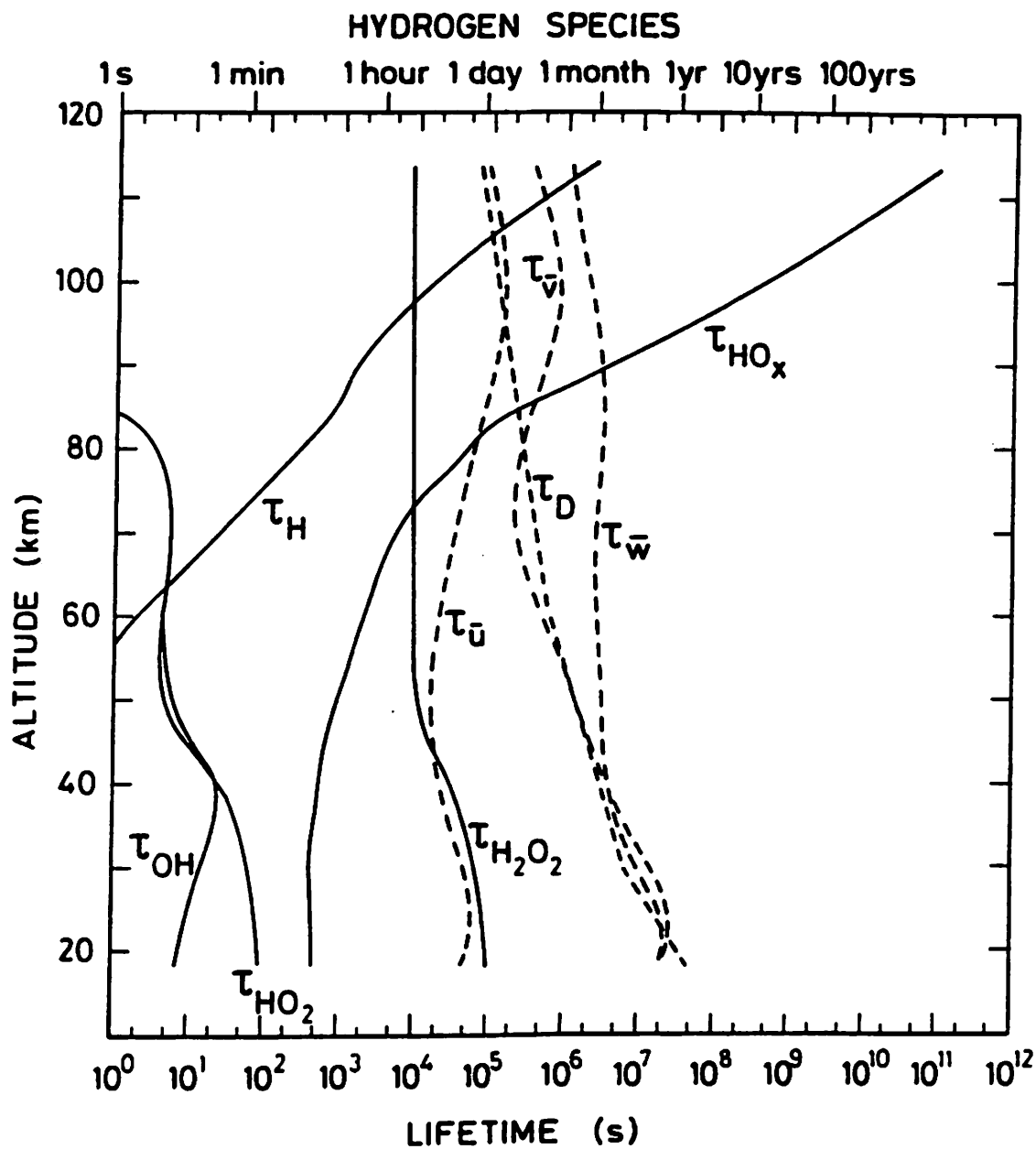


Figure 5



Photochemical lifetimes of O_x , O_3 , and O , and characteristic transport lifetimes.



Photochemical lifetimes of HO_x , H, OH, HO_2 , and H_2O_2 , and the time constants for transport.

Neutral atmospheric composition (60–220 km)

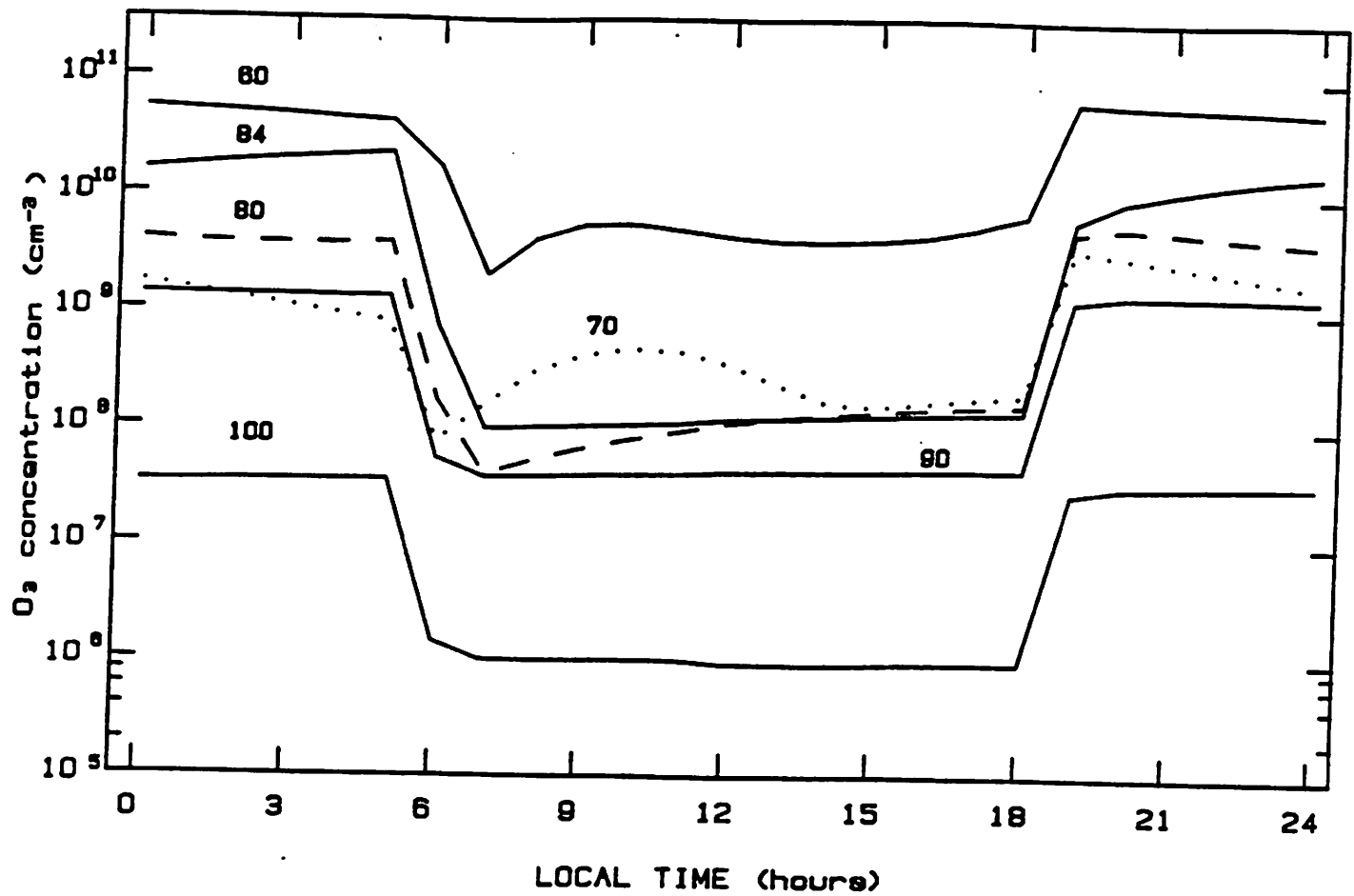


FIG. 13. DIURNAL VARIATION OF OZONE AT SELECTED ALTITUDES.

Neutral atmospheric composition (60–220 km)

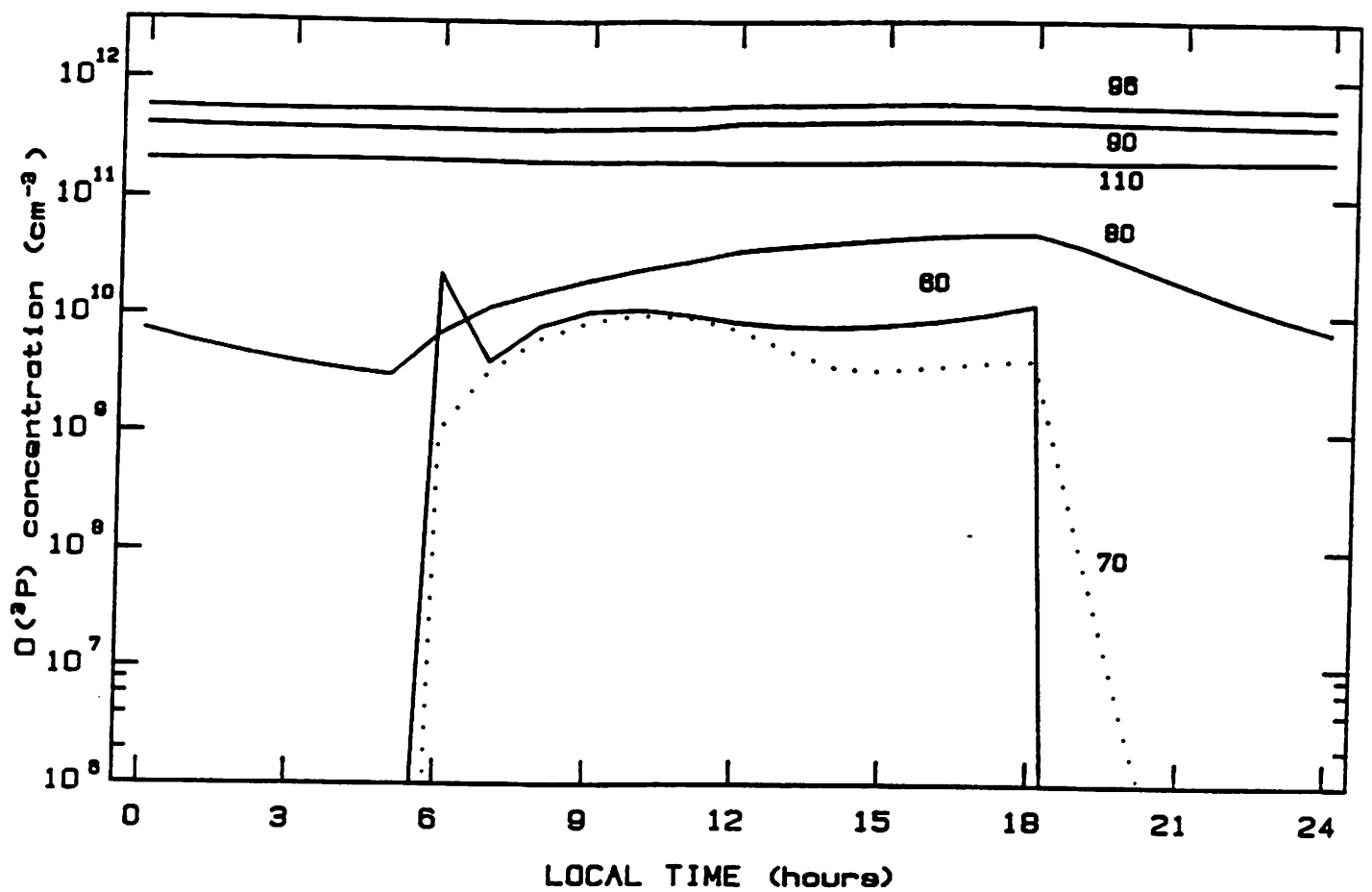


FIG. 11. DIURNAL VARIATION OF $O(^3P)$ AT SELECTED ALTITUDES.

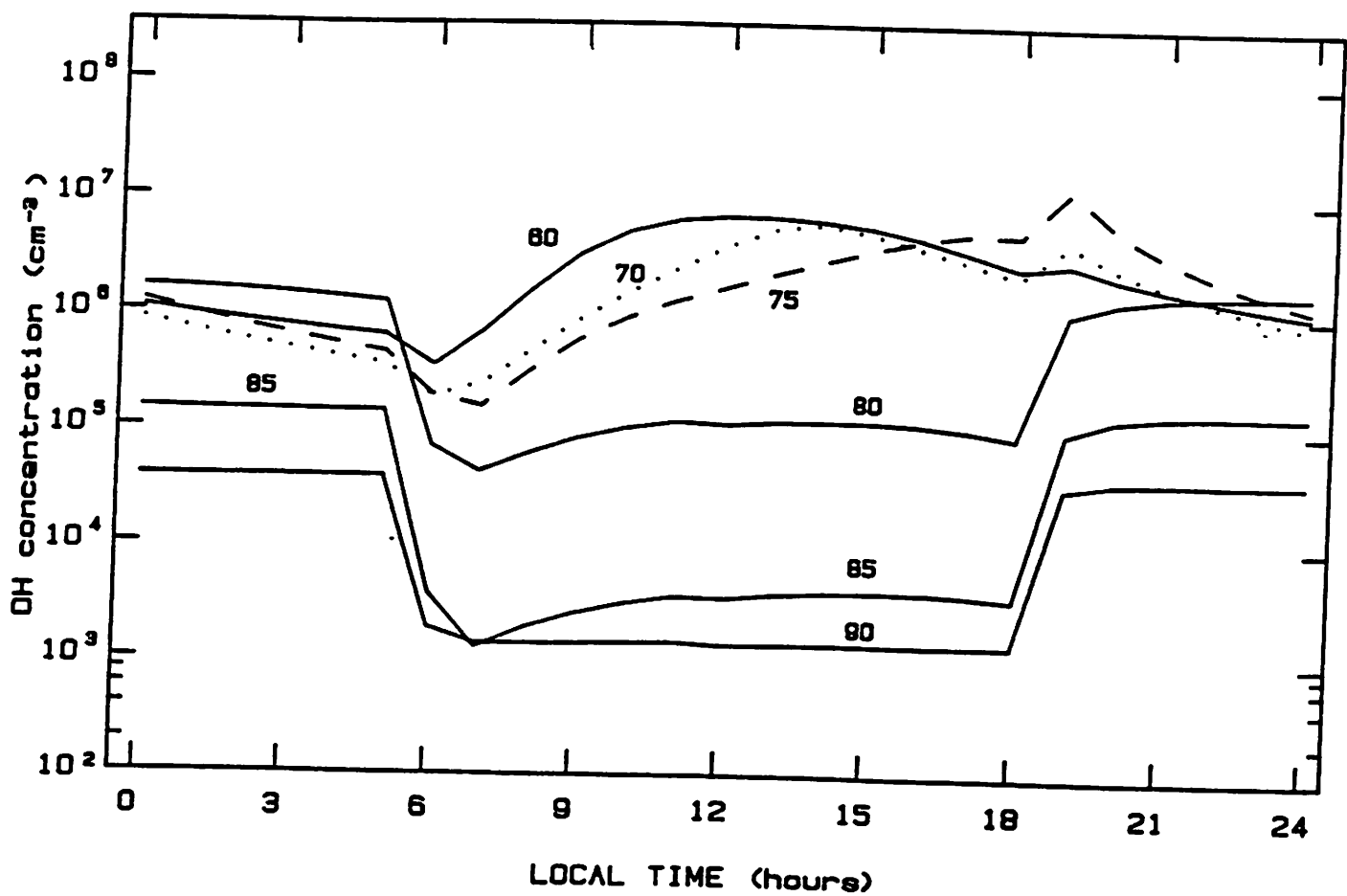


FIG. 15. DIURNAL VARIATION OF HYDROXYL MOLECULE AT SELECTED ALTITUDES.

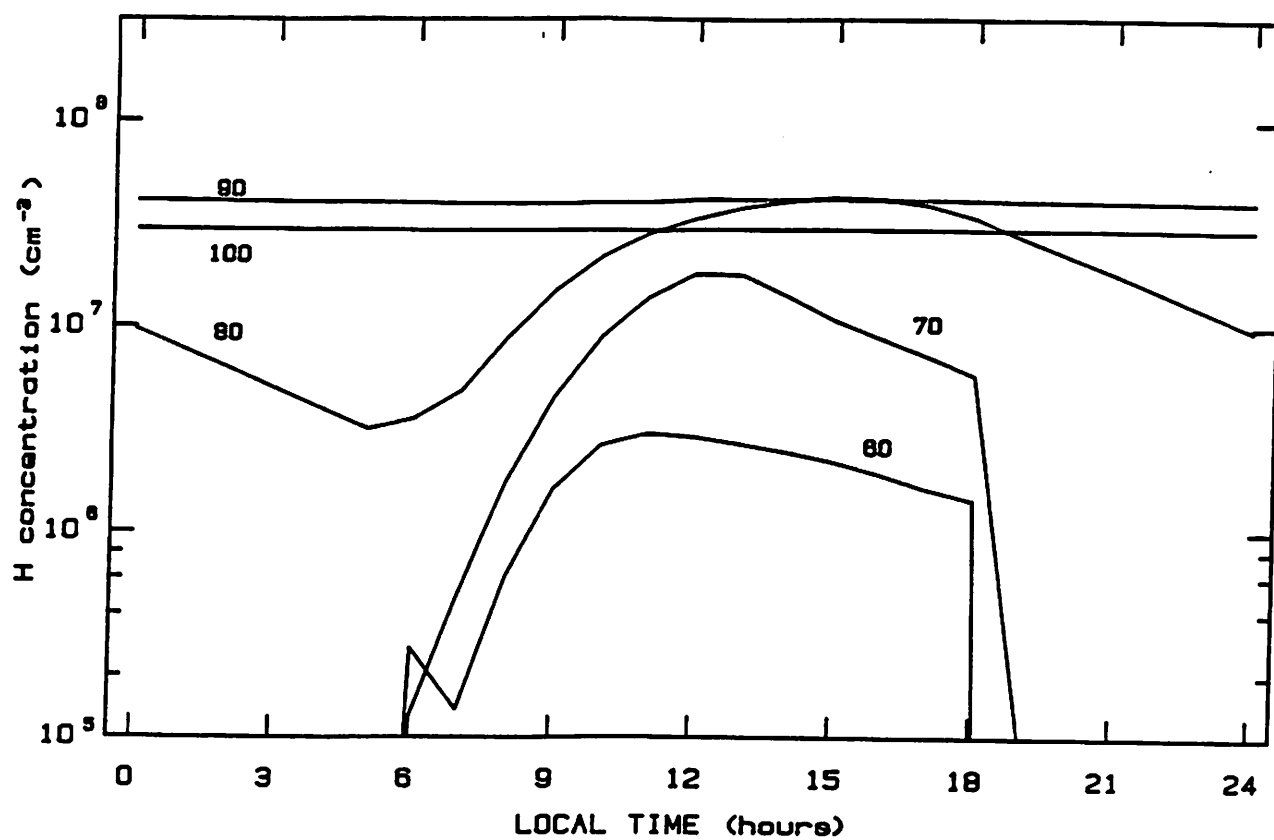


FIG. 17. DIURNAL VARIATION OF ATOMIC HYDROGEN AT SELECTED ALTITUDES.

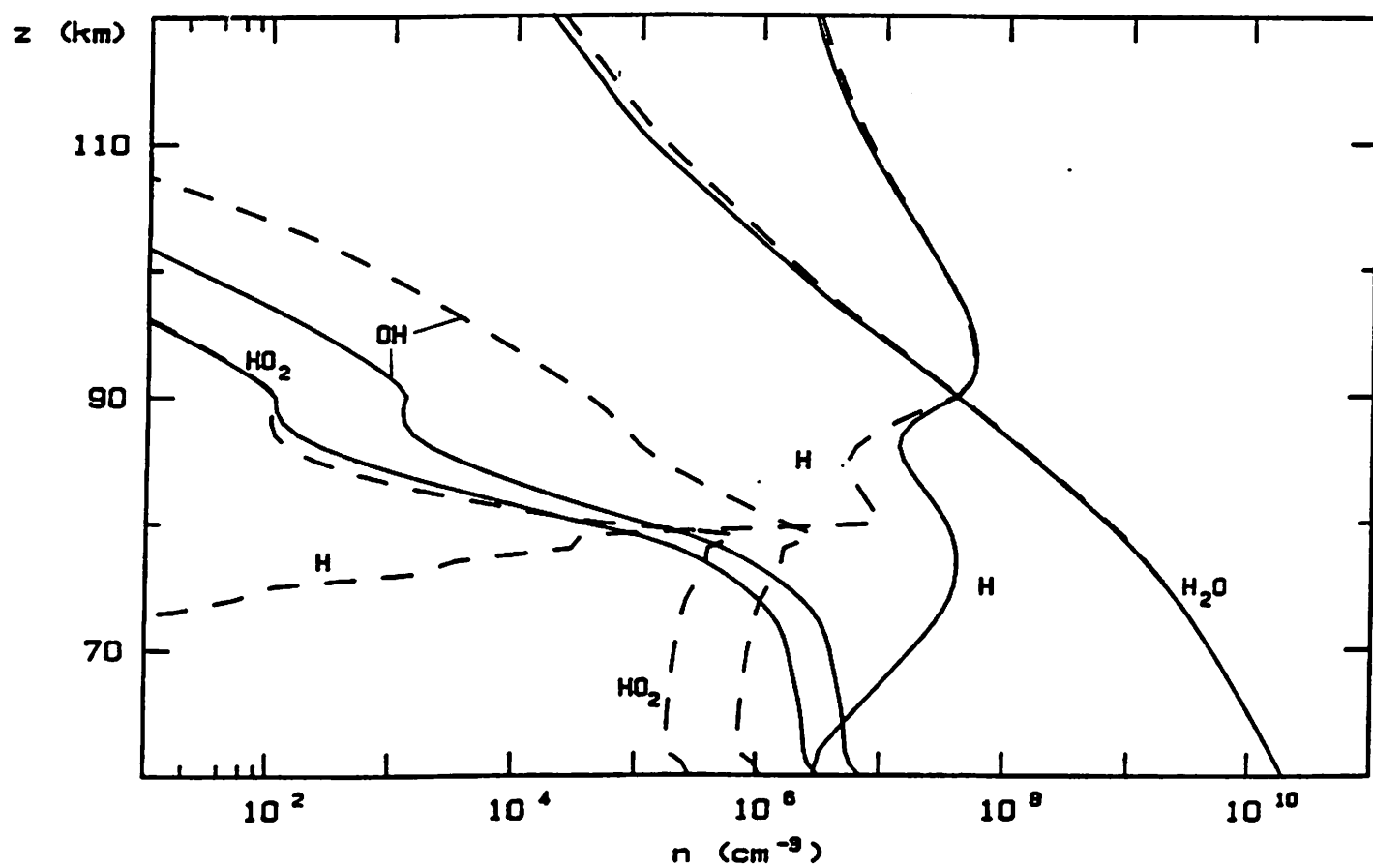


FIG. 14. H-COMPOUNDS CONCENTRATION PROFILES.
Solid lines, noon. Dashed lines, midnight.

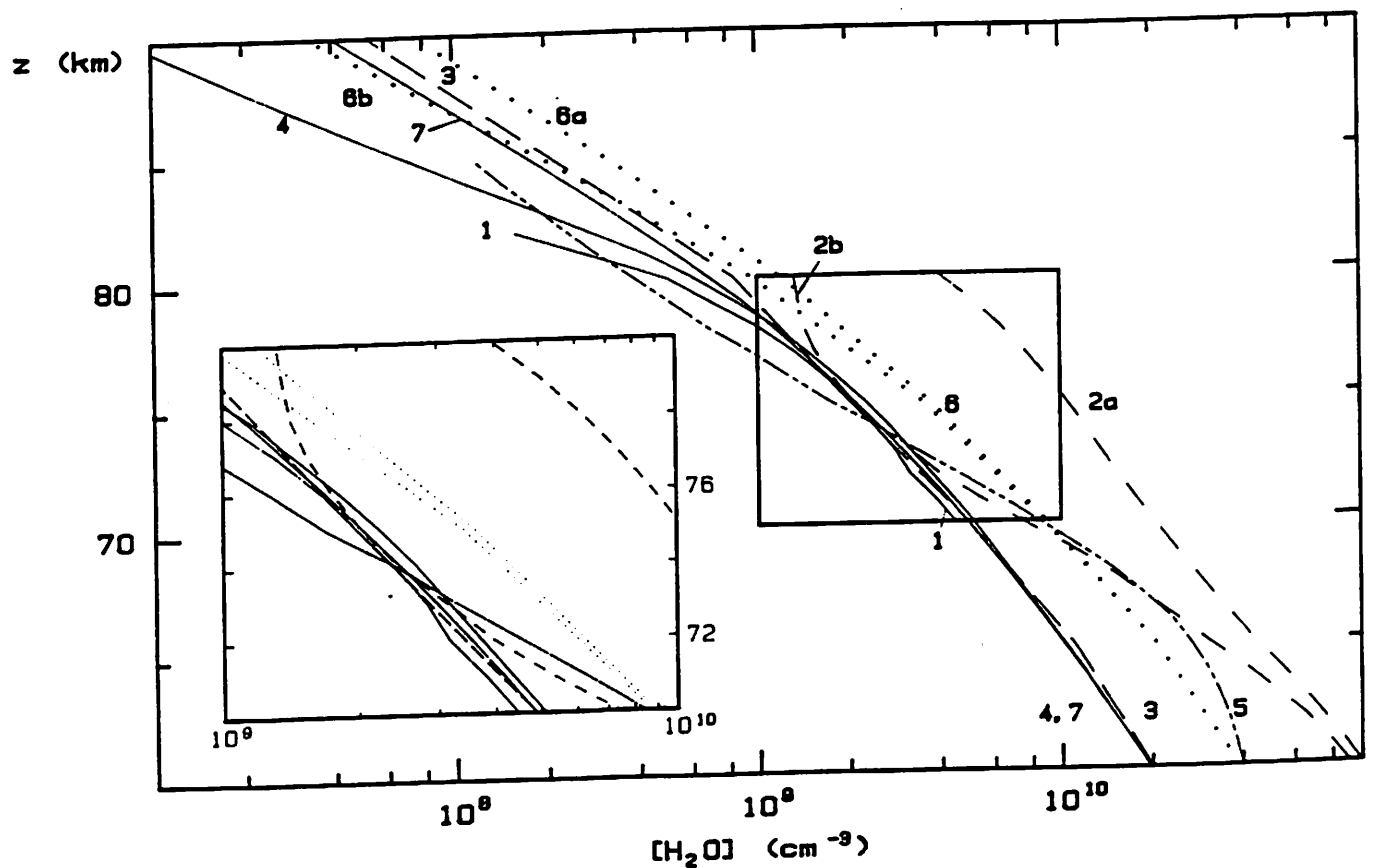
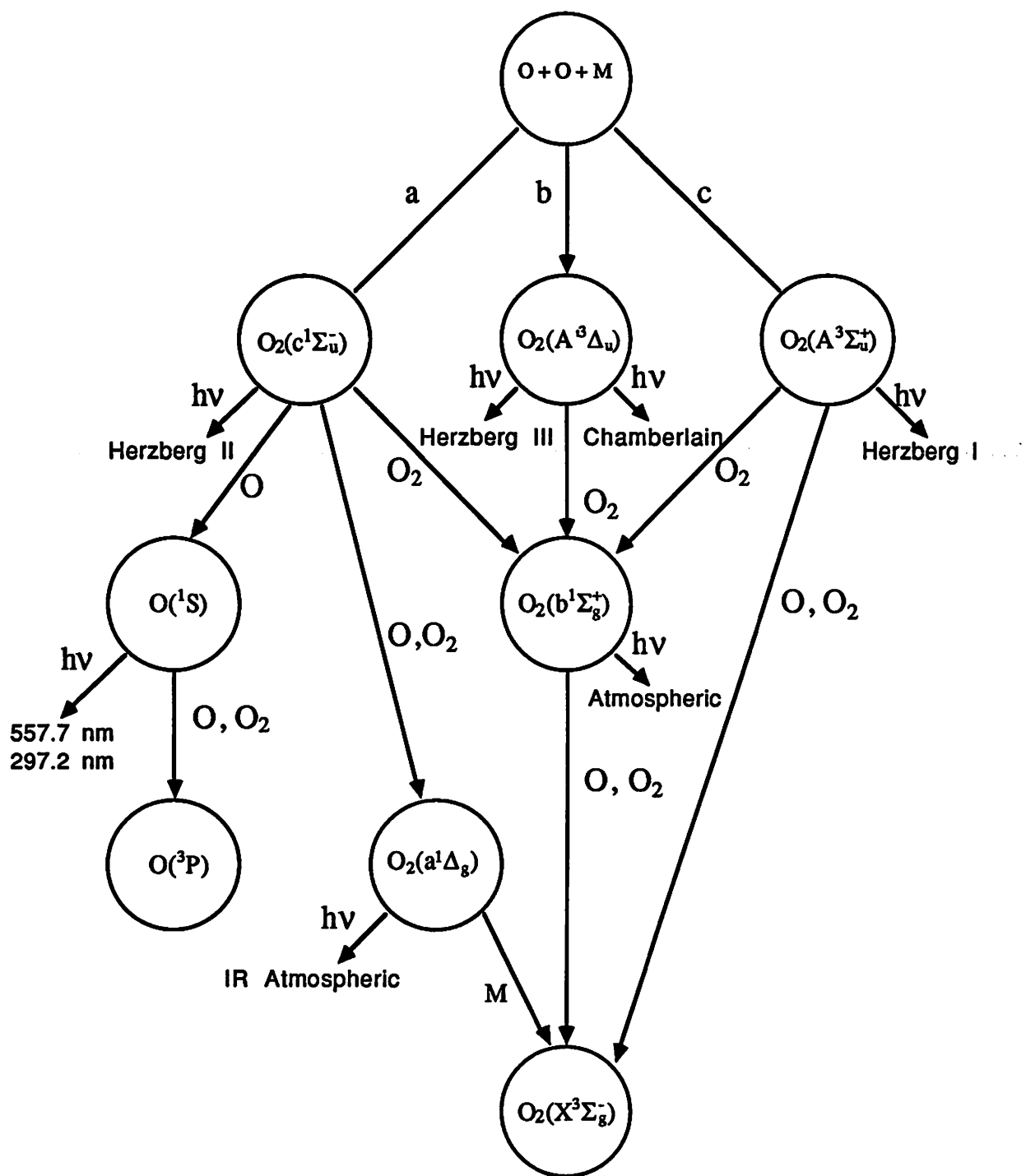


FIG. 18. DIFFERENT WATER VAPOR CONCENTRATION PROFILES.

Curve 1: Swider and Narcisi (1975). Curves 2a and b: Radford *et al.* (1977). Curve 3: Keneshea *et al.* (1979). Curve 4: Battaner and Rodrigo (1981). Curve 5: Gibbins *et al.* (1982). Curves 6a and b: Solomon *et al.* (1982). Curve 7: This model.

MESOSPHERIC METASTABLE O₂
PHOTOCHEMISTRY

METASTABLE O₂ NIGHTTIME CHEMISTRY



EXCITATION MECHANISMS

EXTENSIVELY STUDIED:

BATES, 1964; LLEWELLYN *ET AL.*, 1979; THOMAS *ET AL.*, 1979; THOMAS, 1981, MURTAGH *ET AL.*, 1986a, b; KRASNOPOLSKY, 1986; BATES, 1988a, b, 1992.

RECENT MEASUREMENTS SUPPORT THE DIRECT EXCITATION THROUGH THREE-BODY O RECOMBINATION.

THOMAS, 1981; *ET AL.*, 1986a (ETON CAMPAIGN); SISKIND AND SHARP, 1991.

MODEL RESULTS:

PRODUCTION EFFICIENCY (ϵ) AND QUENCHING RATES (K)

—→ ABSOLUTE INTENSITIES

LOW ϵ AND K —→ LOWER PEAK EMISSION HEIGHTS

GROUNDBASED AND ROCKETBORNE AIRGLOW MEASUREMENTS —→ LAB QUENCHING RATES ARE LOW

CONFIRMED BY RECENT SRI RESULTS FOR $O_2(A)$

$V' = 7, 8, 9$ FOR O_2 AND N_2 —→ HIGH RATES.

PHOTOMETRIC ROCKET RESULTS

HEIGHT PROFILES

SUGGEST ALTITUDE INVARIANT VIBRATIONAL DISTRIBUTION
(MEASUREMENTS FROM HIGH AND LOW VIBRATIONAL LEVELS)

DOUBLE PEAKED VIBRATIONAL DISTRIBUTION

CURRENT MODELS (BASED ON DEGEN, 1972)

3-BODY RECOMBINATION POPULATES $V' \geq 10$ FOLLOWED BY
SINGLE QUANTA COLLISIONAL DEACTIVATION.

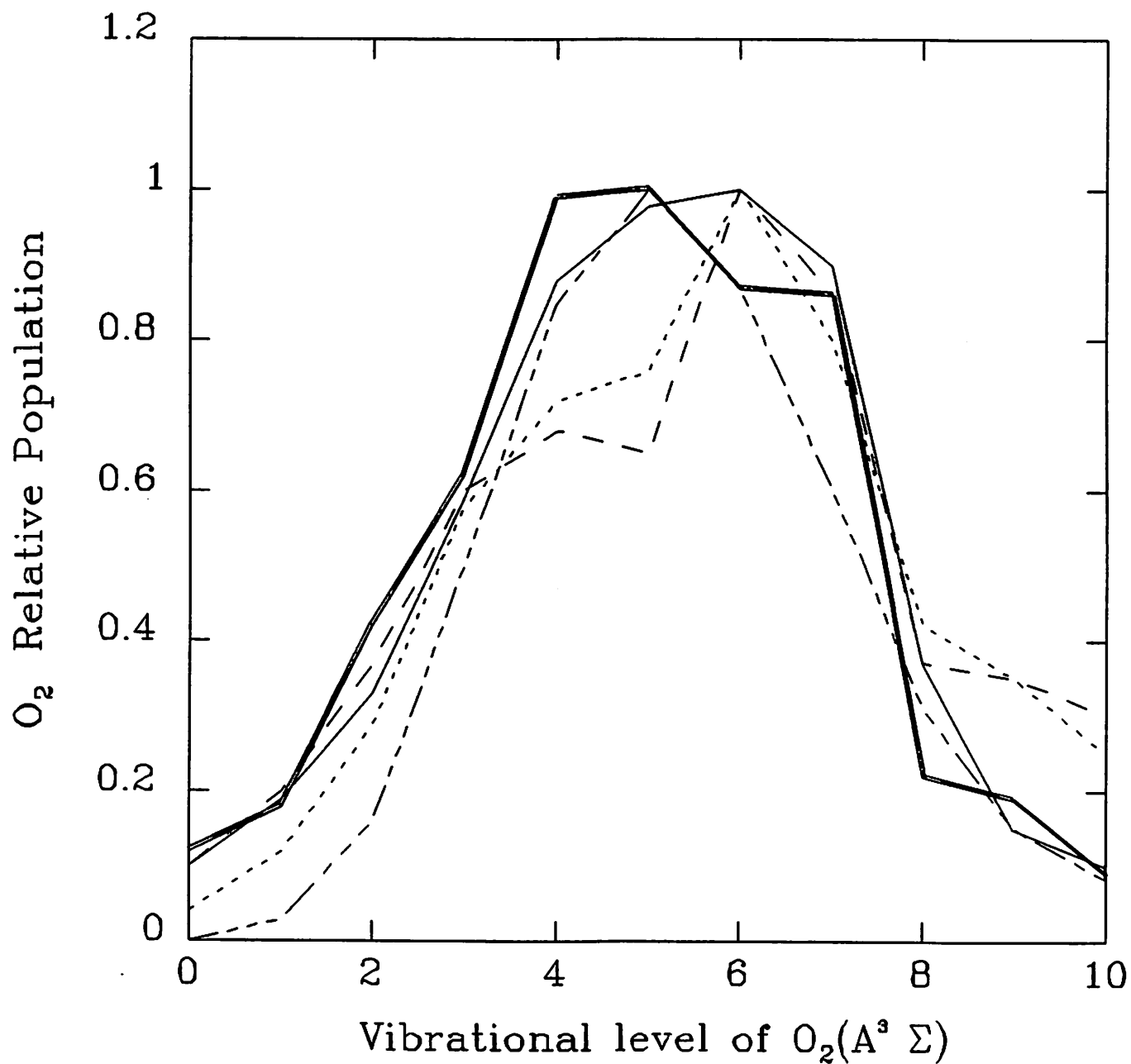
ALTITUDE INVARIANCE IN THE POPULATION DISTRIBUTION
REQUIRES THE CASCADE AND ELECTRONIC QUENCHING
SPECIES TO BE THE SAME

QUENCHING RATES $\gg$ RADIATIVE DECAY

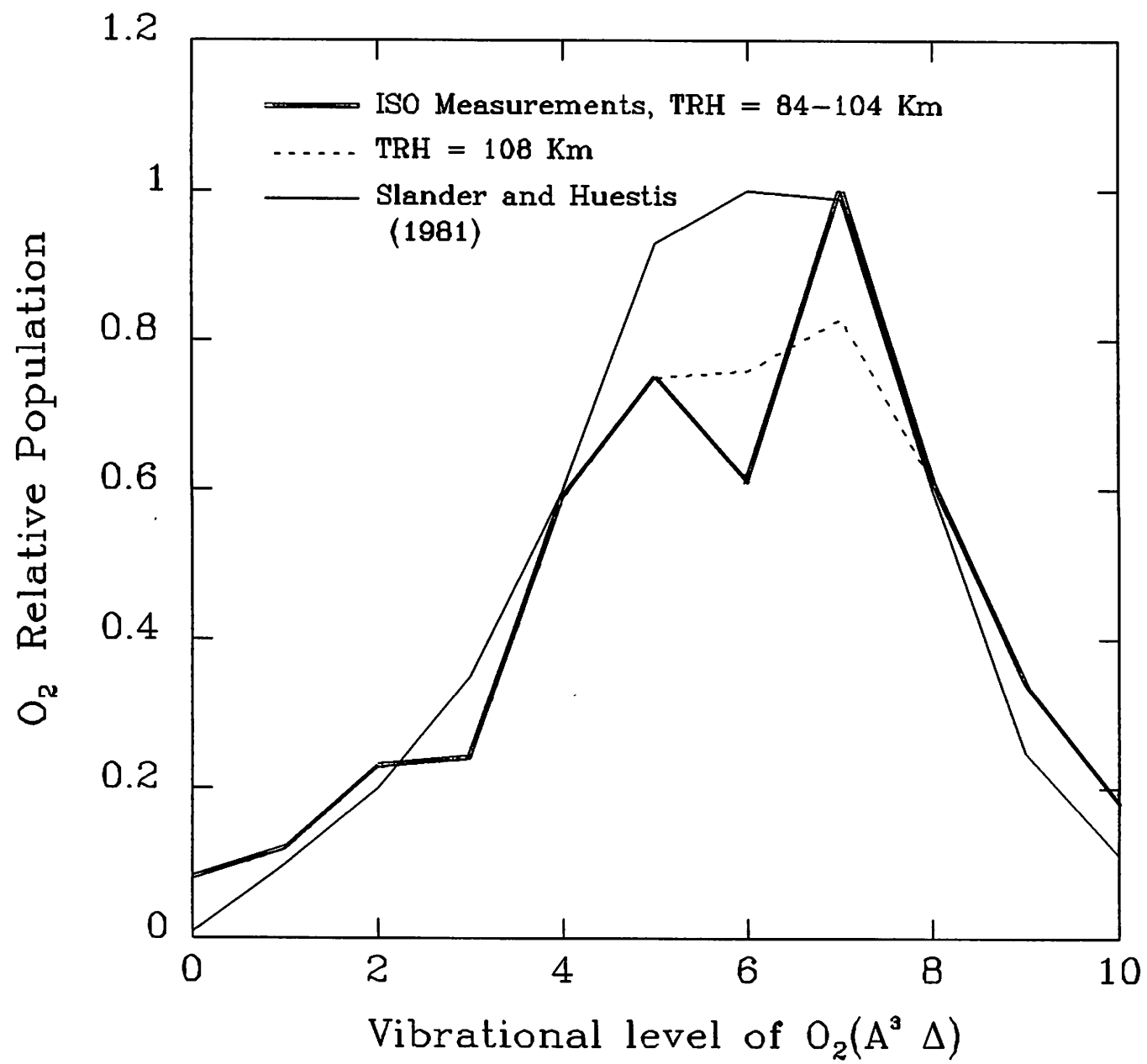
$\Rightarrow$

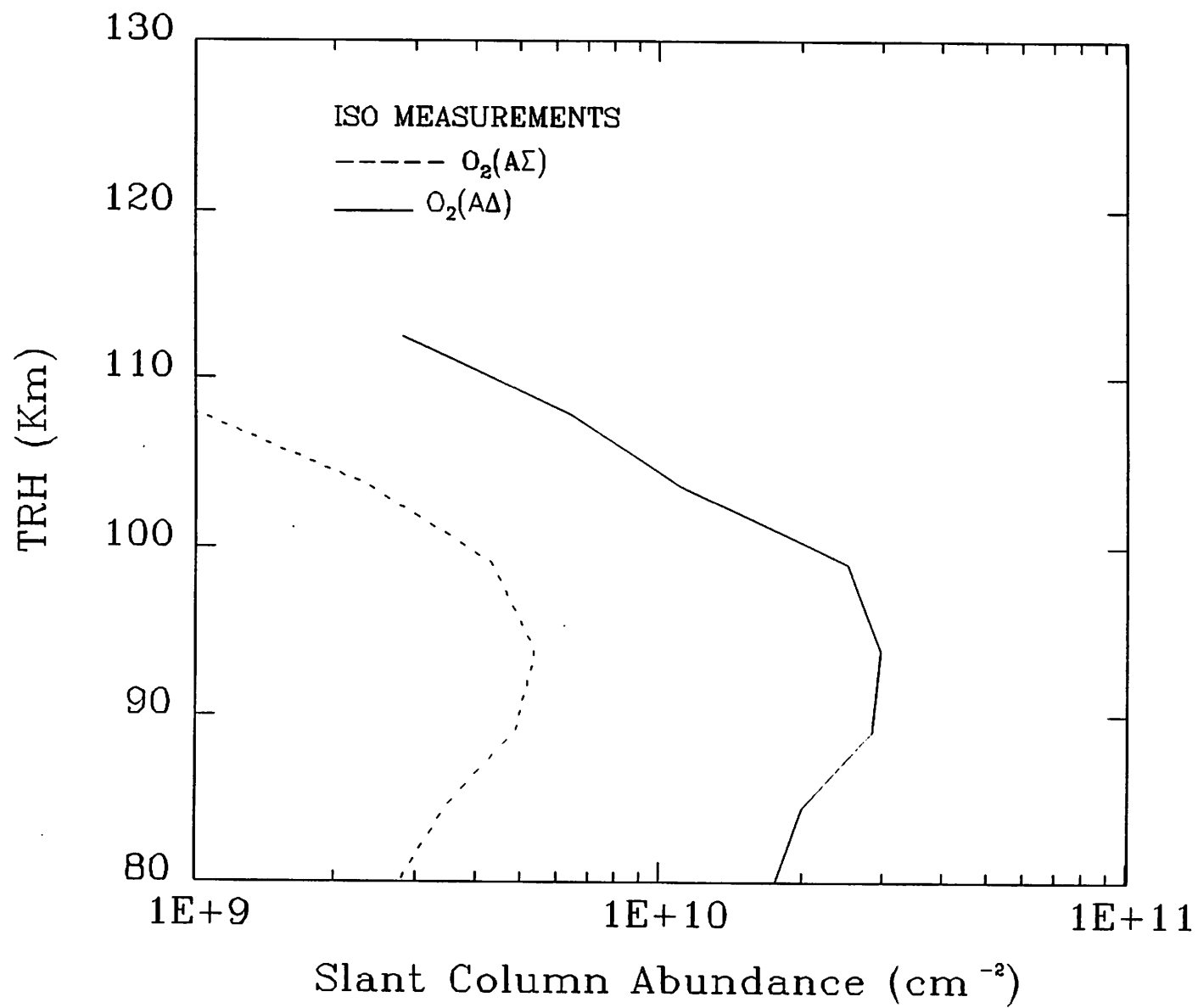
HIGH O₂ QUENCHING RATES AND HIGH YIELDS

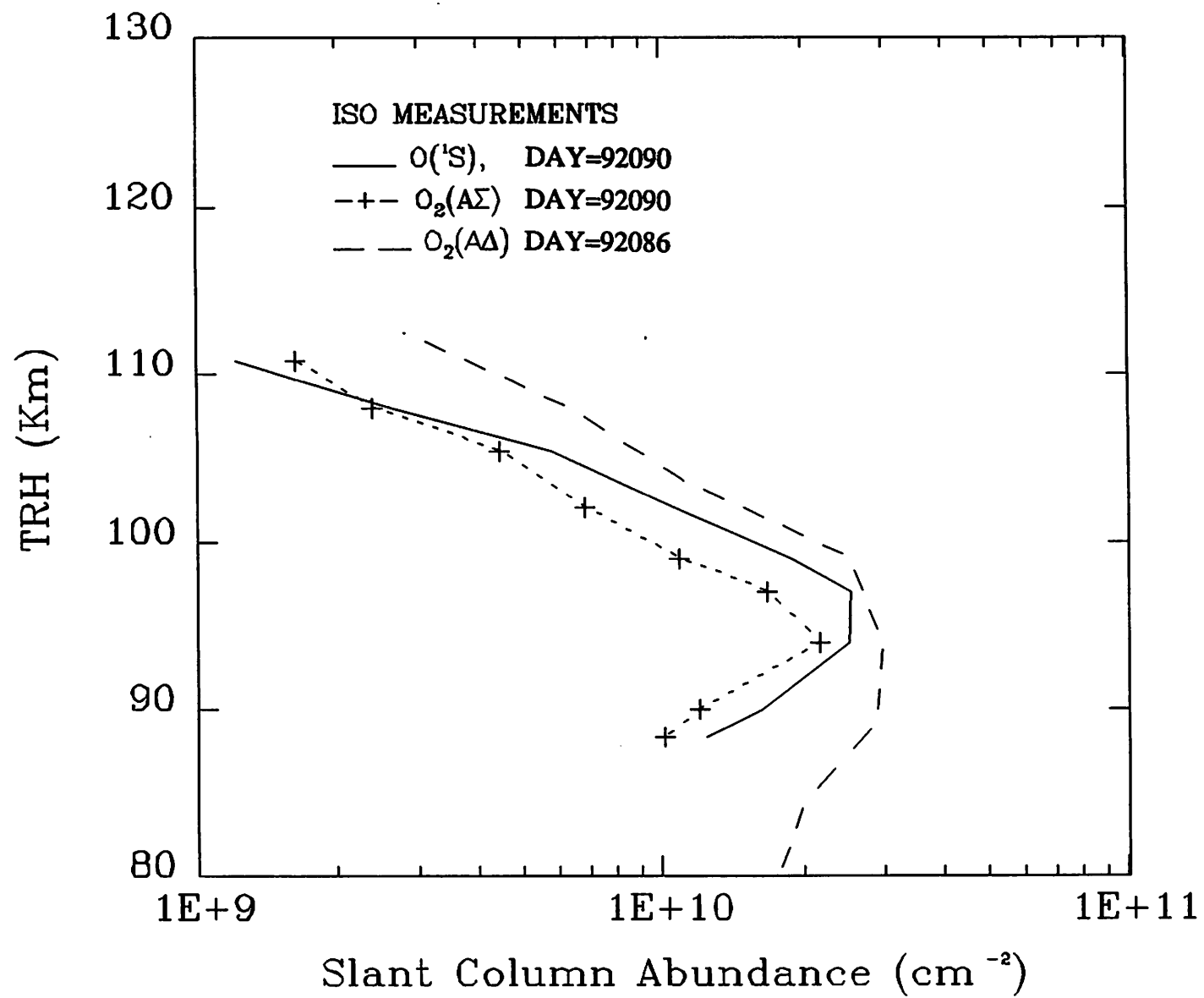
IF O QUENCHES ELECTRONIC STATES, IT MUST ALSO CAUSE
SINGLE QUANTA VIBRATIONAL QUENCHING



Vibrational populations. Thick solid curve: ISO distribution; Long dashed lines: Stegman and Murtagh [1991]; Thin solid line: Slanger and Heustis [1981]; Long dash, three short dashes: Lopez-Gonzales *et al.* [1992]: Model with electronic deactivation vibration independent rate coefficients; Dotted Line: Lopez-Gonzales *et al.* [1992]: Model with electronic deactivation vibration dependent.







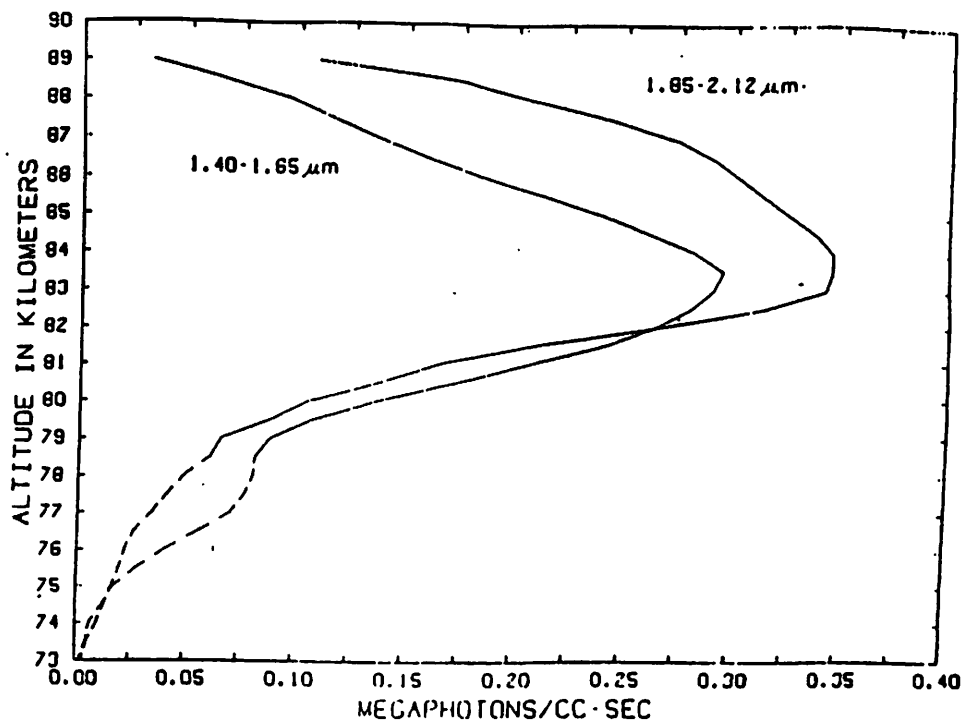


FIGURE 7A

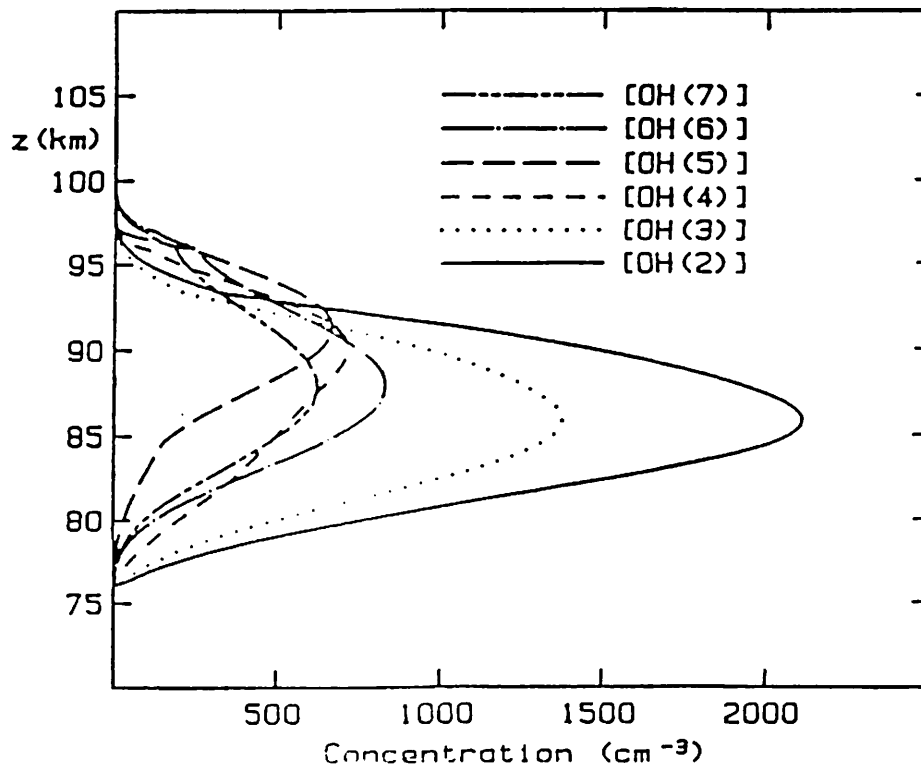
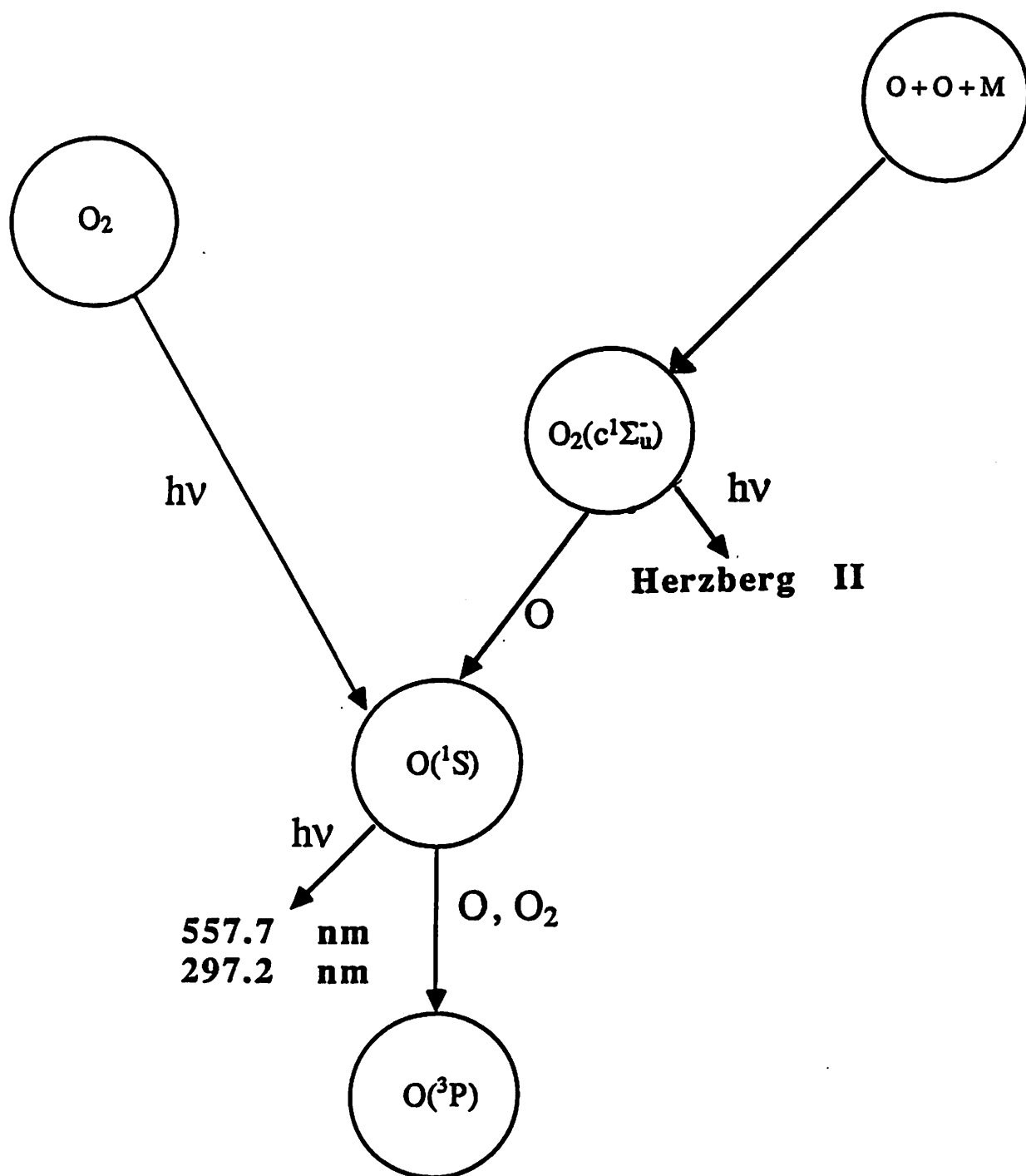
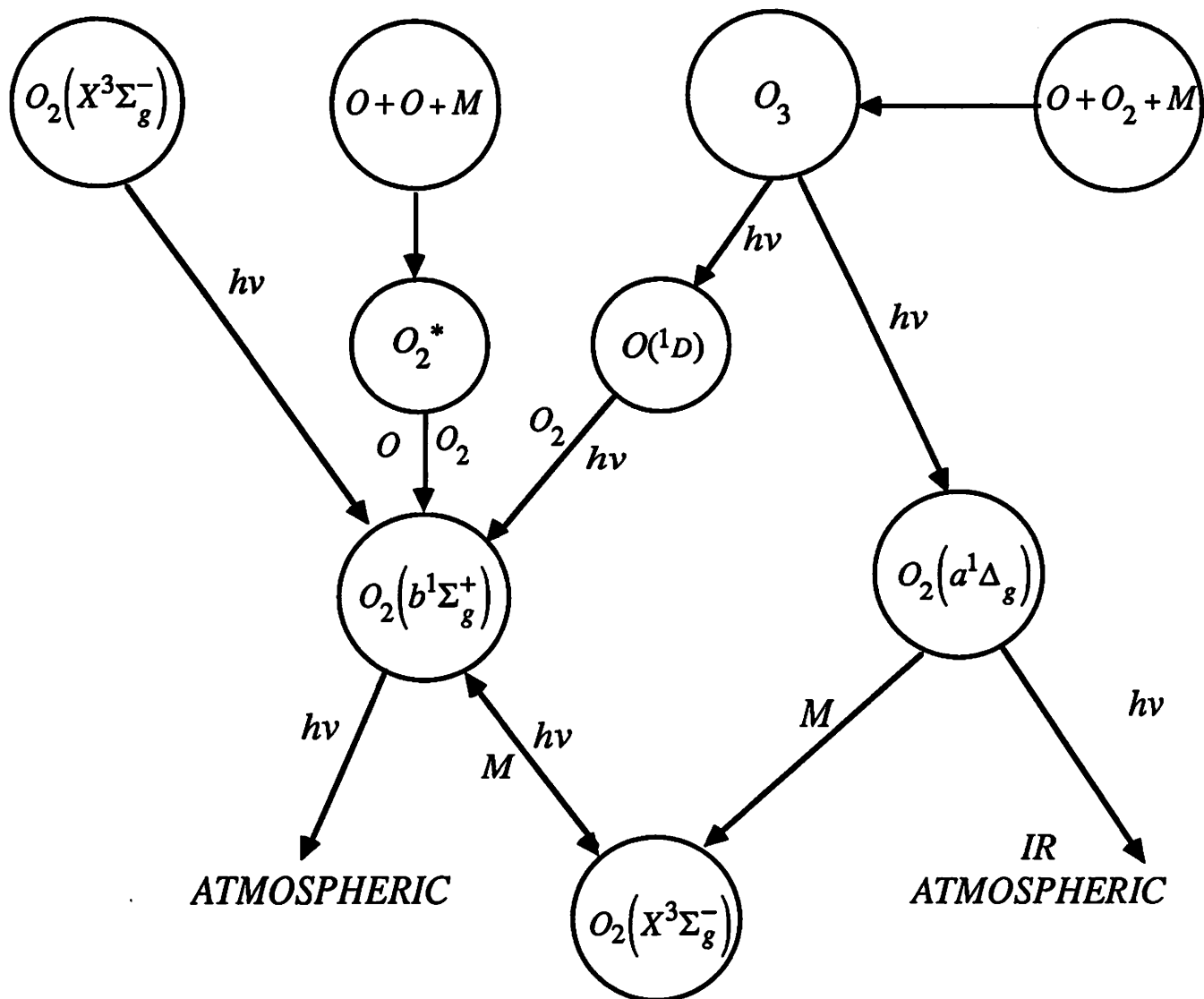


FIGURE 7B

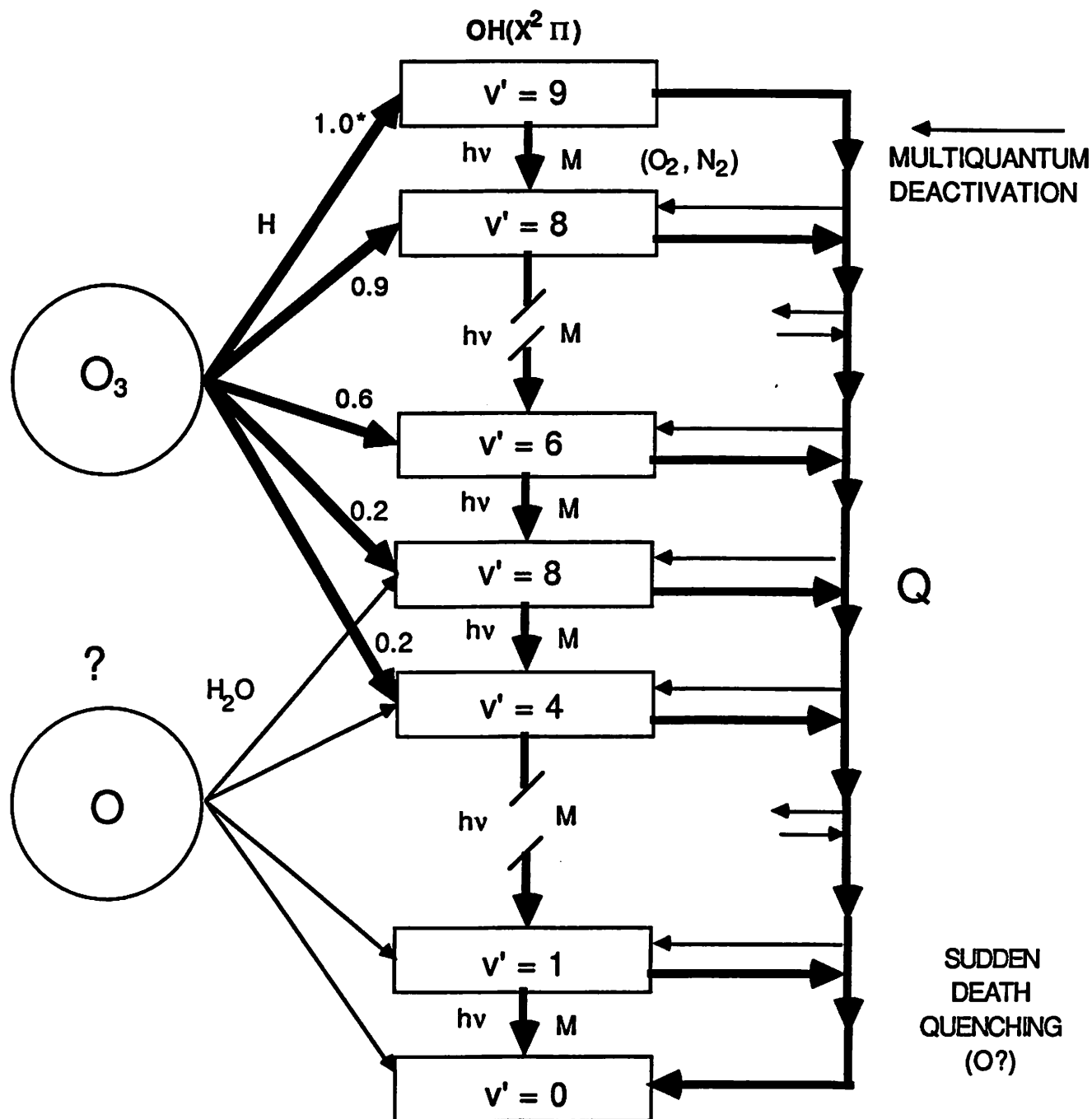
Metastable O₂ Daytime O(¹S) Chemistry



DAYTIME O₂ ATMOSPHERIC BANDS



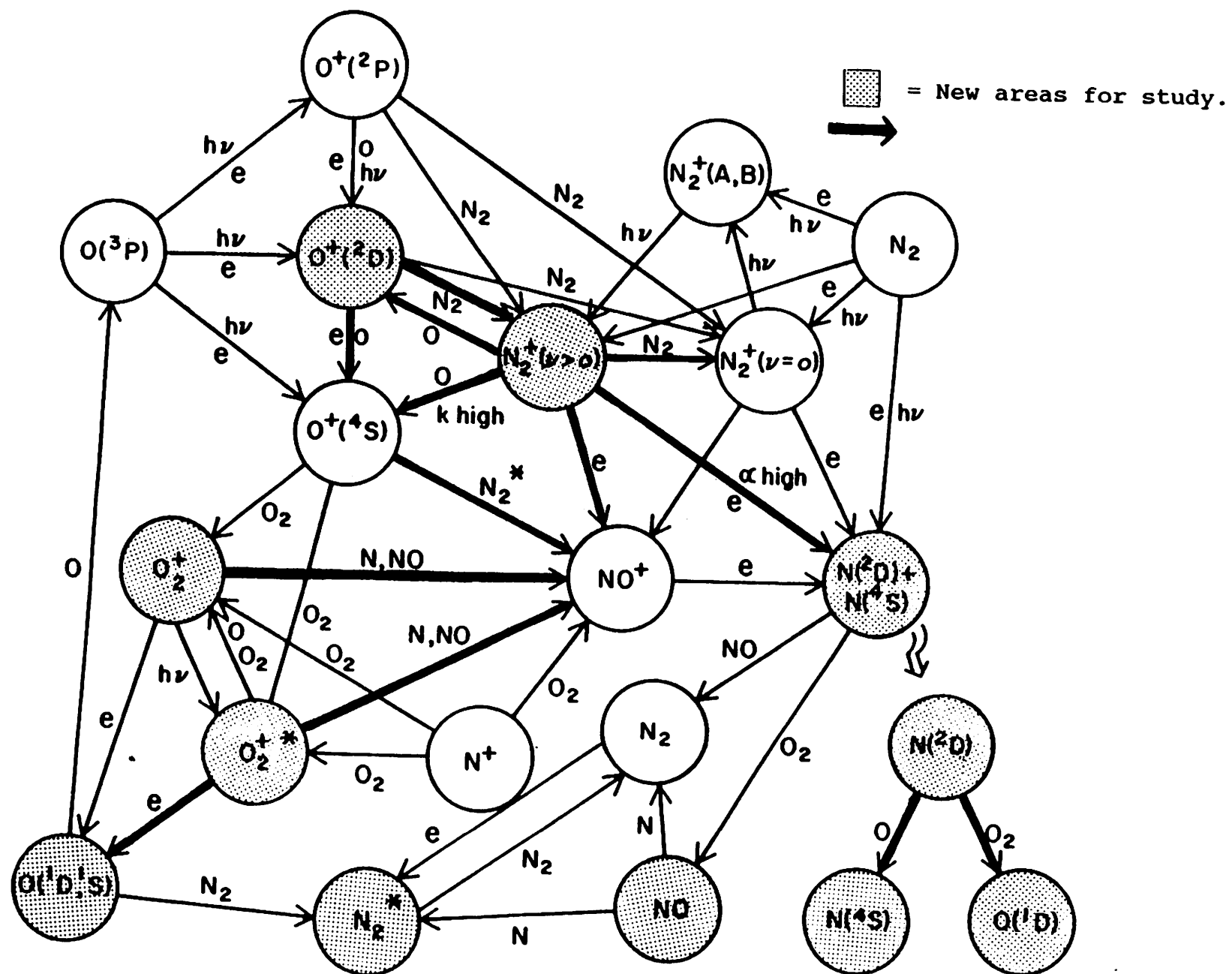
PHOTOCHEMISTRY OF VIBRATIONALLY EXCITED HYDROXYL



***BRANCHING RATIOS: McDade and Llewellyn (1987), Ohoyama et al. (1985)**

UNCERTAINTIES:

1. WHETHER $\text{HO}_2 + \text{O}$ IS A SOURCE.
2. COLLISIONAL DEACTIVATION RATE COEFFICIENTS.
3. ABSOLUTE TRANSITION PROBABILITIES
4. PRODUCTS OF COLLISIONAL DEACTIVATION AS A FUNCTION OF SPECIES.



Schematic of the thermospheric and ionospheric chemistry to be studied

