SUBMILLIMETER HETERODYNE SPECTROSCOPY AND REMOTE SENSING OF THE UPPER ATMOSPHERE

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ABSTRACT

The submillimeter region is rich with spectral lines of atmospheric molecules. Remote sensing by submillimeter heterodyne spectroscopy can provide measurements for studying global change and processes in Earth's atmosphere.

MICROWAVE LIMB SOUNDING

Microwave limb sounding using submillimeter wavelength heterodyne spectroscopy from orbiting satellites is a powerful tool for global-scale studies of Earth's stratosphere, mesosphere and lower thermosphere[1]. It is an outgrowth of microwave atmospheric remote sensing initiated in the 1970's [2]. A millimeter wavelength Microwave Limb Sounder (MLS) experiment is on NASA's Upper Atmosphere Research Satellite to be launched in 1991. A submillimeter MLS is being studied for the future Earth Observing System (EOS).

Atmospheric thermal emission spectra at millimeter and submillimeter wavelengths are measured as the instrument field-of-view (FOV) is scanned through the limb from above. Atmospheric profiles of molecular abundances, temperature, pressure, wind, and magnetic field can be determined from the measured emission spectra. Intensity of the emission can provide abundance and temperature. Measured linewidths, and emission from temperature insensitive O_2 lines, can provide pressure. Differentiation of measured pressure with respect to height differential (inferred from the instrument FOV scan encoder) can also provide temperature through atmospheric hydrostatic equilibrium (which relates temperature to pressure and height differential). Doppler shifts can provide wind; Zeeman splitting can provide magnetic field.

STRATOSPHERE SUBMILLIMETER SPECTRA

The submillimeter spectral region is very rich in atmospheric spectral lines due to rotational and spin transitions of molecules and certain atoms. The JPL spectral line catalog [3] contains spectroscopic parameters for calculating signals from these transitions. The opacity of a stratospheric rotation-spin spectral line is proportional to $f\mu^2/Q_{rs}$, where f is the molecule's volume mixing ratio describing its abundance, μ is the molecule's permanent dipole moment describing its strength of interaction with electromagnetic radiation, and Q_{rs} is its partition function describing the approximate number of states over which the total molecular abundance is distributed. $f\mu^2/Q_{rs}$ is thus a useful 'figure of merit' indicating relative signal strengths expected from various molecule. This is valuable as a guideline to indicate what molecules might be measurable and, equally important, what molecules might introduce unwanted spectral interference. However, $f\mu^2/Q_{rs}$ should only be used as a 'guideline' as strengths of individual lines depend upon other factors (given in the JPL catalog) which generally require knowledge of the molecular spectrum. Table 1 lists stratospheric molecules and atoms in decreasing order of $f\mu^2/Q_{rs}$.

THE EOS MLS EXPERIMENT

Figure 1 gives the projected EOS MLS measurement capability. Measurement sensitivity as a function of height, and examples of scientific value of the data, are discussed in [1]. A 625–650 GHz Submillimeter Limb Sounder (SLS) for scientific studies of the stratosphere from balloon and aircraft has also been developed by J.C. Hardy, R.A. Stachnik and colleagues. The SLS is scheduled for a first flight in 1991, and will also provide valuable experience for EOS MLS.

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REFERENCES

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Table 1: Stratospheric molecules and atoms in descending order of $f\mu^2/Q_{rs}$. Molecules in the JPL catalog are identified by an entry in the SPECTAG column and by the symbol • in the plot. $HD^{17}O$, $N_2O(2\nu_2^0)$ and $N_2O(2\nu_2^2)$ have been added to the catalog since release of Version 3 in March 1991. Values of Q_{rs} given here for the following molecules have been reduced from that given in the catalog in order to account for unresolved overlapping lines in the stratospheric spectrum: ClO and BrO by 8×, HCN (all states and isotopes except $HC^{15}N$) by 3×, $HNO_3(\nu_9)$ by 2×.

$\log_{10} \frac{f\mu^2}{Q_{rs}}$	molecule or atom	JPL SPEC-TAG	μ (D)	Q_{rs} at 225 K	approx. max. strat-ospheric mixing ratio value $\equiv f$	ht/km
−6.4	O_2	32001	0.0186	1.64×10^{2}	2.1×10^{-1}	<∼90
−6.8	H_2O	18003	1.855	1.16×10^{2}	5.0×10^{-6}	50
−9.1	^{18}OO	34001	0.0186	3.47×10^{2}	8.6×10^{-4}	<∼90
−9.1	O_3	48004	0.5337	2.26×10^{3}	7.0×10^{-6}	35
−9.5	$H_2{}^{18}O$	20003	1.85	1.17×10^{2}	1.0×10^{-8}	50
−9.9	HF	20002	1.826	1.05×10^{1}	4.0×10^{-10}	35
−10.1	^{17}OO	33002	0.0186	3.47×10^{2}	1.5×10^{-4}	<∼90
−10.2	$H_2{}^{17}O$	19003	1.85	1.16×10^{2}	1.9×10^{-9}	50
−10.3	HDO	19002	1.732	9.56×10^{1}	1.5×10^{-9}	50
−10.3	OH	17001	1.667	6.03×10^{1}	1.0×10^{-9}	50
−10.4	$O_2(^1\Delta)$	32005	0.0372	1.13×10^{2}	3.0×10^{-6}	70
−10.5	$H^{35}Cl$	36001	1.109	6.09×10^{1}	1.5×10^{-9}	50
−10.7	$O_2(\nu_1)$	32002	0.0186	1.64×10^{2}	1.0×10^{-5}	<∼90
−10.8	CO	28001	0.1098	8.17×10^{1}	1.0×10^{-7}	50
−10.9	N_2O	44004	0.1608	3.74×10^{2}	2.0×10^{-7}	20
−11.0	$O_3(\nu_2)$	48005	0.5261	2.26×10^{3}	7.9×10^{-8}	35
−11.0	$H^{37}Cl$	38001	1.109	6.10×10^{1}	0.5×10^{-9}	50
−11.1	HCN	27001	2.984	1.06×10^{2}	1.0×10^{-10}	30
−11.3	^{16}O	16001	0.0186	6.324	1.0×10^{-7}	50
−11.3	$H_2O(\nu_2)$	18005	1.855	1.16×10^{2}	1.9×10^{-10}	50
−11.7	^{35}ClO	51002	1.298	2.85×10^{2}	3.0×10^{-10}	35
−11.8	^{18}OOO	50004	0.532	4.69×10^{3}	2.9×10^{-8}	35
−11.8	$O^{18}OO$	50003	0.532	2.29×10^{3}	1.4×10^{-8}	35
−12.0	$O_3(\nu_3)$	48006	0.532	2.26×10^{3}	9.0×10^{-9}	35
−12.0	HNO_3	63001	1.99	1.82×10^{4}	5.0×10^{-9}	25
−12.1	^{37}ClO	53002	1.239	2.90×10^{2}	1.0×10^{-10}	35
−12.2	$O_3(\nu_1)$	48006	0.532	2.26×10^{3}	9.0×10^{-9}	35
−12.5	NO	30008	0.1587	8.17×10^{2}	1.0×10^{-8}	40
−12.5	H_2CO	30004	2.331	1.87×10^{3}	1.0×10^{-10}	35
−12.5	$N_2O(\nu_2)$	44009	0.1608	3.74×10^{2}	4.6×10^{-9}	20
−12.6	HO_2	33001	1.541	2.84×10^{3}	3.0×10^{-10}	50
−12.7	OCS	60001	0.715	7.72×10^{2}	3.0×10^{-10}	20
−12.8	^{13}CO	29001	0.11	8.55×10^{1}	1.1×10^{-9}	50
−12.9	NO_2	46006	0.316	8.75×10^{3}	1.0×10^{-8}	40
−13.0	$HD^{18}O$	21001	∼1.73	9.58×10^{1}	3.0×10^{-12}	50
−13.0	$H^{13}CN$	28002	2.984	1.09×10^{2}	1.1×10^{-12}	30
−13.0	$O_3(2\nu_2)$	48007	0.519	2.26×10^{3}	9.1×10^{-10}	35
−13.0	^{18}OH	19001	1.667	6.06×10^{1}	2.0×10^{-12}	50
−13.1	HCN (ν_2^1)	27003	∼2.9	1.06×10^{2}	1.0×10^{-12}	30
−13.2	$O^{17}OO$	49001	0.532	1.30×10^{4}	2.6×10^{-9}	35
−13.2	$CH_3^{35}Cl$	50007	1.899	1.83×10^{4}	3.0×10^{-10}	20
−13.2	SO_2	64002	1.633	3.77×10^{4}	1.0×10^{-9}	<∼30
−13.3	^{17}OOO	49002	0.532	2.73×10^{4}	5.2×10^{-9}	35
−13.3	$HO^{35}Cl$	52006	1.471	6.18×10^{3}	1.6×10^{-10}	35
−13.3	^{15}NNO	45008	∼0.16	3.87×10^{2}	7.3×10^{-10}	20
−13.3	$N^{15}NO$	45007	∼0.16	3.74×10^{2}	7.3×10^{-10}	20
−13.3	$HNO_3(\nu_9)$	63003	∼2.0	1.82×10^{4}	2.7×10^{-10}	25
−13.4	^{81}BrO	97001	1.794	3.69×10^{2}	5.0×10^{-12}	35
−13.4	^{79}BrO	95001	1.794	3.68×10^{2}	5.0×10^{-12}	35
−13.4	H_2O_2	34004	1.573	5.78×10^{3}	1.0×10^{-10}	35
−13.5	$C^{18}O$	30001	0.11	8.58×10^{1}	2.0×10^{-10}	50
−13.5	$HC^{15}N$	28003	2.984	1.09×10^{2}	3.7×10^{-13}	30
−13.6	$NN^{18}O$	46007	∼0.16	3.96×10^{2}	4.0×10^{-10}	20
−13.6	$HNO_3(\nu_7)$	63002	∼2.0	1.82×10^{4}	1.3×10^{-10}	25
−13.7	$^{18}OOO(\nu_2)$	50006	0.532	5.00×10^{3}	3.5×10^{-10}	35
−13.7	$O^{18}OO(\nu_2)$	50005	0.532	2.45×10^{3}	1.8×10^{-10}	35
−13.7	$HO^{37}Cl$	54005	1.471	6.29×10^{3}	5.3×10^{-11}	35
−13.7	$CH_3^{37}Cl$	52009	1.899	1.86×10^{4}	1.0×10^{-10}	20
−13.8	CH_3CN	41001	3.919	9.84×10^{3}	$<1\times10^{-11}$	
−13.8	$HD^{17}O$	20004	∼1.73	9.57×10^{1}	5.5×10^{-13}	50
−13.9	$O_3(\nu_2+\nu_3)$	48008	∼0.52	2.26×10^{3}	1.1×10^{-10}	35
−13.9	DF	21002	1.819	1.48×10^{1}	6.0×10^{-14}	35
−13.9	$HNO_3(\nu_6)$	63004	∼2.0	1.82×10^{4}	8.0×10^{-11}	25
−14.0	^{18}O		0.0186	6.324	2.0×10^{-10}	50
−14.1	$O_3(\nu_1+\nu_2)$	48008	∼0.52	2.26×10^{3}	7.0×10^{-11}	35
−14.1	$N_2O(2\nu_2^0)$	44010	0.1608	3.74×10^{2}	1.1×10^{-10}	20
−14.1	$N_2O(2\nu_2^2)$	44010	0.1608	3.74×10^{2}	1.1×10^{-10}	20
−14.1	$^{35}ClONO_2$	97002	0.72	6.53×10^{4}	1.0×10^{-9}	30
−14.1	$OC^{34}S$	62001	0.715	7.78×10^{2}	1.3×10^{-11}	20
−14.2	$^{35}ClOO^{35}Cl$	102001	∼1	1.07×10^{5}	0.6×10^{-9}	18
−14.2	HO_2NO_2	79001	1.288	8.66×10^{4}	$<5\times10^{-10}$	30
−14.2	$HNO_3(\nu_8)$	63005	∼2.0	1.82×10^{4}	3.9×10^{-11}	25
−14.2	$C^{17}O$		0.11	8.55×10^{1}	3.7×10^{-11}	50
−14.3	$H^{81}Br$	82001	0.828	7.34×10^{1}	2.0×10^{-12}	35
−14.3	$H^{79}Br$	80001	0.828	7.33×10^{1}	2.0×10^{-12}	35
−14.3	$D^{35}Cl$	37001	∼1.1	1.19×10^{2}	2.3×10^{-13}	50
−14.3	$NN^{17}O$		∼0.16	$\sim3.8\times10^{2}$	7.5×10^{-11}	20

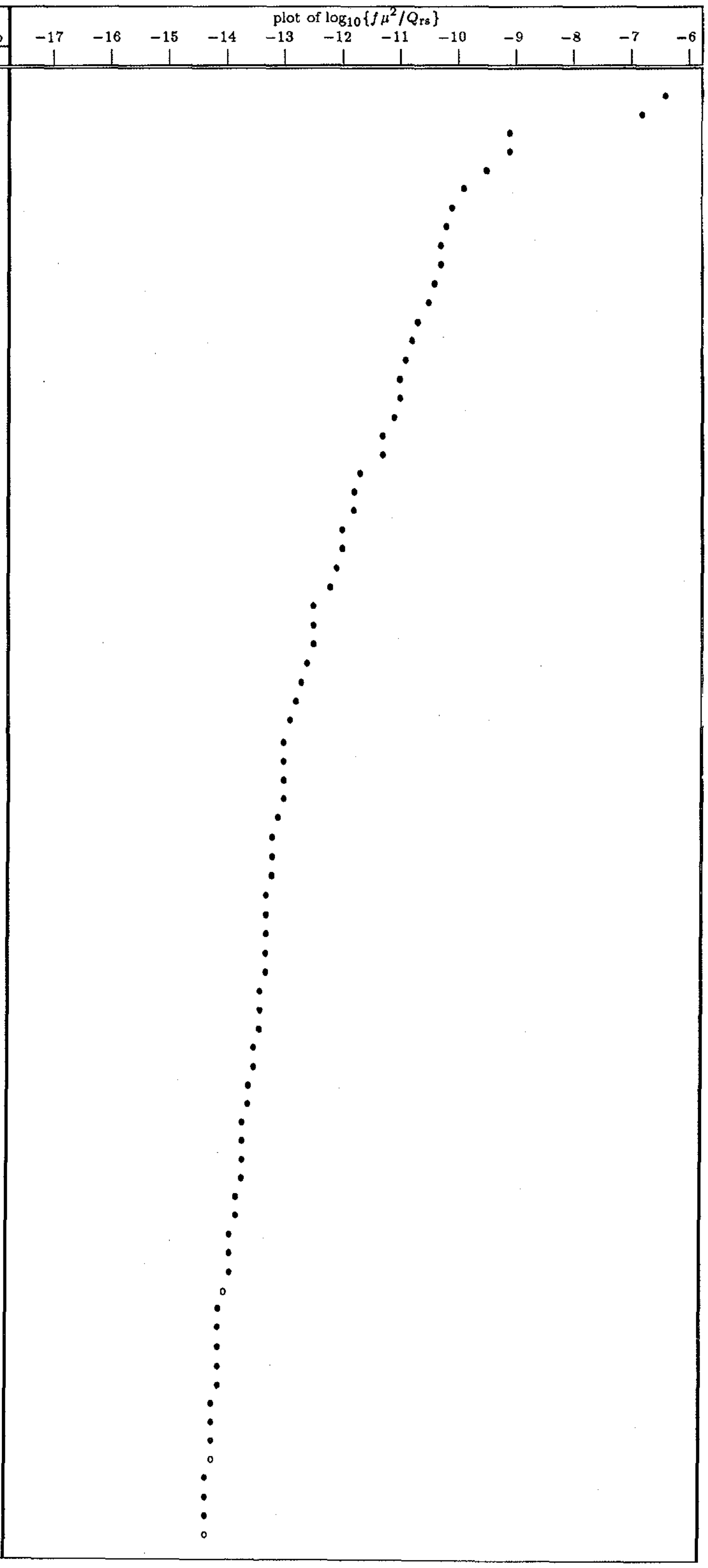
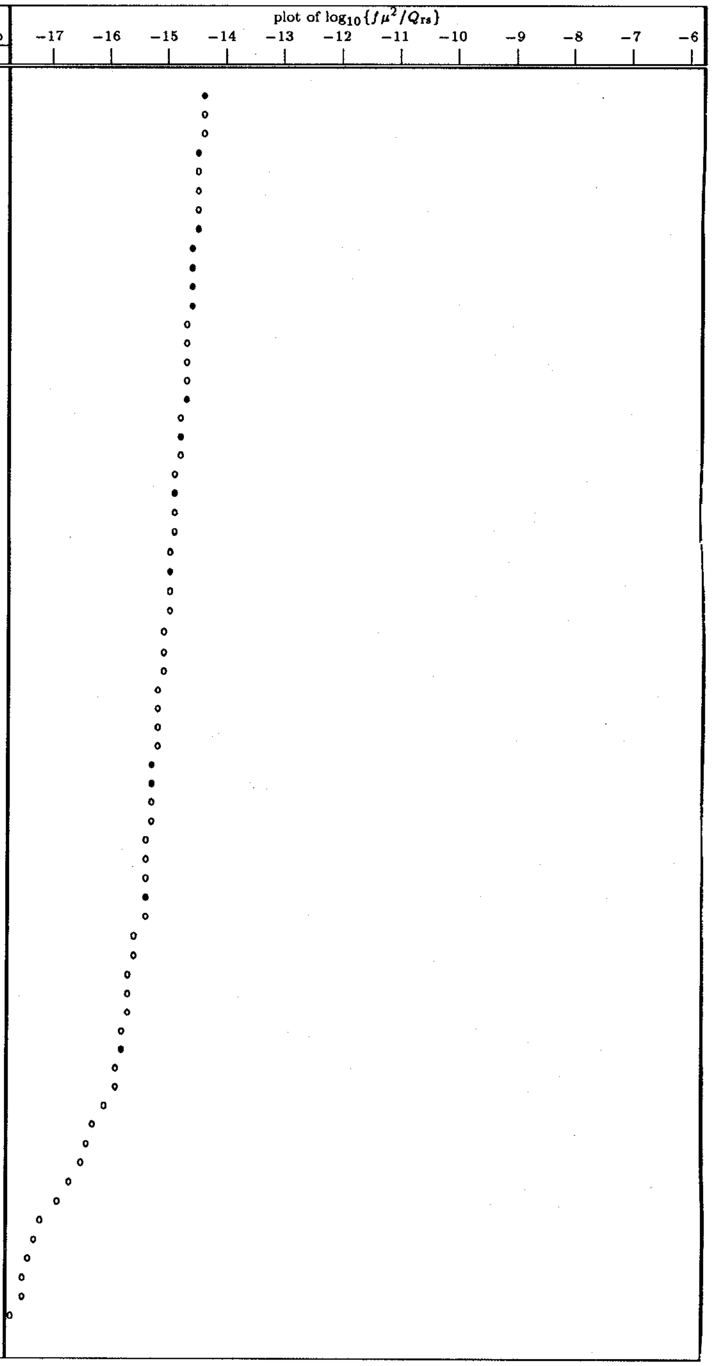


Table 1 (continued): Stratospheric molecules and atoms in descending order of $f\mu^2/Q_{rs}$.

$\log_{10}\frac{f\mu^2}{Q_{rs}}$	molecule or atom	JPL SPEC-TAG	μ (D)	Q_{rs} at 225 K	approx. max. strat-ospheric mixing ratio value $\equiv f$	ht/km
−14.4	$HNO_3(\nu_5)$	63006	~2.0	1.82×10^4	1.8×10^{-11}	25
−14.4	$HO^{15}NO_2$		~2.0	1.82×10^4	1.8×10^{-11}	25
−14.4	$^{34}SO_2$		~1.6	$\sim3.8\times10^4$	4.2×10^{-11}	<30
−14.5	$^{35}ClOO^{37}Cl$	104001	~1	1.07×10^5	0.3×10^{-9}	18
−14.5	$HDO(\nu_2)$		~1.73	9.56×10^1	1.9×10^{-13}	50
−14.5	$N_2O(\nu_1)$		0.1608	3.74×10^2	5.4×10^{-11}	20
−14.5	$HNO_3(2\nu_9)$		~2.0	1.82×10^4	1.5×10^{-11}	25
−14.5	$H_2{}^{13}CO$	31002	2.331	1.93×10^3	1.1×10^{-12}	35
−14.6	OD	18001	1.653	1.53×10^2	1.5×10^{-13}	50
−14.6	$O^{35}ClO$	67001	1.784	3.44×10^4	3.0×10^{-11}	35
−14.6	$^{37}ClONO_2$	99001	0.72	6.70×10^4	3.0×10^{-10}	30
−14.6	COF_2	66001	0.951	3.99×10^4	1.0×10^{-10}	35
−14.7	^{17}O		0.0186	6.324	3.7×10^{-11}	50
−14.7	$H^{18}ONO_2$		~2.0	1.93×10^4	1.0×10^{-11}	25
−14.7	$HON^{18}OO$ (*cis*)		~2.	1.93×10^4	1.0×10^{-11}	25
−14.7	$HON^{18}OO$ (*trans*)		~2.	1.93×10^4	1.0×10^{-11}	25
−14.7	$O^{13}CS$	61001	0.715	7.74×10^2	3.0×10^{-12}	20
−14.8	$O_3(2\nu_3)$		~0.52	2.26×10^3	1.1×10^{-11}	35
−14.8	$D^{37}Cl$	39004	~1.1	1.19×10^2	0.8×10^{-13}	50
−14.8	$OC^{18}O$		0.0007	4.25×10^2	1.4×10^{-6}	<70
−14.9	^{15}NO		~0.16	$\sim8.2\times10^2$	3.7×10^{-11}	40
−14.9	DCN	28004	2.984	1.30×10^2	1.5×10^{-14}	30
−14.9	$O_3(3\nu_2)$		~0.52	2.26×10^3	1.1×10^{-11}	35
−14.9	$HNO_3(\nu_7+\nu_9)$		~2.0	1.82×10^4	6.5×10^{-12}	25
−15.0	$O_3(\nu_1+\nu_3)$		~0.52	2.26×10^3	1.0×10^{-12}	35
−15.0	$O^{37}ClO$	69001	1.784	3.57×10^4	1.0×10^{-11}	35
−15.0	$HO^{18}O$		~1.5	$\sim2.8\times10^3$	1.2×10^{-12}	50
−15.0	HCN $(2\nu_2^2)$		~2.9	1.06×10^2	1.2×10^{-14}	30
−15.1	HCN $(2\nu_2^0)$		~2.9	3.19×10^2	1.1×10^{-14}	30
−15.1	$HNO_3(\nu_6+\nu_9)$		~2.0	1.82×10^4	4.3×10^{-12}	25
−15.1	$CHClF_2$(CFC-22)		1.24	4.31×10^4	2.0×10^{-11}	20
−15.2	$N^{18}O$		~0.16	$\sim8.2\times10^2$	2.0×10^{-11}	35
−15.2	$O_3(2\nu_1)$		~0.52	2.26×10^3	5.6×10^{-12}	35
−15.2	$HNO_3(2\nu_7)$		~2.0	1.82×10^4	3.1×10^{-12}	25
−15.2	CH_3CCl_3		~1.8	1.84×10^5	4.0×10^{-11}	20
−15.3	D_2O	20001	1.845	6.80×10^2	4.4×10^{-13}	50
−15.3	$H_2C^{18}O$	32004	2.331	1.96×10^3	2.0×10^{-13}	35
−15.3	$NO^{18}O$		~0.32	$\sim8.8\times10^3$	4.1×10^{-11}	40
−15.3	$^{15}NO_2$		~0.32	$\sim8.8\times10^3$	3.7×10^{-11}	40
−15.4	$HNO_3(\nu_8+\nu_9)$		~2.0	1.82×10^4	2.1×10^{-12}	25
−15.4	$HNO_3(\nu_6+\nu_7)$		~2.0	1.82×10^4	2.0×10^{-12}	25
−15.4	$SO^{18}O$		~1.6	$\sim3.8\times10^4$	4.0×10^{-12}	<~30
−15.4	^{18}OCS	62002	0.715	8.22×10^2	6.0×10^{-13}	20
−15.4	CCl_2F_2 (CFC-12)		~0.5	1.17×10^5	2.0×10^{-10}	20
−15.6	$HNO_3(\nu_6)$		~2.0	1.82×10^4	1.3×10^{-12}	25
−15.6	$HNO_3(\nu_3)$		~2.0	1.82×10^4	1.2×10^{-12}	25
−15.7	$HNO_3(\nu_4)$		~2.0	1.82×10^4	1.1×10^{-12}	25
−15.7	$HNO_3(\nu_5+\nu_9)$		~2.0	1.82×10^4	1.0×10^{-12}	25
−15.7	$HNO_3(\nu_7+\nu_8)$		~2.0	1.82×10^4	9.4×10^{-13}	25
−15.8	$HNO_3(3\nu_9)$		~2.0	1.82×10^4	8.0×10^{-13}	25
−15.8	$CH_3C^{15}N$	42001	3.919	3.39×10^3	$<4\times10^{-14}$	
−15.9	$HNO_3(\nu_6+\nu_8)$		~2.0	1.82×10^4	6.0×10^{-13}	25
−15.9	$N^{17}O$		~0.16	$\sim8.2\times10^2$	3.7×10^{-12}	40
−16.1	N_2O_5		~0.1	1.13×10^5	1.0×10^{-9}	35
−16.3	$SO^{17}O$		~1.6	$\sim3.8\times10^4$	7.5×10^{-12}	<~30
−16.4	CCl_3F (CFC-11)		0.46	1.77×10^5	8.0×10^{-11}	20
−16.5	CCl_2FCClF_2 (CFC-113)		~0.8	4.40×10^5	2.0×10^{-11}	20
−16.7	$HNO_3(\nu_2)$		~2.0	1.82×10^4	9.0×10^{-14}	25
−16.9	CH_3Br		1.80	2.54×10^4	$<1\times10^{-13}$	20
−17.2	$CClF_3$ (CFC-13)		~0.5	7.19×10^4	2.0×10^{-12}	35
−17.3	$CClF_2CF_3$ (CFC-115)		~0.8	2.50×10^5	1.0×10^{-12}	35
−17.4	$CBrF_3$ (CFC-13B1)		~1	1.13×10^5	5.0×10^{-13}	20
−17.5	NO_3		0.0186	1.05×10^4	1.0×10^{-10}	35
−17.5	$CClF_2CClF_2$ (CFC-114)		<0.5	3.40×10^5	4.0×10^{-12}	20
−17.7	$CBrClF_2$ (CFC-12B1)		~1	1.81×10^5	4.0×10^{-13}	20
−21.9	$HNO_3(\nu_1)$		~2.0	1.82×10^4	7.0×10^{-19}	25



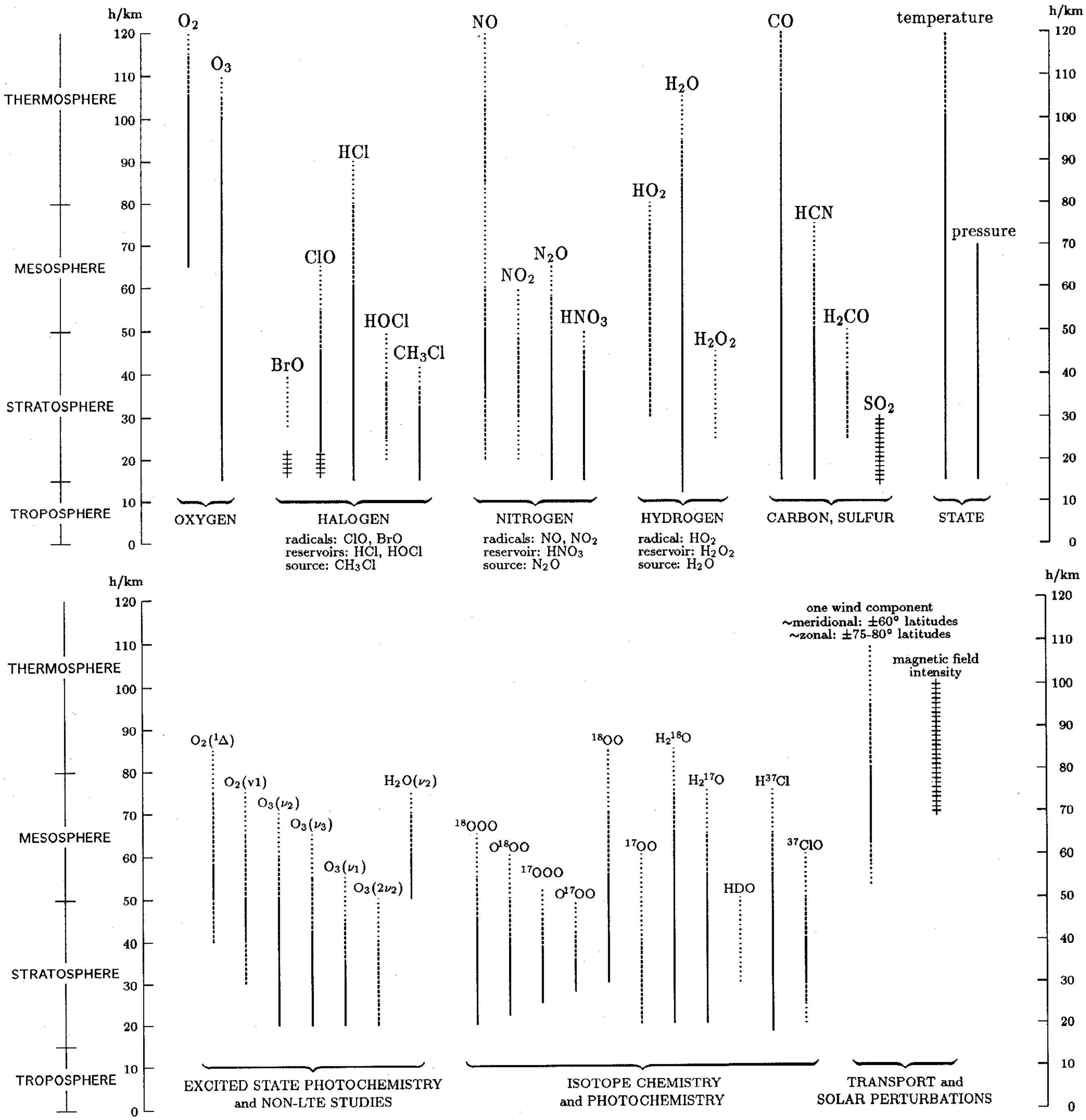


Figure 1: Projected Measurement Capability of EOS MLS. Top: primary objectives. Bottom: additional measurements obtained from the instrument designed for the primary objectives. All measurements can be made simultaneously and continuously — at all times of day and night, and in the presence of aerosols and ice clouds. Vertical resolution is ~2 km and latitude coverage is 82°N – 82°S on each orbit (for the orbit now being considered for EOS). This coverage is expecially well-suited for studying and monitoring high latitude phenomena such as the Antarctic ozone hole and similar processes in the Arctic. Developments now underway for low-noise heterodyne technology in the terahertz region can provide capability for measurements of additionally important upper atmospheric gases such as OH and atomic O.

| ⇒ Individual profiles every 2.5° along great circle of suborbital path

⇒ Daily zonal means (separate day and night); ±80° latitude with 2.5° latitude resolution

⇒ Monthly zonal means (separate day and night); ±80° latitude with 2.5° latitude resolution

⇒ Heterogeneous chemistry enhancements for ClO and BrO; volcanic enhancements for SO_2; solar storms for magnetic field