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ERROR ANALYSIS OF DOBSON SPECTROPHOTOMETER MEASUREMENTS OF THE TOTAL ATMOSPHERIC OZONE CONTENT

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16. Abstract

This report summarizes the results of a study of techniques for measuring atmospheric ozone that was carried out at NASA Wallops Flight Center. This study represents the second phase of program designed to improve techniques for the measurement of atmospheric ozone. This phase of the program studied the sensitivity of Dobson direct sun measurements and the ozone amounts inferred from those measurements to variation in the atmospheric temperature profile. The study used the Plane - Parallel Monte-Carlo Model developed and tested under the initial phase of this program, and a series of standard model atmospheres.

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SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

This report summarizes the results of one phase of a study of techniques for measuring atmospheric ozone that was carried out at NASA Wallops Flight Center. This study represents the second phase of a program designed to improve techniques for the measurement of atmospheric ozone. This phase of the program was concerned with two distinct tasks:

1) A study of the sensitivity of Dobson direct sun measurements and the ozone amounts inferred from those measurements, to variations in the atmospheric temperature profile. The study used the plane-parallel, Monte-Carlo model developed and tested under the initial phase of this program (1) and a series of standard atmospheres taken from Reference 2.

2) Development and testing of a Monte-Carlo simulation of radiative transfer through a spherical shell atmospheric model. Spherical atmospheric models are necessary to study the Dobson Umkehr measurements which use large solar zenith angles.

Under task 1 a plane-parallel Monte-Carlo model of the Dobson measurements systems developed under the initial phase of this program was used to study the effect of variations of atmospheric temperature profiles on the total ozone inferred from Dobson direct sun measurements. The ozone profile and total ozone in each atmospheric model were held constant. The results of the study are summarized in Table 1. The errors listed are for vanishingly small instrumental field of view, which essentially minimizes errors due to single and multiple scattering. The errors listed then reflect the sensitivity of the ozone amounts, inferred from direct sun measurements, to errors in the assumed mean ozone absorption coefficients, and, to a lesser extent, errors in the molecular and aerosol extinction.

TABLE 1

ERRORS IN OZONE AMOUNT INFERRED USING DOBSON GUAGE
(OVERESTIMATE = POSITIVE)

Lines	Std. Atm.	Subarctic Winter Warm 60°N	Subarctic Winter Cold 60°N	Subarctic Jan 60°N	Subarctic July 60°N	Midlatitudes Jan 45°N	Midlatitudes July 45°N	Subtropical Jan 30°N	Subtropical July 30°N	Tropical 15°N
A	-1.49	-2.23	-3.90	-3.19	-1.54	-2.74	-1.74	-2.36	-2.05	-2.25
C	-0.33	-0.72	-3.77	-2.46	0.24	-1.69	-0.14	-1.18	-0.74	-1.10
D	0.75	-1.43	-2.55	-2.09	-0.41	-1.23	-0.23	-0.32	-0.27	-0.45
A-D	-2.13	-2.56	-4.30	-3.59	-1.93	-3.18	-2.23	-2.96	-2.63	-2.84
C-D	-0.01	-0.19	-4.71	-2.73	0.75	-2.06	-0.10	-1.84	-1.11	-1.61
A-D	-3.05	-3.49	-3.82	-3.69	-3.04	-3.54	-3.04	-3.30	-3.10	-3.16

A source of the errors in the ozone estimations is the temperature dependence of the ozone absorption coefficient. Essentially the ozone absorption coefficient used in reducing the direct sun data is an average over the ozone density distribution in the atmosphere. Since the ozone absorption coefficient varies with temperature and hence with height in the atmosphere we will arrive at a different average value for different temperature profiles or ozone profiles.

Under task 2 a Monte-Carlo simulation of radiative transfer through a spherically-symmetric, layered atmosphere was developed and tested against well known solutions. That part of the study will be described in a separate report and is not covered here.

Recommendations: It is recommended that future work should emphasize the following tasks:

1) The ozone absorption spectra of ozone in the Hartley band system (2900Å to 3400Å) should be investigated as a function of wavelength and temperature to

determine whether or not a wide band line pair would reduce or eliminate the ozone absorption temperature dependence.

2) As an interim approach the appropriate values of the average ozone coefficient α should be evaluated for every standard temperature model for a number of possible ozone profiles; from these investigations appropriate values of A_λ and B_λ to be used in Dobson reductions should be derived.

INTRODUCTION

The amount of ozone present in the earth's atmosphere is of considerable interest to the scientific community. Among the reasons for the importance of ozone is its role in the transfer of solar energy in the atmosphere, absorbing harmful ultra-violet radiation, and providing a source of thermal energy in the stratosphere. Ozone is also important as a tracer used to study atmospheric circulation.

Ozone measurements have been made for a number of years using a variety of instruments and techniques. The Dobson spectrophotometer has served as a standard ground-based instrument for the measurement of total atmospheric ozone for over two decades. The Dobson gauge is a double-monochromator that isolates two narrow bands in the ultra-violet spectrum. The wavelengths of the bands are chosen so that one wavelength is strongly absorbed by ozone while the other, longer wavelength is affected very little by ozone absorption. Measurements of the intensities reaching the instrument are used to calculate the amount of ozone that the solar radiation has passed through in arriving at the instrument.

In order to assess the accuracy of the total ozone inferred from Dobson measurements a study was initiated at Wallops Flight Center several years ago. The first phase of that study was concerned with the effects of single and multiple scattering by molecules and particles in the atmosphere on the signals received by the Dobson gauge. That phase was completed last year and concluded that single and multiple scattering can contribute significant errors to the amount of ozone inferred from direct sun measurements. However, these errors could be reduced to a minimum if not completely eliminated by using a narrow instrument field-of-view and using line pair coupling. We also found a significant sensitivity, of the ozone amount inferred, to atmospheric temperature profiles. This report describes the second phase of the study which was concerned with the errors in the total ozone amount estimated from Dobson direct sun measurements for standard atmospheres ranging from tropical through sub-arctic conditions.

DOBSON DIRECT SUN MEASUREMENTS

System Description

The Dobson spectrophotometer is a specialized double beam monochromator used for determining atmospheric ozone by measuring the ratio of the intensities of ultra-violet light at two wavelengths in the solar spectrum. The wavelength pair is selected so that one wavelength is much more strongly absorbed by ozone than the other, so that the intensity ratio can be used to estimate the total amount of ozone in the optical path from the sun to the instrument. By appropriate adjustments of the spectrophotometer one of several specified wavelength pairs can be selected for the measurement, depending on illumination conditions, to provide an estimate of the amount of atmospheric ozone.

The Dobson instrument can be used in three distinct modes: a direct sun measurement, a "zenith sky" measurement and an "Umkehr" mode. In the direct sun mode a prism or "Sun Director" is used to project the sun's image onto the entrance window of the Dobson spectrophotometer. The direct sun mode is the preferred method for measuring total ozone. Details of the Dobson instrument and its use in all three modes are given in Reference 1 and will not be repeated here. In this report we are only concerned with direct sun measurements in a plane parallel atmosphere.

The Dobson instrument measures the relative intensities of the two wavelengths in a given pair by first separating them in a spectroscope, isolating them with slits, and attenuating the beam at the wavelength least absorbed by ozone with a variable thickness optical filter (the filter wedge). The two beams are brought back into coincidence with a second spectroscope so that they impinge on a photo-electric null-meter. The null-meter does not measure absolute intensities, instead it indicates when the difference between the intensities is zero. The null-meter consists of a chopper wheel in the optical path, which passes the two beams sequentially and a photo-multiplier upon which one beam and then the other fall sequentially as allowed by the chopper wheel. An amplifier is used for the A.C. output of the photo-multiplier, then a rectifier converts the alternating current to direct current, and finally a micro-ammeter displays the direct current.

The ratio of the intensities of the two beams is "measured" by adjusting the filter wedge until the micro-ammeter reads zero. Then the intensity ratio is computed from the position of the filter wedge and the instrument calibration data.

Wavelength Doublet and Wavelength-Doublet Pairs. - The Dobson machine can be adjusted to make measurements at any of five wavelength doublets. Table 2 taken from Reference 3 gives the pertinent data on the wavelength doublets A, B, C, D and C'. At present wavelength doublet B is not used, so that only four wavelength doublets are used. Also, when making observations for total ozone, it is desirable to make nearly simultaneous observation on two wavelength doublets. The wavelength doublet pairs used are AD, CD, and CC'.

TABLE 2

TABLE OF WAVELENGTHS AND OTHER CONSTANTS
(absorption coefficients are based on $\log_{10}$)

Designation of Wavelength doublet		Mean Wave-length A.U.	Ozone Absorption Coefficient $(atm\ cm)^{-1}$ α α'	$\alpha-\alpha'$	Atmospheric Scattering Coefficient $(atm)^{-1}$ β β'	$\beta-\beta'$	$\frac{\beta-\beta'}{\alpha-\alpha'}$
A	Short	3055	1.882	1.762	0.491	0.116	0.066
	Long	3254	0.120		0.375		
B	Short	3088	1.287	1.223	0.470	0.113	0.092
	Long	3291	0.064		0.357		
C	Short	3114.5	0.912	0.865	0.453	0.110	0.127
	Long	3324	0.047		0.343		
D	Short	3176	0.391	0.374	0.416	0.104	0.278
	Long	3398	0.017		0.312		
C'	Short	3324	0.047	0.047	0.343		
	Long	4536	Nil				

Theory of Measurement Using Direct Sunlight. - For a plane-parallel stratified atmosphere (Fig. 1) containing Rayleigh scatterers (molecules), ozone molecules and aerosols, the change in sunlight from one layer to the next can be expressed as:

$$dI(h) = -I(h)\ \{\sigma_m(h)\rho_m(h) + \sigma_o(h)\rho_o(h) + \sigma_p(h)\rho_p(h)\}\ \sec Z\ dh \qquad (1)$$

The quantity I(h) denotes the intensity at altitude h while $\sigma(h)$ denotes a cross section for scattering or absorption in cm^2/molecule and $\rho(h)$ denotes the number of molecules or particles per cubic centimeter. Subscripts denote molecules (m), ozone molecules (o), and particles (p). Note that in this analysis we have neglected any light that might be scattered into the path from other parts of the atmosphere; we only considered losses from the beam due to scattering and absorption.

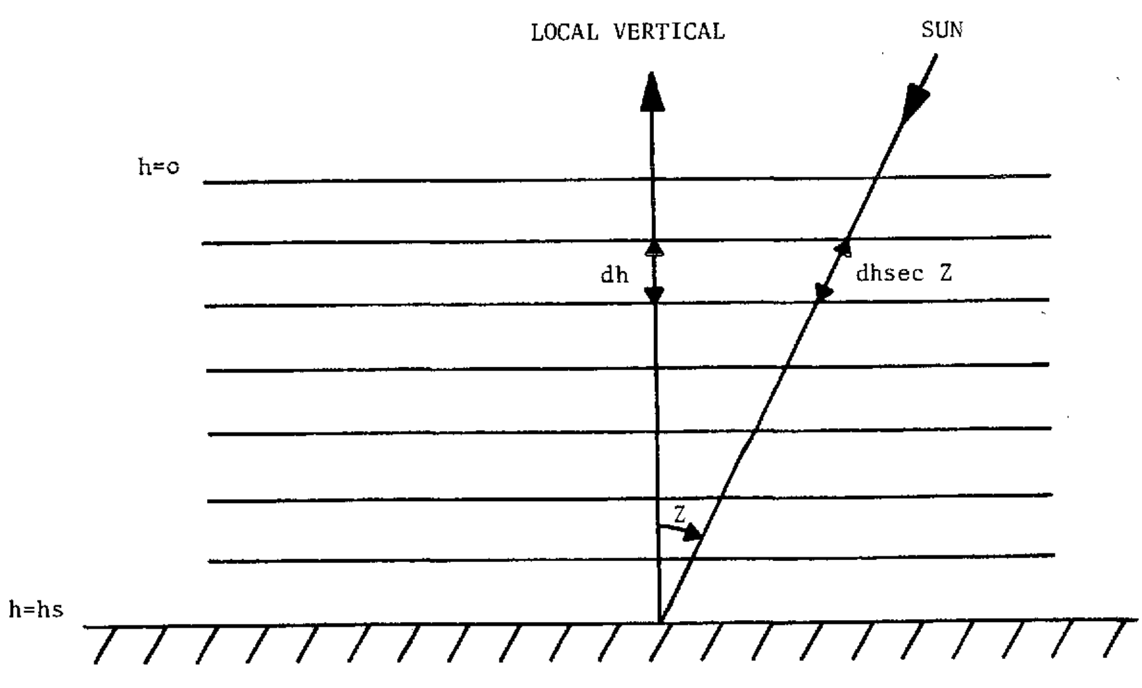

Figure 1 - Geometry of Plane Parallel Case

Integrating the equation from the top of the sensible atmosphere (h=o) to the surface ($h=h_s$) we have:

$$\ln\left[\frac{I(h_s)}{I(0)}\right] = -\int_0^{h_s}\{\sigma_m(h)\rho_m(h) + \sigma_o(h)\rho_o(h) + \sigma_p(h)\rho_p(h)\}\sec Z\, dh \tag{2}$$

If we now define the dimensionless quantities:

$$\int_0^{h_s}\sigma_m(h)\rho_m(h)\, dh = \beta_m T_m \tag{3}$$

$$\int_0^{h_s}\sigma_p(h)\rho_p(h)\, dh = \delta_p T_p \tag{4}$$

and

$$\int_0^{h_s}\sigma_o(h)\rho_o(h)\, dh = \alpha X \tag{5}$$

then the equation for the intensity reaching the ground based instrument is:

$$\ln I(h_s) = \ln I(o) - \{\beta_m T_m + \delta_p T_p + \alpha X\}\sec Z \tag{6}$$

Essentially the quantity T_m represents the "scale height" of the atmosphere, that is, the thickness of the molecular atmosphere if it were reduced to a uniform layer at Standard Temperature and Pressure. Similarly, β_m then represents the Rayleigh volume scattering coefficient for the atmosphere at Standard Temperature and Pressure. The volume coefficient can be calculated from the Rayleigh-Cabannes formulae for the scattering cross section per molecule and Loschmidt's number n_o, the number of molecules per cm^3 at Standard Temperature and Pressure. The product $\beta_m T_m$ then is the normal or vertical optical thickness of the atmosphere due to Rayleigh or molecular scattering. Similarly $\delta_p T_p$ represents the normal optical thickness of the atmosphere aerosol and αX represents the normal optical thickness of the ozone layer. The parameter X is the equivalent thickness of ozone or the ozone scale height, and is the quantity of interest. The quantity α is the average value of the ozone absorption coefficient over the ozone profile. In this plane parallel model, restricted to zenith angles less than 60°, we do not concern ourselves with the effect of refraction on the path length, and we neglect the effect of the earth's curvature.

In Dobson's derivation he sets $\beta = \beta_m T_m$ and $\delta = \delta_p T_p$. Then we have:

$$\ln I(h_s) = \ln I(o) - \{\beta + \delta + \alpha X\}\sec Z \tag{7}$$

where β now denotes the vertical optical thickness of the atmosphere due to molecular scattering and δ represents the vertical optical thickness due to scattering by particulate matter.

In Dobson's derivation for the direct sun measurement the quantity sec Z multiplying the expression for the ozone optical thickness and molecular optical thickness is replaced by quantities μ and m. The parameter m is defined to be the equivalent path length through the molecular atmosphere allowing for atmospheric refraction and the curvature of the earth. When the zenith angle is zero, m is defined to be 1.0. The quantity μ is the relative path length of sunlight through the ozone layer which is presumed to be at 22 km above the earth surface. When the zenith angle is zero, μ is also defined to be 1.0. However in the final equations used m and μ are taken to be essentially the same as sec Z. Since we confine ourselves to zenith angles less than 60°, these distinctions are unnecessary. Then in the interest of brevity and clarity we will use only sec Z.

The preceding derivation used natural logarithms while the original derivation of Dobson employed logarithms to the base ten. Changing to $\log_{10}$ we have

$$\log_{10} I_\lambda = \log_{10} I_{o\lambda} - (\beta + \delta + \alpha X) \sec Z. \tag{8}$$

In this form of the equations, the coefficients are related to the preceding coefficients through relations of the form:

$$\alpha_{10} = \frac{\alpha_e}{\ln(10)} = 0.4342\ \alpha_e,\ \beta_{10} = 0.4342\ \beta_e \text{ and } \delta_{10} = 0.4342\ \delta_e.$$

Writing the equation for two wavelengths λ and λ' and subtracting, we arrive at:

$$\log_{10}\left(\frac{I}{I'}\right) = \log_{10}\left(\frac{I_o}{I_o'}\right) - \left[(\beta - \beta') + (\delta - \delta') + (\alpha - \alpha')\ X\right] \sec Z \tag{9}$$

$$\text{efining } L_\lambda = \log_{10}\left(\frac{I}{I'}\right) \tag{10}$$

$$L_{o\lambda} = \log_{10}\left(\frac{I_o}{I_o'}\right)$$

$$N_\lambda = L_{o\lambda} - L_\lambda$$

$$\text{We have:}\quad -N_\lambda = -\left[(\alpha - \alpha')_\lambda X + (\beta - \beta')_\lambda + (\delta - \delta')_\lambda\right] \sec Z \tag{11}$$

$$\text{or } X = \frac{N_\lambda}{(\alpha-\alpha')_\lambda \sec Z} - \left[\frac{(\beta-\beta')_\lambda + (\delta-\delta')_\lambda}{(\alpha-\alpha')_\lambda}\right] \tag{12}$$

The subscript λ denotes the wavelength dependence of the terms while primes indicate the longer wavelength of the line pair.

The term containing $(\delta - \delta')$ cannot be evaluated explicitly because the attenuation coefficients for particulate scattering usually are not known. As a means of avoiding this difficulty, observations are often made nearly simultaneously on two wavelength pairs, say A and D, and the resulting equations (3-11) subtracted and solved for X. The result for the AD line pairs, using the coefficients given in Table 2 is:

$$X_{AD} = 0.7205\ (N_A - N_D)/\sec Z - 0.009 \tag{13}$$
$$- \left[(\delta-\delta')_A - (\delta-\delta')_D\right] / \left[(\alpha-\alpha')_A - (\alpha-\alpha')_D\right]$$

The last term in equation (13) has been set to be zero, in Dobson's derivation, on the assumption that particulate scattering coefficients are only slightly wavelength dependent, thus cancelling the two terms in the numerator. We then have

$$X_{AD} = 0.7205\ (N_A - N_D) / \sec Z - 0.009 \tag{14}$$

which is identical to Dobson's equation 5.1 in Reference 3 and is the basis for the reduction of AD line pair measurements. A similar equation can be derived for the line pairs CD and AC.

MONTE-CARLO SIMULATION

A Monte-Carlo model of the Dobson ozone estimation scheme was assembled and tested in the initial phase of this study. Details of the Monte-Carlo model are given in Reference 1 and will not be reported here. Briefly, the model can compute the effect of multiple scattered sunlight on the atmospheric ozone density inferred from Dobson spectrophotometer measurements. The program possesses a useful feature. Unlike the earlier Monte-Carlo simulations of Kattawar and Plass[4] and Collins and Wells[5] the present method does not use direct sampling of photons. Rather, it samples hypothetical photons from each scattering on a probability basis. This technique has two important advantages:

1) The variance is considerably reduced.

2) We can sample sky radiance in exactly specified directions and do not have to use averaging techniques.

Polarization is fully treated by applying the Mueller algebra to the Stokes vector associated with each photon. The program can model ten receiver configurations simultaneously, including direct sun observations from ground level, zenith sky observations from ground level and nadir observations from satellite altitudes for any solar zenith angle less than 60°. The constraint on the solar zenith angle is imposed by the plane-parallel atmosphere assumed in the Monte-Carlo simulation. Other receivers at any altitude and with any orientation can also be specified by the user. Thus, as a byproduct of the Dobson computations we can investigate the effect of multiple scattering on observations made in or above the atmosphere.

The Atmospheric Models

The computer program used in this study will accept as data any atmospheric model a user wishes to investigate. In order to limit the amount of computer time used we restricted ourselves to a series of Standard Atmospheres given in Reference 2. The models used are listed in Table 3 and the temperature and molecular density profiles for each model are shown in Fig. 2 through 6. The variation of the molecular densities of the models from the standard atmosphere density is shown in Fig. 7.

TABLE 3

MODEL ATMOSPHERES

Designation	Time of Year	
Standard Atmosphere		
Tropical 15°N		
Subtropical 30°N	January	July
Midlatitude 45°N	January	July
Subarctic 60°N	January	July
Subarctic 60°N	Winter Warm	Winter Cold

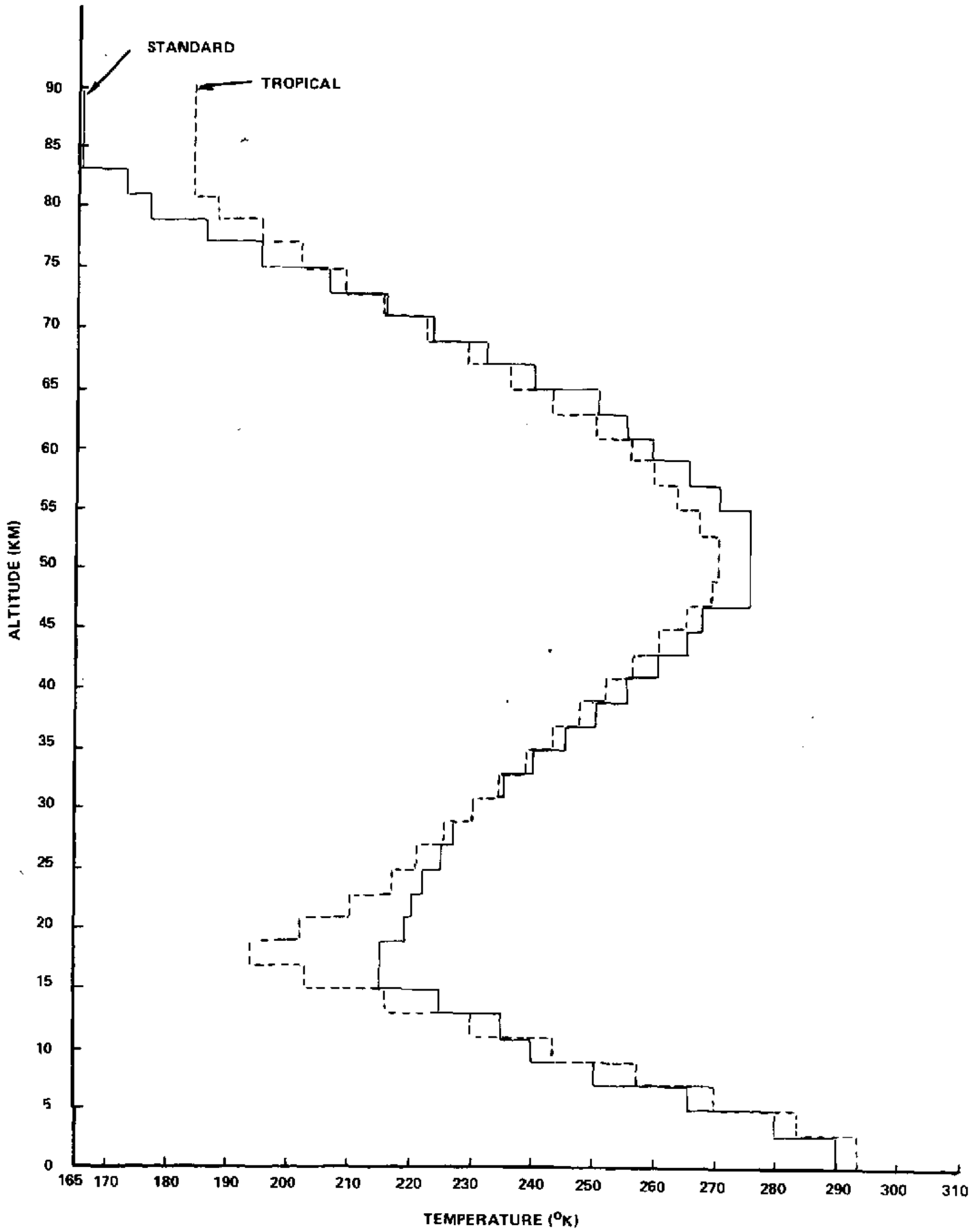

Figure 2 - Vertical Temperature Profile for Tropical (15°N) and Standard Model

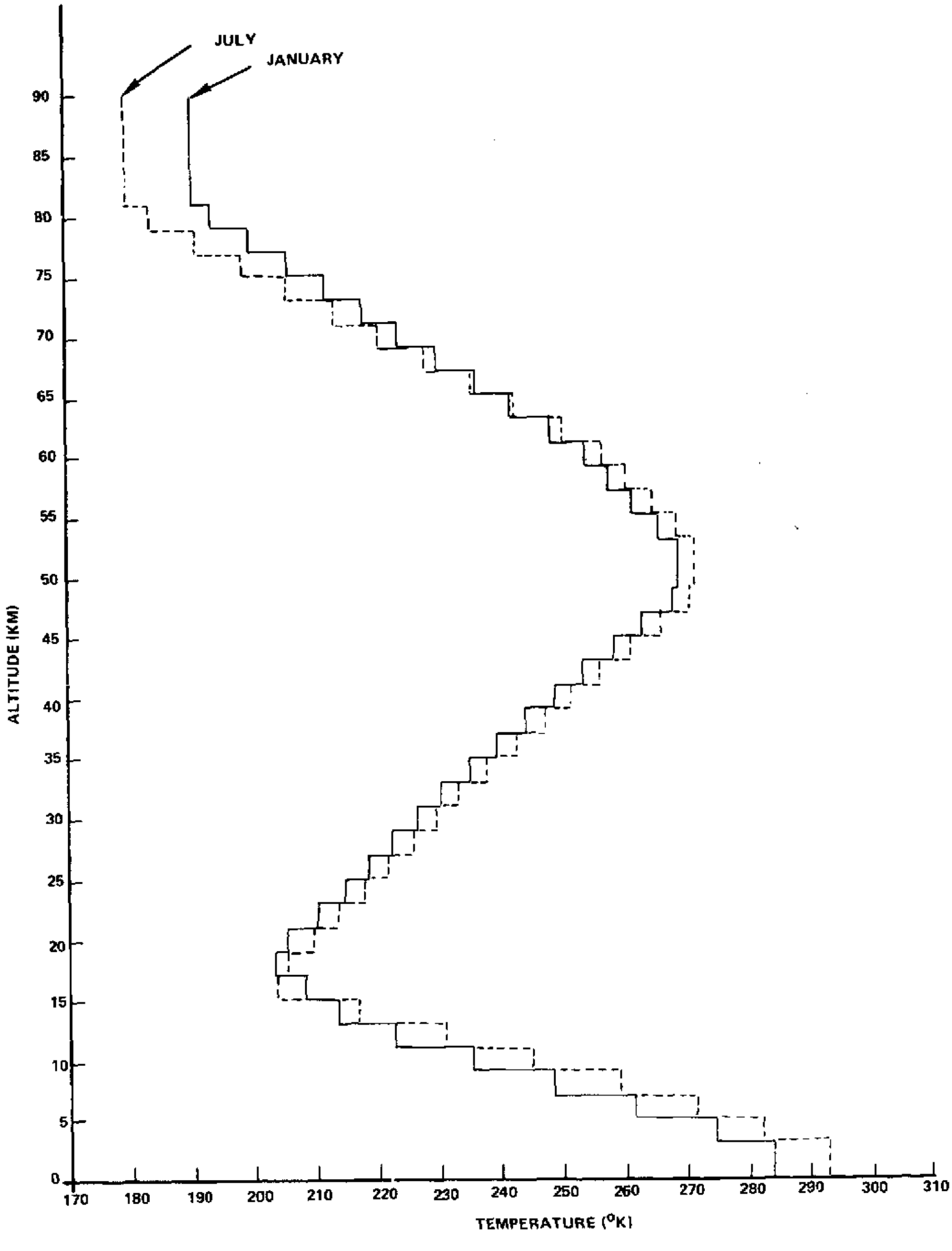

Figure 3 - Vertical Temperature Profile for Subtropical (30°N)

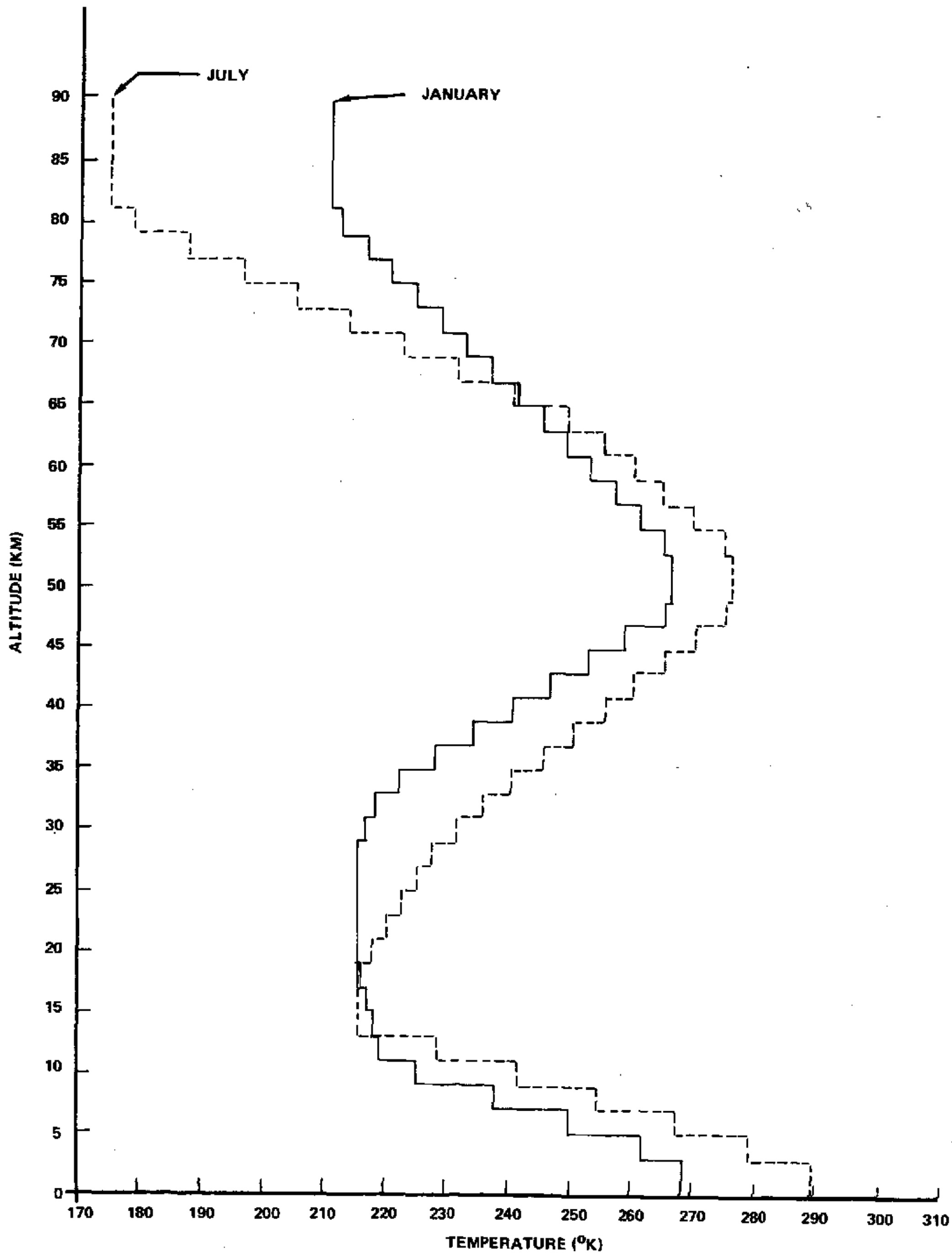

Figure 4 - Vertical Temperature Profile for Midlatitude (45°N)

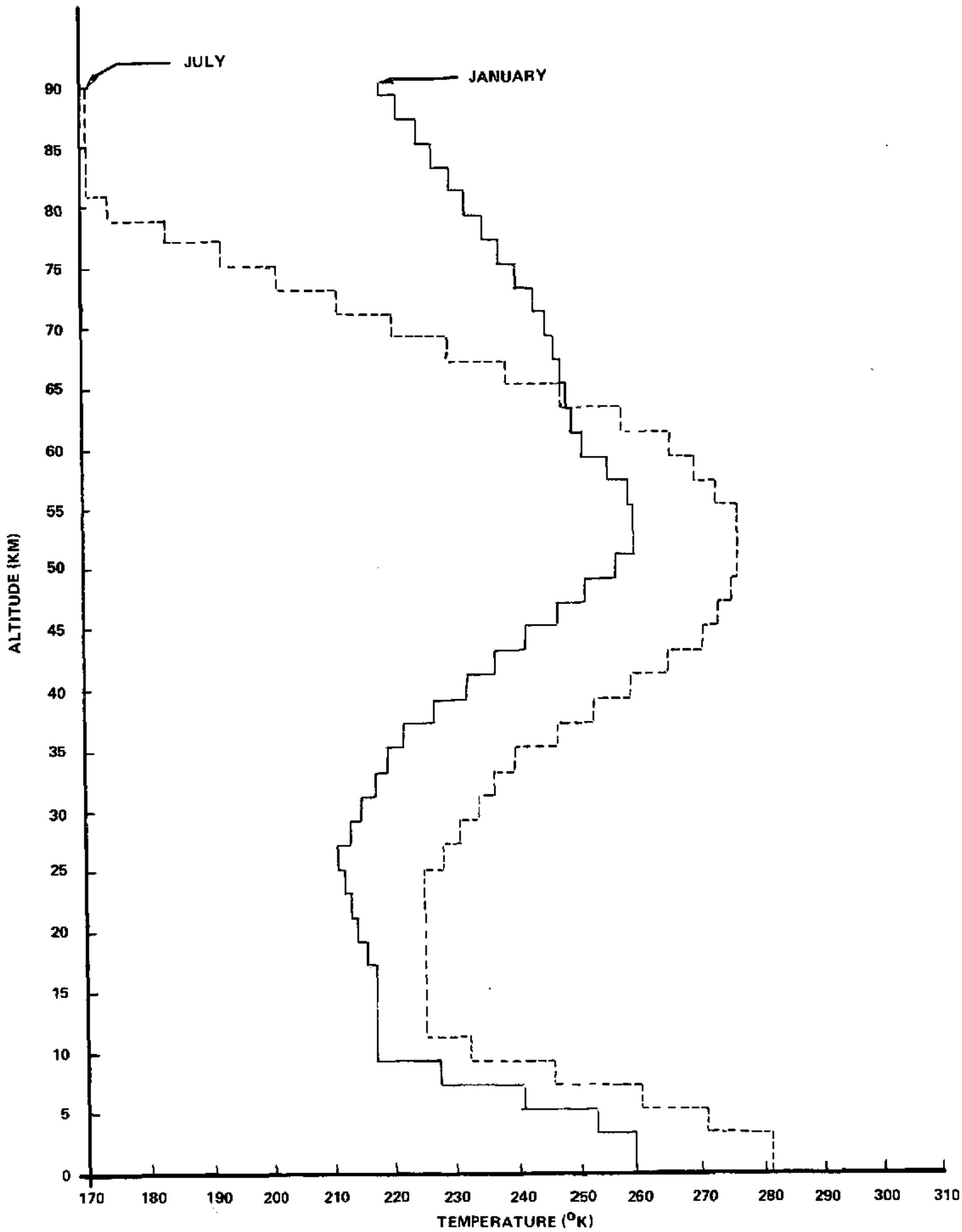

Figure 5 - Vertical Temperature Profile for Subarctic (60°N)

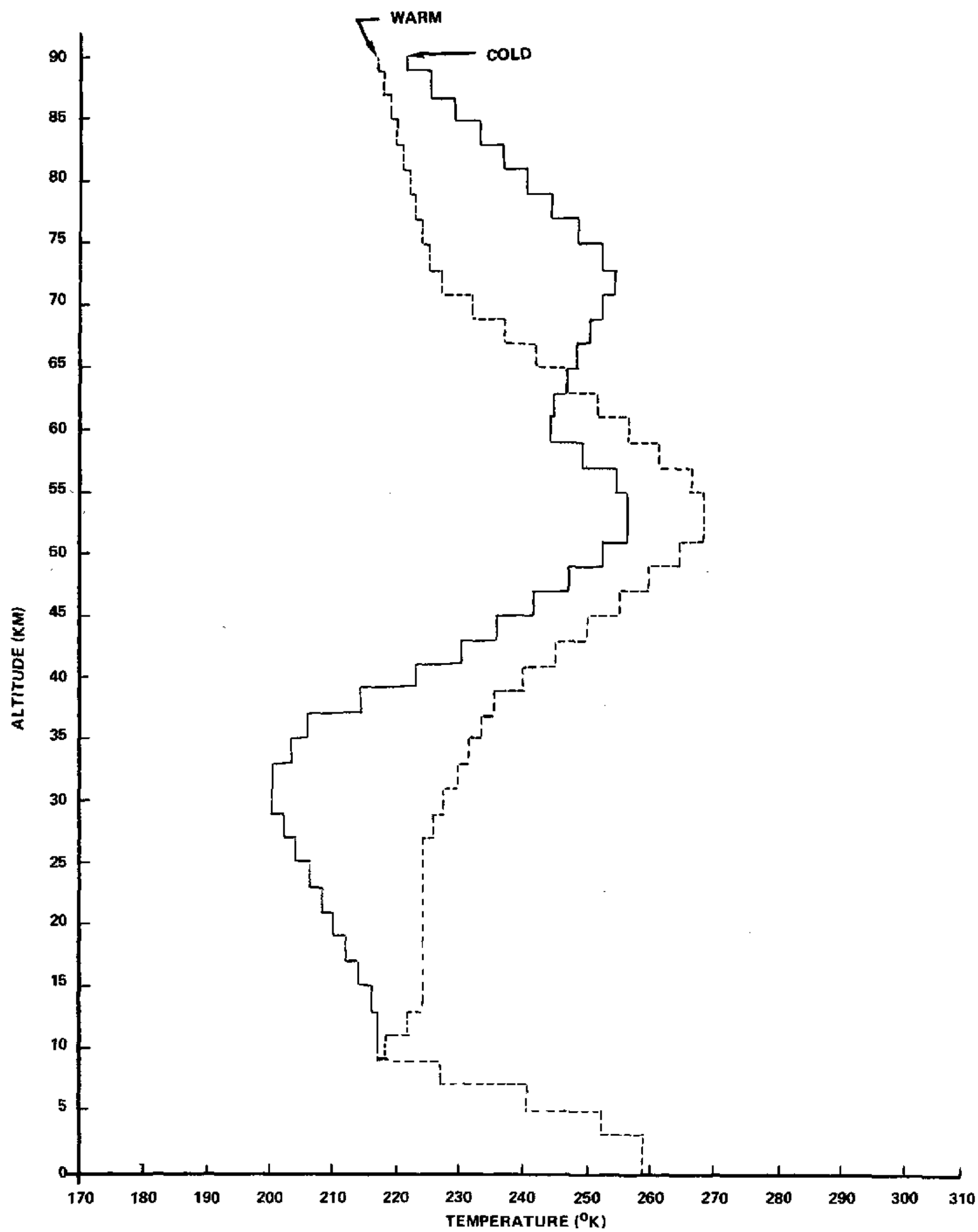

Figure 6 - Vertical Temperature Profile for Subarctic (60°N)

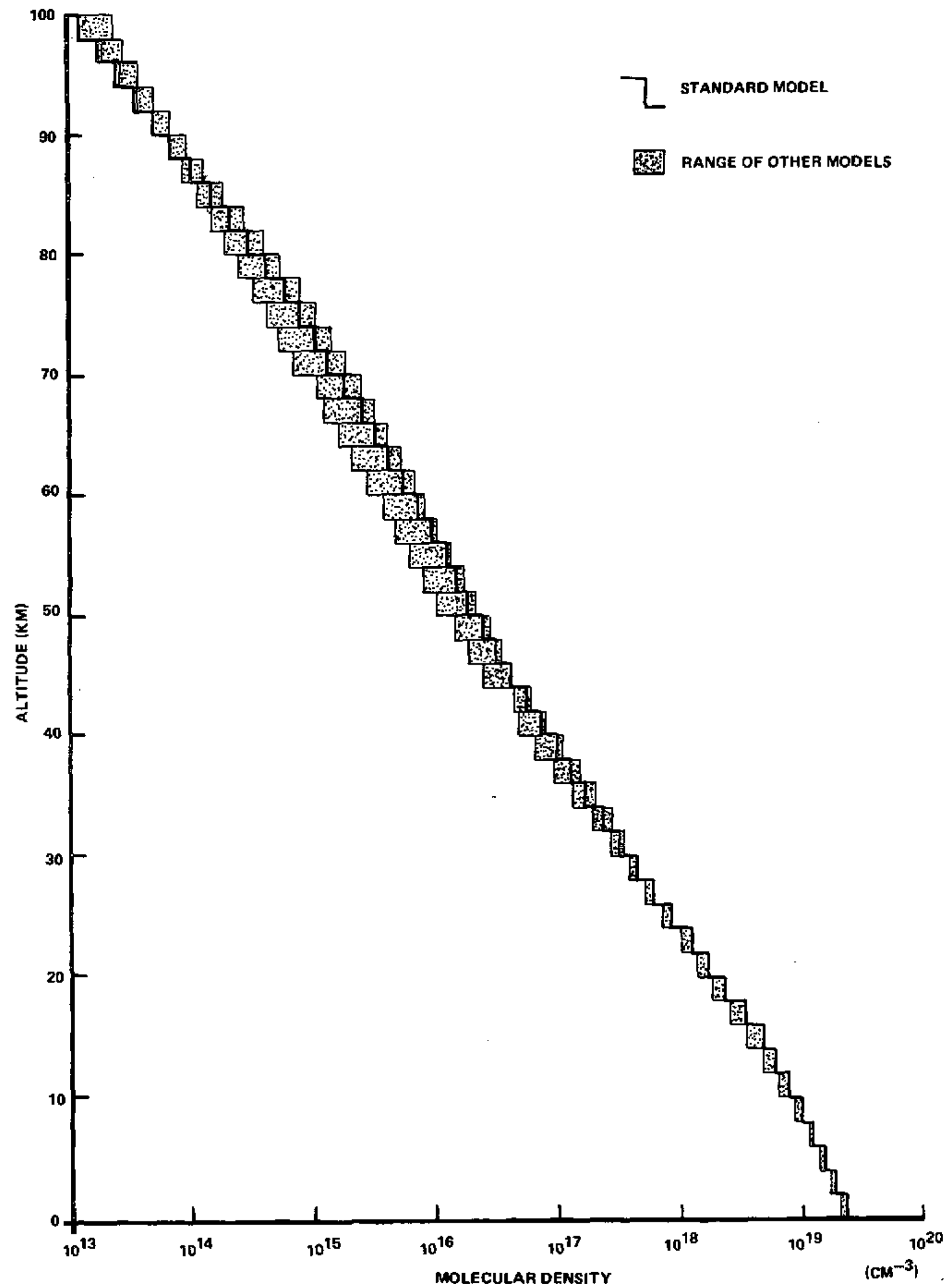

Figure 7 - Model Molecular Densities as Function of Altitude

Our standard atmosphere used the July temperature model of the U.S. Standard Atmosphere while the molecular densities were taken from Champion's atmospheric model (6) which represents mean conditions throughout the year for latitudes near 30 degrees above 30 km. Below 30 km we used an average of the Cole and Kantors (7) 30 degree latitude summer and winter atmospheres to provide a smooth fit between Champion's densities and those of the U.S. Standard Atmosphere (2), which were used exclusively below 10 kms. For the other models, molecular densities were calculated from tabulated values of atmospheric density and mean molecular weights as functions of altitude (2). For aerosol densities we employed the Elterman model (8). The size distribution used was assumed to be that of Junge; i.e., the number of particles with diameters in the range D to D + dD was:

$$n(D)dD = (\nu-1)D_o^{\nu-1}\ D^{\nu}\ dD \qquad = D \geq D_o$$

$$= 0 \qquad D < D_o$$

In this investigation we used:

$D_o = 0.2\mu$
$\nu = 4.0$

The aerosol density was kept constant in all of the atmospheric models investigated. The aerosol scattering properties are computed with a Mie scattering computer program supplied by Holland (9). We assumed that all aerosol particles were spherical with a real refractive index of (1.55-0i). Wavelength dependence of the aerosol refractive index was ignored so that the sole effect of changing wavelength was to alter the Mie size parameter $X = \frac{\pi D}{\lambda}$ for the particles in the distribution. The ozone density profile used in these studies was taken from data by Dutsch (10). The ozone absorption cross sections used were taken from reference 8 and are summarized in Table 4. The variation of the ozone coefficients with temperature is shown in Fig. 8. For temperatures intermediate to the published values, linear interpolation was used. The ozone density was kept constant for all of the atmospheric models studied.

In these simulations we assumed that all other molecular components behaved as Rayleigh scatterers, with scattering cross sections per molecule as given in Table 4.

TABLE 4

ABSORPTION CROSS-SECTIONS FOR OZONE
AND RAYLEIGH SCATTERING CROSS-SECTION
(Values based on $\log_e$)

DOBSON PAIRS	LINE $\lambda(\mu)$	219°K 18°C σ_{ABS} cm^2/molecule	229°K -44°C σ_{ABS} cm^2/molecule	214°K -59°C σ_{ABS} cm^2/molecule	σ_R cm^2/molecule
"A" Lines	.3055	1.757×10^{-19}	1.608×10^{-19}	1.582×10^{-19}	5.187×10^{-26}
	.3254	1.526×10^{-20}	1.254×10^{-20}	1.221×10^{-20}	3.964×10^{-26}
"C" Lines	.31145	8.634×10^{-20}	7.778×10^{-20}	7.554×10^{-20}	4.798×10^{-26}
	.3324	4.578×10^{-21}	3.461×10^{-21}	3.312×10^{-21}	3.621×10^{-26}
"D" Lines	.3176	3.745×10^{-20}	3.259×10^{-20}	3.223×10^{-20}	4.396×10^{-26}
	.3398	1.451×10^{-21}	1.116×10^{-21}	1.042×10^{-21}	3.297×10^{-26}

The Rayleigh scattering cross sections were calculated from the equation:

$$\sigma_R = \frac{3.327\times10^{-28}}{\lambda^{4.258}} \text{ cm}^2\text{/molecule}$$ where λ, the wavelength is expressed in microns.

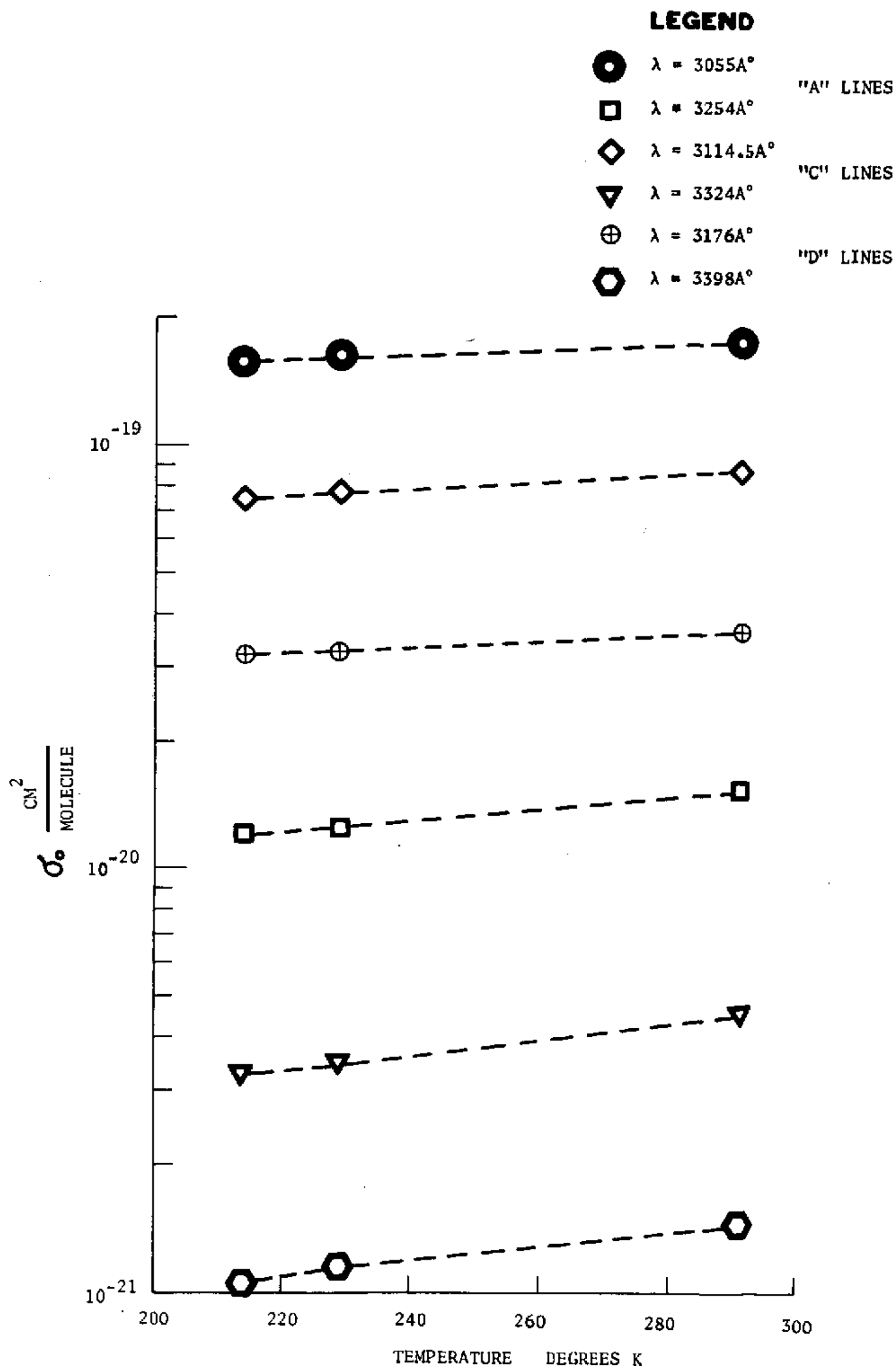

Figure 8 - Ozone Absorption Cross Sections VS Temperature

Analysis of Dobson Direct Sun Measurements

For each model atmosphere described above we simulated radiative transfer through the model for each wavelength in the line pairs A, C and D. The parameter N_λ defined in equation 9 was calculated as a function of receiver field of view using the sum of the direct and scattered intensities reaching the receiver in the direct sun mode. The parameters N_λ so calculated were then used to determine the total ozone in the atmosphere through Dobson's equation using the Dobson coefficients given in Table 2. That is, we calculated the quantities eqs. (13) or (14).

$$X_\lambda = (\alpha-\alpha')^{-1} N_\lambda \ (\sec Z)^{-1} - \left[(\beta-\beta') + (\delta-\delta')\right] (\alpha-\alpha')^{-1}$$

$$= A_\lambda \ N_\lambda \ (\sec Z)^{-1} - B_\lambda$$

Now in equation (10), N_λ is defined as:

$$N_\lambda = \log_{10} \left(\frac{I_0}{I_0'}\right) - \log_{10} \left(\frac{I}{I'}\right)$$

and appears to depend on the values of the solar flux outside the sensible atmosphere for the three line pairs used. Normally these ratios are inferred by making observations at a large number of zenith angles or air masses and extrapolating to zero air mass. However it is easy to show that the scattered intensity for any receiver field of view is always directly proportional to the intensity incident at the top of the atmosphere as is the direct attenuated intensity so we can write $I = K\ I_0$ and $I' = K'I'_0$. Hence $N_\lambda = \log_{10} (I_0/I_0') - \log_{10} (I/I') = \log_{10} (K'/K)$. Or equivalently we can set $I_0 = I_0'$ for each wavelength pair so that $N_\lambda = \log_{10} (K'/K)$. The values of K and K' are calculated by the Monte-Carlo simulation. Thus the values N_λ are independent of the ratios of the incident intensities.

In our calculations we know the true value of the equivalent ozone thickness X since we could integrate the model ozone profile over height to obtain the integrated column count. Dividing by Loschmidt's number, the number of molecules in a cubic centimeter at Standard Temperature and Pressure, gave us the value of X. We could then obtain the true value of α, the average ozone absorption coefficient, by performing the integral in eq 5 namely:

$$\alpha\ X = \int_0^{h_s} \sigma_0 \ (h)\ \rho_0(h)\ dh$$

and divide by X to obtain α in $(\text{atm cm})^{-1}$ or cm^{-1} STP. In our model the value of X was 0.36567 cm STP.

In the same way we could obtain the proper values of β and δ, and so calculate the correct values of A_λ and B_λ eq. (4) used in Dobson's equation, for each model atmosphere. Details of the calculation of the coefficients are contained in Appendix A.

DISCUSSION

The results of our model simulations are summarized in Table 5. These results are for extremely small instrument fields of view so that errors due to singly or multiply scattered light are minimized. These results then reflect the sensitivity of the ozone amounts inferred from Dobson direct sun measurements, to atmospheric temperature profiles.

The source of the errors can be appreciated by neglecting the effects of scattering by molecules and aerosols. We have shown in Reference 1 that the errors due to scattering can be essentially eliminated by narrowing the instrument field of view and by using line pair coupling. Then, viewed as a simple absorption experiment, the Dobson gauge measures

$$\frac{I}{I_o} = 10^{-\alpha X} \text{ or } \log_{10}\left(\frac{I_o}{I}\right) = \alpha X, \text{ for a zenith sun.} \tag{15}$$

Now the quantities αX are defined by equation (5) as:

$$\alpha X = \int_0^{h_s} \sigma_o(h)\ \rho_o(h) dh \tag{16}$$

where $\sigma_o(h)$ is the ozone absorption coefficient (cm^2/molecule) and $\rho_o(h)$ is the ozone number density $\left(\frac{\text{molecules}}{\text{cm}^3}\right)$.

$$\text{Now} \quad n_o X = \int_0^{h_s} \rho_o(h) dh \tag{17}$$

is the integrated column count or the number of ozone molecules in a column with a base area of one square centimeter reaching to the top of the atmosphere. The symbol n_o denotes Loschimdt's number ($2.687\text{x}10^{19}$ molecules/cm^3) the number of molecules per cm^3 at standard temperature and pressure. So we can write

$$\int_0^{h_s} \sigma_o(h)\ \rho_o(h) dh \approx \bar{\sigma}_o n_o X = \alpha X \tag{18}$$

TABLE 5

PERCENTAGE ERROR (OVERESTIMATE) USING DOBSON COEFFICIENTS

MODEL	A LINES	C LINES	D LINES	A-D LINES	C-D LINES	A-C LINES
Standard (30°N)	-1.49	0.33	0.75	-2.13	-0.01	-3.05
45°N Jan	-2.74	-1.69	-1.23	-3.18	-2.06	-3.54
45°N July	-1.74	-0.14	-0.23	-2.23	-0.10	-3.04
60°N Winter Warm	-2.23	-0.72	-1.43	-2.56	-2.01	-3.49
60°N Winter Cold	-3.90	-3.77	-2.55	-4.30	-4.71	-3.82
60°N Jan	-3.19	-2.46	-2.09	-3.59	-2.73	-3.69
60°N July	-1.54	0.24	-0.41	-1.93	0.75	-3.04
30°N Jan	-2.36	-1.18	-0.32	-2.95	-1.84	-3.30
30°N July	-2.05	-0.74	-0.27	-2.63	-1.11	-3.10
15°N	-2.25	-1.10	-0.45	-2.84	-1.61	-3.16
STATISTICS						
Maximum	-1.49	0.33	0.75	-1.93	0.75	-3.04
Minimum	-3.90	-3.77	-2.55	-4.30	-4.71	-3.82
Mean	-2.20	-1.12	-0.82	-2.83	-1.54	-3.32
Standard Deviation	0.76	1.26	1.02	0.72	1.58	0.29

Overall Mean = -2.00 Overall Standard Deviation = 0.99

where $\bar{\sigma}_0$ denotes an average ozone absorption cross section averaged over the ozone density profile.

But what we really have in hand is the quantity αX and to arrive at a correct value for X we need the correct value of α or σ_0. But since σ_0 varies with temperature and so with height in the atmosphere, then in order to calculate the true average value, we need to know the ozone density profile with height.

In practice the value of X we get will depend on the value of α that we use, as long as the value of the absorption coefficient for ozone depends on temperature and hence on height. If the temperature dependence could be eliminated then we could remove the absorption coefficient from the integral eq. (16) and have

$$\int_0^{h_s} \sigma\, \rho_0(h)dh = \sigma \int_0^{h_s} \rho_0(h)dh = \sigma n_0 X = \alpha X$$

According to Mitra (11) the temperature sensitivity of the ozone absorption coefficients has been investigated by Wulf and Melvin (12) from -78°C to 250°C. They found that in the Hartley Bands between 2900Å to 3400Å when the temperature was decreased there was an increase in the maxima in the bands and a decrease in the minima. Similar investigations by Vassy (13) for temperatures between -80° to 20°C did not show a corresponding increase in the band maxima, but confirmed the decrease in the minima. Vassy also investigated the effects of varying pressures (between 19 mm Hg to 760 mm Hg) and found practically no pressure effect. The absorption data of Vigroux quoted in Reference 8 show a consistent decrease in both maxima and minima with decreasing temperature. These conflicting results should be investigated in the laboratory, since Wulf and Melvin's results, if correct, suggest that a broad band line pair might be chosen so that temperature effects are eliminated or considerably reduced. However the results of Vassy and Vigroux appear to contradict Wulf's results.

Table 6 compares the correct values of the parameters A_λ and B_λ calculated for each temperature model with those of Dobson (3). The discrepancy in the values of A_λ reflect the temperature sensitivity of $A_\lambda = \frac{1}{(\alpha-\alpha')}$ or $\frac{1}{(\alpha-\alpha')_A - (\alpha-\alpha')_B}$ say to the average value of the ozone absorption coefficient. Another approach to this problem is to study the variation in values A_λ for each standard atmospheric temperature model for various reasonable ozone density profiles with height. In a sense one could derive an average value for the standard models that would yield better estimates of total ozone than the values now in use.

TABLE 6

CORRECTED VALUES OF A_λ AND B_λ

COMPARED WITH DOBSON VALUES

Lines		Std. Atm.	Subarctic Winter Warm	Subarctic Winter Cold	Subarctic Jan	Subarctic July	Midlatitudes Jan	Midlatitudes July	Subtropical Jan	Subtropical July	Tropical	Dobson Coefficients Ref (3)
			60°N	60°N	60°N	60°N	45°N	45°N	30°N	30°N	15°N	
A	A_λ	0.5754	0.5781	0.5879	0.5836	0.5739	0.5817	0.5754	0.5800	0.5776	0.5787	.5675
	B_λ	0.0665	0.0656	0.0668	0.0663	0.0650	0.0665	0.0655	0.0666	0.0659	0.0661	.0660
C	A_λ	1.1488	1.1560	1.1920	1.1763	1.1448	1.1638	1.1507	1.1660	1.1584	1.1625	1.1560
	B_λ	0.1257	0.1242	1.1396	0.1263	0.1229	0.1265	0.1240	0.1267	0.1251	0.1256	0.1270
D	A_λ	2.6885	2.7129	2.7441	2.7316	2.6843	2.7213	2.6874	2.7070	2.6932	2.6972	2.6730
	B_λ	0.2842	0.2822	0.2854	0.2841	0.2791	0.2849	0.2804	0.2848	0.2817	0.2820	0.2780
A-D	A_λ	0.7322	0.7346	0.7482	0.7422	0.7300	0.7398	0.7322	0.7382	0.7352	0.7368	0.7205
	B_λ	0.0098	0.0096	0.0096	0.0096	0.0096	0.0096	0.0096	0.0097	0.0096	0.0096	0.0090
C-D	A_λ	2.0016	2.0143	2.1074	2.0658	1.9961	2.0520	2.0124	2.0480	2.0326	2.0432	2.0370
	B_λ	0.0035	0.0034	0.0034	0.0034	0.0034	0.0035	0.0034	0.0035	0.0035	0.0035	0.0120
A-C	A_λ	1.1513	1.1561	1.1601	1.1586	1.1509	1.1569	1.1511	1.1541	1.1518	1.1523	1.1147
	B_λ	0.0062	0.0061	0.0061	0.0061	0.0061	0.0062	0.0062	0.0062	0.0062	0.0062	0.0064

In summary then we have reached the following conclusions.

1) The equations used in the reduction of Dobson direct sun measurement depend on the atmospheric temperature profile and the ozone density profile. This dependence is due to the temperature dependence of the ozone absorption coefficient.

2) The absorption spectra of ozone in the Hartley band system (2900Å to 3400Å) should be investigated as a function of wavelength and temperature to elucidate the discrepancy in the published data, determine whether or not a wide band line pair would reduce or eliminate the ozone absorption temperature dependence and to provide more reliable data for interpolating between temperatures.

3) As an interim approach, the appropriate values of the average ozone coefficient α should be evaluated for every standard temperature model for a number of possible ozone profiles; from these investigations appropriate values of A_λ and B_λ to be used in Dobson reductions should be derived.

APPENDIX A

DERIVATION OF THE COEFFICIENTS OF THE TOTAL OZONE ESTIMATION EQUATION

Referring to equation (12) we see that the form of the ozone estimation equation is

$$X = A_\lambda N_\lambda \cos Z - B_\lambda \tag{A-1}$$

where

$$N_\lambda = \log_{10}\left(\frac{I_o}{I_o'}\right) - \log_{10}\left(\frac{I}{I'}\right) \tag{A-2}$$

and A_λ and B_λ are constants which may be derived from the properties of the atmosphere for each line pair or set of coupled line pairs. Values of A_λ and B_λ have been derived for standard conditions making certain assumptions in regard to scattering and absorption cross sections of the atmospheric constituents. In this section we explain how we used the information generated by the Monte-Carlo program "INPUT" subroutine to derive new values of these coefficients which would be relevant for our particular model atmospheres and ozone temperature sensitivity coefficients.

Five sets of coefficients were derived for the following cases:

1) A lines
2) C lines
3) D lines
4) A-D lines
5) C-D lines

We shall treat the line pairs first and then explain the procedure for the coupled line pairs.

Equation (12) shows that for uncoupled line pairs we may write

$$A_\lambda = \frac{1}{\alpha-\alpha'} \tag{A-3}$$

and

$$B_\lambda = \frac{(\beta-\beta') + (\delta-\delta')}{(\delta-\delta')} \tag{A-4}$$

Referring back to equation (8) we can see that αX can be related to the contribution of absorption to the optical thickness of the atmosphere. Neglecting aerosol and molecular scattering we would obtain for an overhead sun (i.e., zenith angle equal to zero)

$$\log_{10}\left(\frac{I_\lambda}{I_{o\lambda}}\right) = -\alpha X \tag{A-5}$$

But the contribution of absorption by ozone to the total optical thickness can be represented as

$$\tau_{oz} = \log_e\left(\frac{I_{o\lambda}}{I_\lambda}\right) = -2.313 \log_{10}\left(\frac{I_\lambda}{I_{o\lambda}}\right) \tag{A-6}$$

$$= 2.303\ \alpha X$$

Hence, we can write $\alpha-\alpha'$ as

$$\alpha-\alpha' = \frac{\tau_{oz} - \tau'_{oz}}{2.303X} \tag{A-7}$$

Now in the computer program we compute specifically the total optical thickness τ_t in each case and the contribution of scattering to this value, τ_s. Since absorption in the wavelengths of interest is attributed to ozone alone we have that $\tau_{oz} = \tau_t - \tau_s$.

Thus (A-7) may be rewritten as

$$\alpha-\alpha' = \frac{\tau_t-\tau_s - \tau_t'+\tau_s'}{2.303X} \tag{A-8}$$

All of the parameters of the right hand side of equation (A-8) are available from the atmospheric model and cross section assumptions and are explicitly evaluated and output on a routine basis. Thus we have

$$A_\lambda = (\alpha-\alpha')^{-1} = \frac{2.303X}{\tau_t-\tau_s - \tau_t'+\tau_s'} \tag{A-9}$$

By a similar argument we are able to derive the value of B_λ from the scattering contribution to the total optical thickness. If we neglect absorption by ozone in equation (8) we obtain for an overhead sun

$$\log_{10}\left(\frac{I_\lambda}{I_{o\lambda}}\right) = -(\beta+\delta) \tag{A-10}$$

The contribution of scattering to the total optical thickness is in this case,

$$\tau_s = \log_e \frac{I_{o\lambda}}{I_\lambda} = -2.303 \log_{10} \frac{I_\lambda}{I_{o\lambda}} \tag{A-11}$$

$$= 2.303\ (\beta+\delta)$$

Thus

$$\beta+\delta = \frac{\tau_s}{2.303} \tag{A-12}$$

Hence,we can write $(\beta+\delta)$ - $(\beta'+\delta')$ as $(\tau_s-\tau_s')/2.303$ and (A-4 becomes)

$$B_\lambda = \frac{(\tau_s-\tau_s')}{2.303}\ A_\lambda \tag{A-13}$$

where A_λ is computed by equation (A-9).

Equation (A-9) and (A-13) are employed to evaluate corrected coefficients A_λ and B_λ for the A, C and D lines. For line pair coupling we rewrote (A-1) as

$$N_\lambda \cos Z = \frac{X}{A_\lambda} + \frac{B_\lambda}{A_\lambda} \tag{A-14}$$

When we couple line pairs we subtract another equation of this type from (A-16) obtaining

$$(N_\lambda-N_\lambda')\cos\ Z = X\left(\frac{1}{A_\lambda} - \frac{1}{A_\lambda'}\right) + \frac{B_\lambda}{A_\lambda} - \frac{B_\lambda'}{A_\lambda'} \tag{A-15}$$

where the dash now stands for another line pair. Inverting (A-15) we obtain

$$X = \left(\frac{1}{A_\lambda} - \frac{1}{A_\lambda'}\right)^{-1} (N_\lambda-N_\lambda')\cos Z - \left(\frac{B_\lambda}{A_\lambda} - \frac{B_\lambda'}{A_\lambda'}\right)\left(\frac{1}{A_\lambda} - \frac{1}{A_\lambda'}\right)^{-1} \tag{A-16}$$

Equation (A-16) gives us the appropriate coefficients for coupled line pairs in terms of parameters evaluated in the computer model set-up. These are employed to obtain the coefficients attributed to Thomas in the computer output and are applied to evaluate errors as a function of the field of view.

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