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ON THE SCATTERING OF ULTRAVIOLET SOLAR RADIATION IN THE ATMOSPHERE WITH THE OZONE ABSORPTION CONSIDERED

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Abstract. In this paper an attempt has been made to give observational evidence of the existence of multiple molecular scattering and non molecular scattering of light in the ultraviolet region where the ozone absorption is very strong. An approximate method for calculating secondary scattered light considering ozone absorption has been developed and used for analysing the observed data. Information about the effects of multiple molecular and non molecular scattering processes has been obtained which should be taken into account when the vertical distribution of the ozone in the atmosphere is deduced by the «Umkehr Method».

CONTENTS

I. THE PRIMARY AND SECONDARY SCATTERING OF SUNLIGHT IN A PLANE-STRATIFIED ATMOSPHERE OF UNIFORM COMPOSITION

1. Introduction. The existence of multiple molecular scattered radiation and light scattered from large sized scattering material in the atmosphere is theoretically well established. In spite of the importance of this subject to meteorology and illumination problems, good measurements to support the rather complicated theories are few [1].

In this paper an attempt has been made to give observational evidence of the existence of multiple molecular scattering of light in the ultraviolet region. In the ultraviolet region the ozone absorption is very strong and the influence of ozone absorption on the scattering processes has been studied.

In the attempt which is made to give this observational evidence, particular directions of observation are introduced. The problem of analysing the observed data, however, presents many difficulties. An exact mathematical treatment has been abandoned in favour of an approximate method, developed by the author, for calculating secondary scattered light considering ozone absorption. Comparison between observed effects and calculated effects of secondary molecular scattering has given information about multiple molecular and non-molecular scattering processes which should not be neglected when the vertical distribution of ozone in the atmosphere is deduced by analysing zenith light measurements.

As was done by Hammad and Chapman [2], primary and secondary scattering of sunlight is considered, in a plane-stratified atmosphere of uniform composition. Later, an absorbing ozone layer is introduced.

Any transformation of energy from or to other wavelengths by absorption and re-emission, is neglected. Attention is restricted to a monochromatic constituent of the light, between the wavelengths λ and $\lambda + d\lambda$. Refraction and polarization are not considered. Thus the problem is treated in restricted form, and the treatment deals with only a part of the actual problem of atmospheric illumination.

2. The attenuation and scattering of sunlight. When a beam of light of intensity $Id\lambda$, passes through an air-mass, it loses energy by scattering. The rate of loss per unit mass of air is $\sigma Id\lambda$, where σ or $\sigma(\lambda)$ denotes the scattering coefficient of the air per unit mass for light of wavelength λ. When we consider only a single monochromatic constituent of light, usually the reference to λ is omitted.

If a small volume of air, dv of mass ϱdv, is that part of the region traversed by a pencil of the incident radiation of normal crossection ds, which is intercepted between the heights h and $h + dh$, then $dv = \sec z\, dh\, ds$, where z is the zenith distance of the incident radiation. The rate of loss of energy along the pencil will be

$$dI d\lambda\, ds = \sigma \varrho \sec z\, dh ds\, I d\lambda$$

or

$$dI = - sI \sec z\, d\overline{m}$$

Here the fraction of air mass above our operating level at height h in the atmosphere, is denoted by $\overline{m}$. If M is the total mass of air in a vertical column of unit crossection area, we have

$$\overline{m} = \frac{1}{M}\int_h^{\infty} \varrho\, dh \text{ and } m = \frac{1}{M}\int_0^{h} \varrho\, dh$$

where ϱ denotes the air density. s, the total scattering coefficient for vertically incident light, is defined by $s = \sigma M$. By logarithmic integration we get

$$I = Io\, e^{-s \sec z \overline{m}}$$

which gives the attenuation of direct sunlight in the atmosphere where Io denotes the solar radiant energy which is received per unit time on a unit area normal to the unit vector S directed towards the sun.

$\sigma Id\lambda$ is the rate of loss of energy by scattering per unit mass of air per unit time for a beam of incident light. This energy abstracted from the beam is reemitted as primary scattered light in all directions at the rate $\sigma Id\lambda$ per unit mass per unit time. Rayleigh showed that the intensity of the light scattered in directions lying within the cone denoted by $\overline{K}d\overline{K}$ is proportional to $(1 + \cos^2 \psi)\, d\overline{K}$ where ψ is the scattering angle, the angle between $\overline{K}$ and $\overline{S}$, the direction of incident radiation. Integration over all directions $\overline{K}$ gives

$$\int_{\overline{K}} (1 + \cos^2 \psi)\, d\overline{K} = \frac{16}{3}\pi$$

The actual fraction of the light emitted by this scattering, within the cone $\bar{K}d\bar{K}$ is $3/16\,\pi\ (1 + \cos^2\psi)\ d\bar{K}$. The intensity of primary scattered sunlight emitted per unit mass of air at the height h, within the cone $\bar{K}d\bar{K}$ is given by

$$E_1(\lambda, h, z, \bar{K}) = \frac{3}{16\,\pi}\,\sigma\, I_0\,(1 + \cos^2\psi)\, e^{-s \sec z \bar{m}}\, d\bar{K}$$

3. The reception of primary scattered light. Suppose B in Fig. 1 denotes the point of observation. $\bar{K}$ denotes the direction of observation with zenith distance θ. $\bar{S}$ denotes the direction of sun rays with zenith distance z. $r = oB$. Element dV, the element with $\bar{K}$ as its axis, is represented by

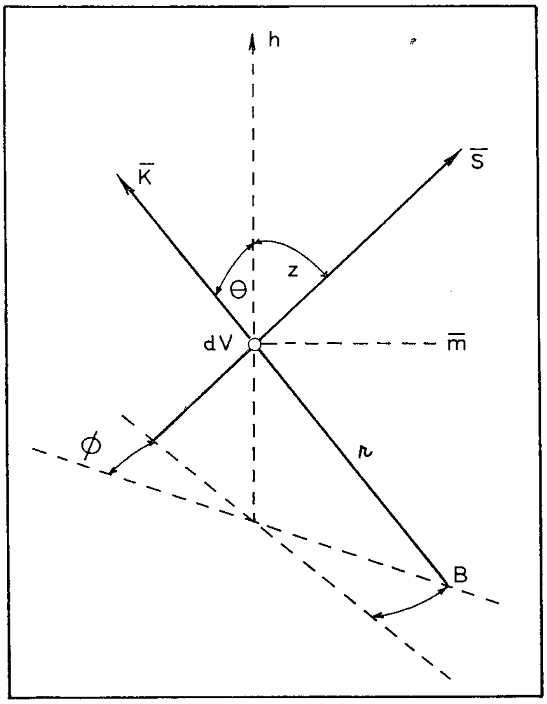

Fig. 1.

$$dV = rd\varphi\, rd\theta\, dr = r^2 d\bar{K}\, dr$$

Light from the sun at dV has an intensity I_1, and primary scattered light towards B, i.e. in direction ψ where ψ is the scattering angle, is dI_1 where

$$dI_1 = I_1 \frac{3}{16\,\pi}\,\frac{s}{M}\,\varrho dV\,(1 + \cos^2\psi)$$

The intensity of the light falls at the rate $1/r^2$ from the point of scattering. Also this radiation passes through an air mass $(\bar{m} - \bar{m}')$ sec θ before reaching B, and the intensity of the scattered light received at B from dV will be dI_R where

$$dI_R = I_1 \frac{3}{16\,\pi}\,\frac{s}{M}\,\varrho dV\,(1 + \cos^2\psi)\,\frac{1}{r^2}\, e^{-s \sec\theta(\bar{m} - \bar{m}')}$$

Now we have

$$I_1 = I_0\, e^{-s\bar{m}' \sec z}$$

$$dV = r^2 d\bar{K}\, dr \text{ and } dr = -\frac{M}{\varrho}\, d\bar{m} \sec\theta$$

and we get

$$dI_R = I_0 \frac{3}{16\,\pi}\, sd\bar{K}\,(1 + \cos^2\psi)\, e^{-s(m - \bar{m}')\Theta}\, e^{-sm Z}\,(-d\bar{m}')\Phi$$

where $Z = \sec z$,
$\Theta = \sec\theta$.

Integration from $\bar{m}' = 0$ *to* $\bar{m}' = m$ i.e. from the top of the atmosphere to depth $\bar{m}$, gives

$$I_R/d\bar{K} = R_D = \frac{3}{16\pi} I_0 s \,(1 + \cos^2\psi)\, \frac{1}{s}\, \frac{\Theta}{Z - \Theta} \left\{ e^{-s\Theta\bar{m}} - e^{-sZ\bar{m}} \right\}$$

or

$$R_D/Ks = (1 + \cos^2\psi)\, \frac{1}{s}\, \frac{\Theta}{Z - \Theta} \left\{ e^{-s\Theta\bar{m}} - e^{-sZ\bar{m}} \right\} \tag{3.1}$$

where R_D means intensity of primary scattered light downwards and where $K = \frac{3}{16\pi} I_0$.

Integration from $\bar{m} = o$, the top of the atmosphere, to $\bar{m} = 1$, the ground, gives

$$R_D/Ks = (1 + \cos^2\psi)\, \frac{1}{s}\, \frac{\Theta}{Z - \Theta} \left\{ e^{-s\Theta} - e^{-sZ} \right\} \tag{3.2}$$

If $Z = \Theta$ we get

$$R_D/Ks = (1 + \cos^2\psi)\, Z\bar{m} e^{-s\bar{m}Z} \tag{3.3}$$

where $\bar{m}$ gives the depth of the point of observation. For a point of observation at ground level and $Z = \theta$ we get

$$R_D/Ks = (1 + \cos^2\psi)\, Z e^{-sZ} \tag{3.4}$$

If a part of the atmosphere is considered, we have to integrate from the depth $\bar{m}_1$ to the depth $\bar{m}_2$ where the point of observation is at depth $\bar{m}_2$. In this case we get

$$R_D/Ks = (1 + \cos^2\psi)\, \frac{1}{s}\, \frac{\Theta}{Z - \Theta}\, e^{-\bar{m}_2 s\Theta} \left\{ e^{-(Z-\Theta)\bar{m}_1 s} - e^{-(Z-\Theta)\bar{m}_2 s} \right\} \tag{3.5}$$

For upward scattered light, we have to integrate from m' $= 0$, ground level, to $m' = m$ the level of observation. Remembering that $\bar{m} = 1 - m$ we get

$$R/Ks = (1 + \cos^2\psi)\, \frac{\Theta}{s\,(\Theta + Z)}\, e^{-sZ} \left\{ e^{+Zms} - e^{-\Theta ms} \right\} \tag{3.6}$$

4. The emission and reception of secondary scattered light. The air at any height h receives primary scattered light from all directions $\bar{K}'$ with zenith angle θ', and all such light is scattered in all directions as secondary scattered sunlight. The light emitted by secondary scattering per unit mass of air at height h in directions lying within the cone $\bar{K}d\bar{K}$ is $E_2 d\lambda d\bar{K}$. The contribution to this, made by the primary scattered sunlight coming from directions $\bar{K}'$ may be calculated in a way analogous to the calculation of emission of primary scattered sunlight. We were there concerned with the scattering of direct sunlight coming only from direction $\bar{S}$, so now $R_1 d\lambda d\bar{K}'$ must be subtituted for $R_0 d\lambda d\bar{S}$. Therefore we have

$$dE_1 = \frac{3}{16\,\pi}\,\sigma\,(1 + \cos^2 \psi')\;R_0 d\bar{S}$$

and

$$dE_2 = \frac{3}{16\,\pi}\,\sigma\,(1 + \cos^2 x)\;R_1 d\bar{K}'$$

representing the contribution made to E_2 by primary scattered light from directions $\bar{K}'d\bar{K}'$. By summing this expression over all directions $\bar{K}'d\bar{K}'$, we obtain E_2, and

$$E_2 = \frac{3}{16\,\pi}\,\sigma \int (1 + \cos^2 x)\,R_1\,d\bar{K}'$$

where the integration extends over all directions of K' except at the ground and at the top of the atmosphere where it extends over one hemisphere only. We can write $\sin\,\theta'\;d\,\theta'\;d\,\Phi$ in place of $d\bar{K}'$ and we get

$$E_2\,(\lambda, h, z, K) = \frac{9\,\sigma\,s}{256\,\pi^2}\,I_1 \int_0^{2\pi}\int_0^{\pi/2}\int_0^{1} e^{-Zms-\Theta' s(m-m')}\;(1 + \cos^2 \psi')\;(1 + \cos^2 \chi)\;\times$$

$$\times\;\sec\,\theta'\;\sin\theta'\;dm'\;d\,\theta'\;d\,\Phi'$$

as the expression for the emission of secondary scattered light. The calculation of the secondary scattered sunlight received at any level, in terms of the secondary emitted sunlight, is similar to the corresponding calculation of reception of primary scattered light. The result is obtainable by changing the suffix 1 to 2. We had

$$R_1 = M\,\Theta' \int_m e^{-\Theta'(m-m')\,s}\;E_1 dm'$$

and

$$R_2 = M\,\Theta' \int_m e^{-\Theta'(m-m')\,s}\;E_2 dm'$$

The evaluation of the expression for R_2 is however rather complicated. HAMMAD and CHAPMAN's paper discusses and completes the exact formal solution. But still, as mentioned in their paper, it is necessary to evaluate the formula for R_1 and R_2 numerically before the solution may be of any use in connection with actual observation. It was eight years after the formal solution had been published in 1939, before numerical tables and discussion of primary and secondary scattered light received at the ground, were presented [3].

In this paper the principal question is how an absorbing ozone layer acts upon primary and secondary scattering. HAMMAD and CHAPMAN are considering a pure Rayleigh atmosphere with no absorbing matter present, where attenuation of light is due to scattering alone. Walton, in his thesis [4], has calculated secondary scattered light with an ozone layer present. But he has dealt with direction of observation towards zenith only, whereas in this work other directions of observation are preferable in order to study secondary and higher orders of scattering by observation. The author has found it necessary to develop an approximate method for calculating intensities of secondary scattered light where ozone absorption is considered. In this approximate calculation the problem is easier to follow physically and simpler to handle, and complicated exact mathematical treatment has been abandoned in favour of it.

In the approximate method attention is restricted to a monochromatic constituent of the light. Refraction and polarization are not considered, but an absorbing layer of ozone is brought in, which plays an important role in the problem of atmospheric illumination in the ultraviolet. The atmosphere is presumed to be resting on a flat earth.

5. Mean scattering level. We have found for dI_R the primary scattered light received at depth $\bar{m}$ and emitted from a mass element at depth $\bar{m}'$

$$dI_R = K \frac{s}{M} \varrho\, r^2\, d\bar{K} dr\ (1 + \cos^2 \psi)\ \frac{1}{r^2}\ e^{-s(\bar{m}-\bar{m}')}\ e^{-s\bar{m}'Z}$$

When light scattered from the zenith and received at the ground is considered, dI_R will be reduced to

$$dI_R = K \frac{s}{M} \varrho\, r^2\, d\bar{K} dr\ (1 + \cos^2 z)\ \frac{1}{r^2}\ e^{-s(1-\bar{m}')}\ e^{-s\bar{m}'Z}$$

The expression for the mass of scattering material in the element dv will be

$$dM = \varrho\, r^2\, dK dr = M \left| dm \right| r^2\, dK$$

remembering $dr = \dfrac{M}{\varrho} \left| dm \right|$

Mdm is interpreted as the mass concentration at the depth $\bar{m}$ in direction $\bar{K}$, and we can write

$$\frac{dI_R}{dK} = K \frac{s}{M}\ Mdm\ (1 + \cos^2 z)\ e^{-s}\ e^{-s(Z-1)\bar{m}}$$

or

$$R_1/K = \frac{s}{M} \triangle M\ (1 + \cos^2 z)\ e^{-s}\ e^{-s(Z-1)\bar{m}}$$

where $\triangle M$ is the mass of scattering material in an emitting scattering mass element at depth $\bar{m}$, which can be denoted as a scattering mass point. If $\triangle M = M$, the whole scattering air mass is concentrated in one such scattering mass point at depth $\overline{m}_z$ representing a summation of all contributory scattering elements along $\overline{K}$.

The amount of light which is received at the ground and scattered from a scattering mass point with the whole scattering air mass concentrated, depends on the attenuation of both direct sunlight and scattered light. The value of $\overline{m}_z$ may be adjusted to a representative depth, at which the whole re-emitting atmosphere is concentrated, and we call $m_z = 1 - \overline{m}_z$ the mean scattering level.

The mean scattering level is a function, when considering zenith light, of z and s, the sun's zenith distance and the total scattering coefficient respectively. When the sun's zenith distance increases, the mean scattering level will ascend, and will ascend more rapidly when we go to shorter wavelength.

By concentrating the whole air mass which is scattering in a direction, θ, in a mass scattering point at depth, $\overline{m}$, we get $\triangle M = M \sec \theta$. For a direction of observation with the same zenith distance as the sun, i.e. $\theta = z$, the light scattered from the mass scattering point and received at the ground will be

$$I_R = \frac{3}{16\,\pi} I_0 \,(1 + \cos^2 \psi) \sec z \, e^{-\sec z s}$$

We see that we have here the exact formula, and the mass scattering point may be at any level.

If the point of observation is at a depth $\overline{m}$, the mass concentration will be $\triangle M = \overline{m} M \sec \theta$, and we get

$$R_1/K = (1 + \cos^2 \psi) \, \overline{m} \sec \theta \, e^{-\overline{m} \sec z s}$$

again the exact formula.

6. Approximate method for calculating intensities of secondary scattered sunlight.

For this method the atmosphere is divided into three sections:

$$\begin{aligned} \overline{m} &= 0 \text{ to } \overline{m} = \cdot 3 \ (\triangle M_1) \\ \overline{m} &= .3 \text{ to } \overline{m} = .6 \ (\triangle M_2) \\ \overline{m} &= .6 \text{ to } \overline{m} = 1.0 \ (\triangle M_3) \ \text{(fig. 2)}. \end{aligned}$$

We concentrate the emitting scattering air mass for each section at depths

$$\begin{aligned} \overline{m}_c &= .15 \text{ for } \triangle M_1 \\ \overline{m}_c &= .45 \text{ for } \triangle M_2 \\ \overline{m}_c &= .80 \text{ for } \triangle M_3 \end{aligned}$$

For each section we calculate exact intensities of primary scattered light received in $\triangle M$ from directions $\overline{K}'$, say $\sec \theta' = 1, 2, 3, 5$ and ∞, in halfplanes through $\Phi' = 0$,

π and $\pm\,\pi/2$ where Φ is azimuth relative to the half-plane through the sun. Calculation is carried out for scattered light upwards. If we write $f = (1 + \cos^2 \psi')$, primary scattered light along $\bar{K}'$ received in $\triangle M$ at $\bar{m}_c$ may be expressed by

$$(f_{\Theta'} \times r_{\Theta'})_{\Phi', m_c} = R_1/Ks$$

for down- and upwards light, and where for downwards light equation (3.1) is used, and for upgoing light equation (3.6) is used. $\triangle M$ will then, as a mass scattering point representing a section of the atmosphere, re-emit or transfer part of the light received, as secondary scattered light. Secondary scattered light emitted from $\triangle M$ along direction $\bar{K}$ will have the scattering angle χ, the angle between $\bar{K}'$ and $\bar{K}$.

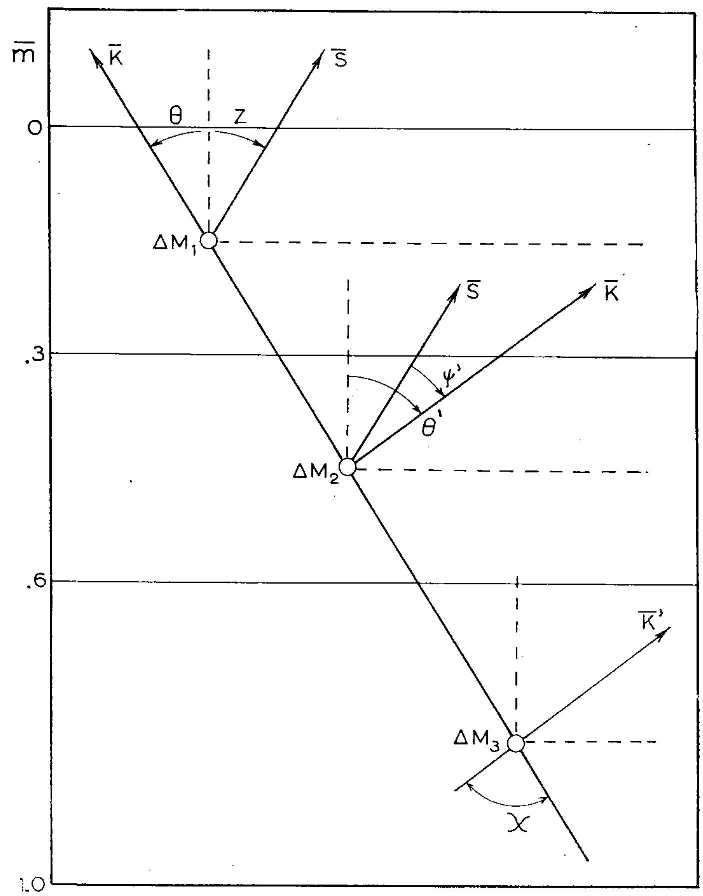

Fig. 2.

$$\text{We have } \bar{K}' = \bar{K}'\,(\Theta', \Phi')$$
$$\bar{K} = \bar{K}\,(\Theta, \Phi)$$

and

$$\cos \chi = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos (\Phi - \Phi')$$

We write $g = (1 + \cos^2 \chi)$, and light emitted as secondary scattered light may be expressed as E_2 where

$$E_2 = (f \times g)\,(r)\,Ks\,\frac{3}{16\,\pi}\,\frac{s}{M}\,\triangle M$$

for a given $\bar{K}' = \bar{K}'\,(\theta', \Phi')$
a given $\bar{K} = \bar{K}\,(\theta, \Phi)$
a given $\bar{S} = \bar{S}\,(z)$

and a given $\triangle M$ at depth $\bar{m}_c$ .s is the total scattering coefficient.

Light emitted from $\triangle M$ as secondary scattered light along $\bar{K}$, will be attenuated before reaching ground level. Secondary scattered light received at ground level due to primary scattering along $\bar{K}'$ may be expressed in terms of $R_2\ (\bar{K}')$ where

$$R_2\ (\bar{K}') = E_2\ (\bar{K}')\ e^{-\bar{m}_c \Theta_s}$$

The contribution due to primary scattered light from all directions $\bar{K}'$ is making up the intensity of secondary scattered light emitted from $\triangle M$. If we say

$$\underset{\text{Mean}}{E_2\ (\bar{K}')} = \frac{1}{n} \sum_n E_2\ (\bar{K}')$$

this mean represents an average value of secondary scattered light emitted from $\triangle M$ in direction $\bar{K}$ per unit solid angle when a certain half-plane through Φ' is considered for either up- or downgoing primary contributory scattering. Hence

$$\left\{ \begin{matrix} E_2\ (\bar{K}') \\ \text{Mean} \end{matrix} \right\} \times \underset{(\theta')}{\frac{\pi}{2}} \times \underset{(\varphi')}{\frac{\pi}{2}}$$

will give the contribution of secondary scattered light emitted from $\triangle M$ due to primary scattering received from one quarter of the hemisphere above or below the mass scattering point $\triangle M$ considered. The procedure is carried out for halfplanes through $\Phi = 0$, π and $+ \pi/2$. The secondary scattered light received at ground level in a direction $\bar{K}$ from mass scattering points $\triangle M_1$, $\triangle M_2$ and $\triangle M_3$ will make up the total amount of secondary scattered light which is scattered along direction $\bar{K}$ and received at ground level.

The mass concentrated in $\triangle M$ is the mass of scattering matter in the sloping column in the direction $\bar{K}$ from the mass scattering point $\triangle M$ to the top of the atmospheric section when primary scattering downwards is considered. When primary scattering upwards is considered, $\triangle M$ must contain the mass of scattering material in the sloping column intercepted between the mass scattering point $\triangle M$ and the lower boundary of the section in direction K.

One probably introduces an error by putting the mass scattering point at the center of pressure in each section. This will however, facilitate the calculation, and the error may not be serious when a section of the atmosphere is represented in each mass scattering point.

7. Numerical tables of primary and secondary scattered light received at ground in direction z $= 0$, $\Phi = \pi$. Following this procedure of calculating secondary scattering values of R_2/Ks^2 have been derived and are tabulated in Table 1. Values of R_1/Ks and the ratio R_2/R_1 are given in the same table, and HAMMAD's values for R_2/Ks^2 are given in brackets. The author is aware that it has been pointed out by WALTON [4] that HAMMAD and CHAPMAN's theory is not quite correct. WALTON has, very kindly worked out one value for R^2/Ks^2 for contour measurement, following his theory, but with depolarization factor $\partial = 0$. This value is, for comparison, shown in the table.

It is seen from the table that the values of R_2/Ks^2 derived, are in reasonable agreement with those of HAMMAD, considering that the method used is an approximate one. The intensity ratio R_2/R_1 increases towards shorter wavelengths and for a lower sun. For a low sun, the pathlength through the atmosphere is very long and the chance for secondary scattering to predominate is greater, especially at shorter wavelengths. As will be shown later, this feature will be more pronounced when an absorbing ozone layer is present in the atmosphere.

Table 1. *Values of R_1/Ks and R_2/Ks^2 and R_2/R_1.*
Direction of observation: $\Phi = \pi$, $\theta = z$.

s	(sec z) sec θ	R_1/Ks	R_2/Ks^2	R_2/R_1	*Hammad* R_2/Ks^2	*Walton* R_2/Ks^2
.4	1	1.341	.663	.20	(.755)	
	2	1.123	1.305	.46	(1.254)	
	4	1.426	1.403	.39	(1.340)	
.8	1	.899	.309	.28	(.389)	
	2	.505	.392	.62	(.421)	
	4	.288	.221	.61	(.245)	
1.0	1	.736	.231	.31	(.289)	
	2	.338	.235	.70	(.258)	(.241)
	4	.129	.096	.74	(.115)	

8. An approximate method for calculating secondary scattering where ozon absorbtion is considered. A model of the atmosphere where the atmospheric ozone is represented by a thin layer, is used. This is assumed to be a good approximation. For our purpose we have put the ozone layer at a depth $\bar{m} = .150$ (approximately 150 mb). This may be too low down, but we are bound by the distribution of the mass scattering points we have selected. If we had all three mass scattering points below the ozone layer, we would have no secondary scattering source above the ozone, and this would certainly not be the best approximation.

We consider primary scattered light, downwards, from direction $\bar{K} = \bar{K}\ (\theta', \Phi')$ which is received at a mass scattering point $\triangle M_1$ at a depth $\bar{m}_1$. The thin ozone layer has been put just under this mass scattering point, but at the same depth[1]. The ozone layer will attenuate the secondary scattered light emerging from $\triangle M_1$ along direction

[1] By doing this, one introduces a model of the atmosphere which physically is not quite consistant. one ought to divide $\triangle M_1$ into two scattering mass points with the thin ozone layer in between. The numerical calculations showed, however, that the error introduced by not dividing $\triangle M_1$ is negligible.

$\bar{K}$. The attenuation due to the ozone layer is expressed by exp (— a sec θ) where a is the absorption coefficient. Including the attenuation due to the air between $\triangle M_1$ and ground level, the secondary scattered light received at ground level will be attenuated by an amount,

$$e^{-a \sec \theta} \; e^{-s m_1 \sec \theta}$$

which is valid for secondary scattering emitted from $\triangle M_1$ due to primary scattered light from all downwards directions $\bar{K}'$.

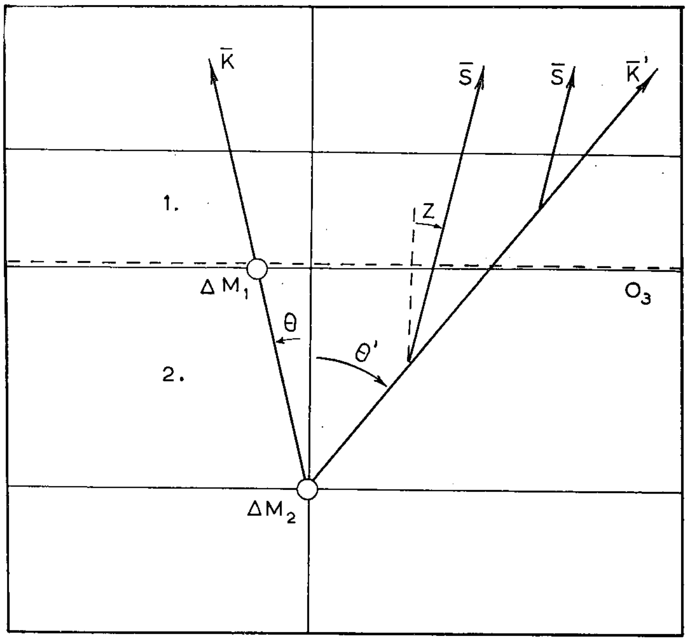

Fig. 3. Dividing of atmosphere into two separate regions.

Primary upwards scattered light, from direction $\bar{K}'$ also is received in $\triangle M_1$. Sunrays creating this primary scattered light upwards along $\bar{K}'$, have to penetrate the ozone layer before reaching $\bar{K}'$. Hence, the sunlight will be attenuated at the rate exp (— a sec z). The primary scattered light will have to pass the ozone layer before reaching the mass scattering point $\triangle M_1$, and will be attenuated at the rate exp (— a sec θ'). The ozone layer will again attenuate the secondary scattered light emerging $\triangle M_1$ along direction $\bar{K}$, at the rate exp (— a sec θ). The air mass intercepted between $\triangle M_1$ and ground level will further attenuate the light before it reaches the point of observation. Hence, we will have secondary scattered light emerging from $\triangle M_1$, reaching ground level and, because of primary upwards scattered light along $\bar{K}' = \bar{K}' (\theta)'$ attenuated at the rate

$$e^{-a \sec z} \; e^{-a \sec \theta'} \; e^{-a \sec \theta} \; e^{-\sec \theta \, m_1 s}$$

When considering the mass scattering point $\triangle M_2$, we divide the atmosphere which contributes to downwards primary scattered light received at $\triangle M_2$, into two sections, denoted by 1 and 2 (Fig. 3). Section 1 is the section above the ozone layer. Section 2 is the section between the ozone layer and $\triangle M_2$.

Section 1 contributes to primary scattered light at $\triangle M_2$ if no ozone absorption is considered, with intensity R_D, where

$$R_D = Ksf \frac{\Theta'}{Z - \Theta'} \left\{ e^{-\Theta' \overline{m}_1} - e^{-Z \overline{m}_1} \right\} e^{-\Theta' (\overline{m}_2 - \overline{m}_1) s}$$

Primary scattered light from section 1 will be attenuated as it passes through the ozone layer along direction $\overline{K}'$. Hence, primary scattered light received at $\triangle M_2$ from section 1 will have the intensity (R_D)exp(-a sec θ').

The primary scattered light, from section 2, received at $\triangle M_2$ will have the intensity R_D where

$$R_D = Ksf \frac{\Theta'}{Z - \Theta'} e^{-\Theta' \overline{m}_2} \left\{ e^{-(Z - \Theta') \overline{m}_1} - e^{-(Z - \Theta') \overline{m}_2} \right\}$$

when no ozone absorption is considered. The direct sunrays will, however, be attenuated by the ozone layer before reaching section 2, and the light scattered from section 2 along direction $\overline{K}'$ and received at $\triangle M_2$, will have the intensity (R_D)exp(-a sec z). The secondary scattered light emitted from $\triangle M_2$ and due to primary scattering downwards, will have no further attenuation due to ozone.

Direct sunlight giving primary upwards scattered light along $\overline{K}'$, will be attenuated in the ozone layer before reaching the section intercepted between $\triangle M_2$ and ground level, at a rate exp(-a sec z). Secondary scattered light, emitted from $\triangle M_2$ and due to primary scattered light upwards, will have no further attenuation due to ozone.

We may say that light received at $\triangle M_2$, including both upwards- and downwards scattered light will be

$R_D\, e^{-a \sec \theta'}$ (from sect. 1)
$R_D\, e^{-a \sec z}$ (from sect. 2)
$R_U\, e^{-a \sec z}$ (from sect. below $\triangle M_2$).

which in turn is transferred as secondary scattered light. When considering the mass scattering point $\triangle M_3$, the atmosphere has to be divided into the sections 1 and 3, where section 1 is that part of the atmosphere above the ozone layer, and section 3 is the part of the atmosphere intercepted between ozone layer and depth $\overline{m}_3$, the depth of $\triangle M_3$. The procedure when considering $\triangle M_3$ is analogous to that for $\triangle M_2$.

Solar radiation reaching ground level as secondary scattered sunlight, will have penetrated the ozone layer either once or three times. It is however, only the secondary scattered light emitted from M_1, which passes the ozone layer after secondary scattering.

The procedure of calculating secondary scattering with ozone absorption taken into account is the same as that for no ozone absorption when the rate of attenuation due to the ozone layer is applied to the products (f $\times$ g) (r).

As to primary scattered light received at ground level from direction of observation $\theta = z$ and $\Phi = \pi$, we have

$$R_1/Ks = f \sec z\, e^{-\sec z\, s}$$

for no ozone absorption, and

$$R_1/Ks = f \sec z\, e^{-\sec z\, s}\, e^{-\sec z\, a}$$

when ozone absorption is considered.

9. Numerical results. Primary and secondary scattering received at ground from an atmosphere with ozone. Applying the approximate method for calculating secondary scattering, when an absorbing ozone layer at depth $\overline{m} = .150$ in the atmosphere is considered, the following numerical values of primary and secondary scattering received at ground are derived. Values of primary and secondary scattering, with and without ozone absorption, are tabulated in Table 2.

Table 2. *Intensities of primary and secondary scattering, R_1 and R_2, received at ground level.* Direction of observation: $\theta = z$, $\Phi = \pi$. a = ozone absorption coefficient, s = scattering coefficient.

$\sec \theta = \sec z$	s	a	O_3 *in cm*	R_1/Ks	R_2/Ks^2	R_2/R_1
1	1.0	1.0	.360	.2707	.0702	.26
2				.0458	.0281	.61
4				.0024	.0036	1.53
1	1.0	.5	.180	.446	.119	.27
2				.124	.076	.61
4				.017	.016	.94
1	1.0	0	0	.763	.231	.31
2				.338	.235	.70
4				.129	.096	.75
1	.8	0	0	.899	.309	.28
2				.505	.392	.62
4				.288	.221	.61

The ozone layer effects both primary and secondary scattering, but when the sun is high, the secondary will suffer more than the primary scattering. Hence, at high sun the primary scattering will be more predominant due to the atmospheric ozone than if no ozone absorption had been considered. For low sun, primary scattering will suffer more than secondary by ozone absorption, secondary scattering will be more predominant as the ozone absorption increases, and for larg ozone absorption the intensity of secondary will exceed the intensity of primary scattering. It would be of great importance to be able to support these interesting effects, by observation. This cannot be done directly. Any observation will give primary plus multiple scattering, and it would be impossible to distinguish between different orders of scattering. In the next section however, it will be shown how the particular direction of observation $z = \theta$, sky contour measurement, shows an effect when considering an intensity ratio, which can be interpreted as an effect of secondary and higher order of scattering. It will be an intimation of multiple scattering by observation, partly confirmed by applying an approximate method for calculating secondary scattering.

II. OBSERVATIONAL EVIDENCE OF THE EXISTENCE OF SECONDARY AND HIGHER ORDER OF SCATTERING.

10. The log intensity ratio of scattered light. The instrument at the author's disposal has been a DOBSON's Spectrophotometer. The instrument reads a difference between two log intensity ratios, actually

$$\log I'c_3/Ic_2 - \log I_0'c_3/I_0C_2 = \log I'/I - \log I_0'/I_0 = \mathcal{N}$$

where I' is the intensity of light of the longer wavelengths between λ' and $\lambda' + \triangle \lambda'$, and I the intensity of light of the shorter wavelengths between λ and $\lambda + \triangle \lambda$.

Light of wavelength λ passes through a narrow slit, s_2, in the instrument, as light of wavelength λ' passes through a wider one, s_3. c_2 and c_3 are constants, including such instrumental effects as slit width, absorption in the optical components and so on. The instrument is not designed for absolute determination of a log intensity ratio, but for estimating the difference between two log intensity ratios. One may say that c_2 and c_3 further include a factor which places $\log I'c_3/Ic_2$ values at a convenient level. In the difference, the constants c_3 and c_2 go out.

Log $I_0'c_3/I_0c_2$ is the log intensity ratio of direct sunlight as the instrument would see it, if it was brought outside the atmosphere. Hence, $\log I_0'c_3/I_0c_2$ is an extraterrestrial constant for the instrument involved, determined for each instrument by calibration, after a basic extrapolation. Under the same exterior conditions, two instruments should read the same $\mathcal{N}$ value. Outside the atmosphere the actual $\mathcal{N}$ value would be zero.

When scattered light is entering the instrument, this gives response to $\log R'c_3/Rc_2$ where R' and R denotes the intensity of scattered light of wavelengths λ and λ' respectively. Applying the extraterrestrial constant, we get

$$\log \frac{R'c_3}{Rc_2} - \log \frac{I'_0c_3}{I_0c_2} = \log \frac{R'}{R} - \log \frac{I'_0}{I_0}$$

as the $\mathcal{N}$ value of the scattered light which the instrument actually reads.

When the direction of observation is $\theta = z$, we have, for primary scattered light received at the ground,

$$R_1 = 3/16\,\pi\, s\, I_0(1 + \cos^2 \psi) \sec z\, e^{-\sec z(s+a)}$$

and we will have

$$\mathcal{N}_p = \log \frac{e^{-Z(s'+a')}}{e^{-Z(s+a)}} - \log \frac{s}{s'}$$

where $\mathcal{N}_p$ denotes the $\mathcal{N}$ value for primary scattered light.

For direct sunlight received at the ground we have

$$I = I_0 \, e^{-Z(s+a)}$$

and we get

$$\mathcal{N}_{sun} = \log \frac{e^{-Z(s'+a')}}{e^{-Z(s+a)}}$$

Hence we have

$$\mathcal{N}_p = \mathcal{N}_{sun} - \log s/s'$$

or

$$\log R'_1/R_1 = \log I'/I - \log s/s'$$

This is an important relation which tells that the log intensity ratio for primary scattered light received from the direction of observation with the same elevation as the sun and for any azimuth angle, is equal to the log (intensity ratio for direct sunlight), minus log (ratio of scattering coefficients). The primary scattered light is given in a known relation to the observed $\mathcal{N}$ value of direct sunlight, in fact a basic reference value for the instrument. Hence, any observed deviation from the primary scattering value of $\mathcal{N}$ estimated as

$$\underset{\text{observed}}{\mathcal{N}_{sun}} - \log s/s'$$

will be interpreted as an observed evidence of the existence of scattering processes different from primary molecular scattering.

We will denote any deviation from the primary scattering value by $\triangle\mathcal{N}$, and we may write

$$\triangle \mathcal{N} = \mathcal{N}_p - \mathcal{N}_{p+s}$$

where the suffix $(p+s)$ denotes primary plus secondary scattering. The $\mathcal{N}$ value for light of all orders of scattering is denoted by $\mathcal{N}_{p+M}$ where the suffix $p + M$ stands for primary plus multiple scattering.

An expression for $\triangle\mathcal{N}$ in terms of the ratio R_2/R_1, secondary over primary scattering, is expressed by

$$\triangle \mathcal{N} = \log \frac{1 + \frac{R_2}{R_1}(\lambda)}{1 + \frac{R_2}{R_1}(\lambda')}$$

Applying the calculated values of R_2/R_1 we can estimate the value of $\triangle\mathcal{N}$ theoretically. $\triangle\mathcal{N}$ is usually called the primary scattering correction. In table 3 such theoretical values of $\triangle\mathcal{N}$ are given, which should be directly comparable with the observed deviation from the primary scattering value of $\mathcal{N}$.

The absorption and scattering coefficients used refer to the light of wavelengths λ and λ', approximately 3150 and 3300 Å. respectively. The ozone amount is varied from zero to .360 cm $\mathcal{N.P.T.}$

Table 3. *Primary scattering correction* $\triangle N = Np - Np{+}s$.
Direction of observation: $\Theta = Z$, $\Phi = \pi$.

sec z	*s*	*s′*	*a*	*a′*	*Ozone in cm*	$\triangle N$ (*in log unit*)
1	1.0	.8	0	0	0	+ .014
2						+ .021
4						+ .036
1	1.0	.8	.5	0	.180	− .0034
2						− .0027
4						+ .0810
1	1.0	.8	1.0	0	.360	− .0068
2						− .0027
4						+ .1963

11. Sky countour measurements. Before giving the observational results, some details about the observations with a Dobson's Spectrophotometer will be given.

A Dobson's Spectrophotometer, equipped with sun director, is placed on a level platform. By turning the instrument, the direction of observation will follow a sky contour (θ = constant), and the elevation of the direction of observation is adjusted to that of the sun, by the sundirector. In order to control the azimuth relative to sun (Φ), a scale is placed upon the instrument and the shadow of the sundirector indicates the operating azimuth during an observation. To prevent direct sunlight from falling upon the sundirector prism during a sky observation, a long tube is fitted to the front of the sundirector prism, and one can carry out measurements up to about 5° from the the sun.

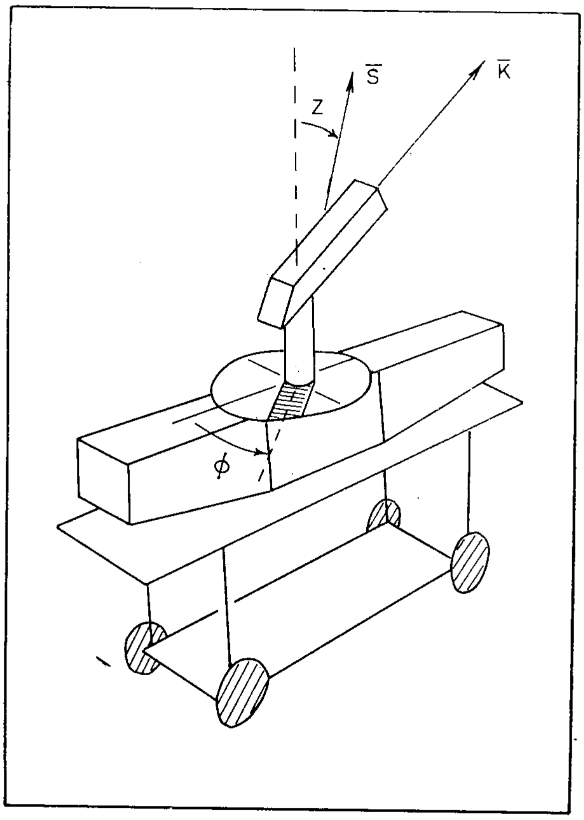

Fig. 4. The Dobson's spectrophotometer.

Observed N values from contour runs are fairly evenly levelled, following the constant primary scattering value almost parallel from $\Phi = 180°$ to $\Phi = 60°$. Between $\Phi = 60°$ and $\Phi = 10°$, the observed

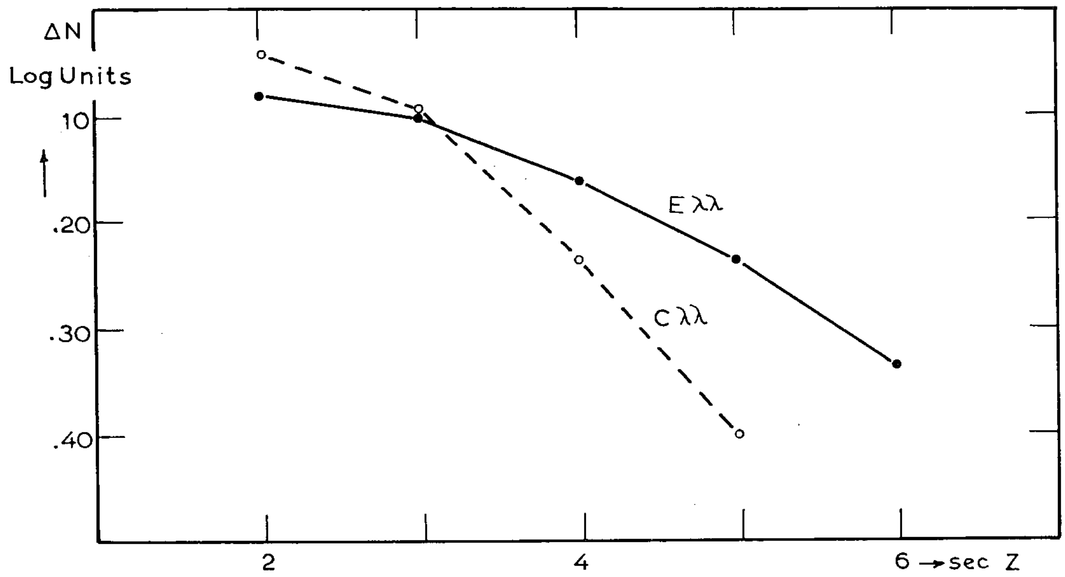

Fig. 5. Observed variation of $\triangle N$, the deviation from primary scattering. $E\ \lambda\lambda$ has no ozone absorption. $C\ \lambda\lambda$ has the ozone absorption coefficient a = .5.

curve rises, the N values increase. Near the sun the rise is steeper, presumably caused by large particle scattering. By taking contour measurements for different zenith distances of the sun, one will be aware that the deviation from the primary scattering value of N, the $\triangle N$, increases with sun's zenith distance. To demonstrate this striking feature, one has to carry out an efficient method of observation. To select one point on the sky contour, namely $\Phi = \pi$, and take runs of (Sun — Sky — Sun) observations for different heights of sun, appears to be the best. In this particular direction of observation, large particle scattering may be presumed to have negligible influence on the log intensity ratio. It will be shown later that it really is so. Further, for a low sun the polarization is small at this point of the contour.

As to the observational technique, this direction of observation is advantageous, because one does not need to turn the instrument, only the sundirector, and this means less time difference between the sun- and the sky observation, which is important.

Such observations for different heights of the sun, and for different wavelengths with different ozone absorption coefficients, have been undertaken at Oxford and Tromsø. Observational results of such contour point measurements at Oxford are given in the following diagram, fig. 5. In the diagram N_p, the primary scattering value, is used as a reference line, and the variation of

$$\triangle N = N_p - N_{Observed}$$

at $z = \theta$, $\Phi = \pi$, with sec z, is shown.

The observed log intensity ratio of scattered light must include all orders of molecular scattering. If one ignores the effects the large particle scattering may have on the intensity ratio, we can say that

$$\triangle \mathcal{N} = \mathcal{N}_p - \mathcal{N}_{p+M} = \mathcal{N}_{Sun} - \log s/s' - \mathcal{N}_{Observed}$$

is an observed effect of multiple scattering. It is seen from the diagram that for $E\lambda\lambda$, where there is practically no ozone absorption, the deviation from the primary scattering value increases with sec z, which means that the multiple scattering becomes more predominant as the sun gets lower. It is further seen from the diagram that for a low sun an increasing ozone absorption will give a larger deviation from primary scattering. One may say that the secondary scattering becomes still more predominant due to ozone absorption when the sun is low. Presumably the average pathlength through the ozone for multiple scattered light is shorter than for primary scattered light. This will increase the value of the ratio R_2/R_1 for the shorter wavelength at a greater rate than for the longer, which could explain the observed effect. This particular change in $\triangle\mathcal{N}$ has been found for secondary scattering by the numerical calculation (Table 3 page 17), and it seems reasonable to assume that in a sky countour measurement with a very low sun and large ozone absorption, the instrument will receive light where the main contribution is through higher orders of scattering.

When the sun is fairly high, it is seen from the diagram that ozone absorption will change the multiple scattering effect, so that the deviation $\triangle\mathcal{N}$ has a smaller positive value for increasing ozone absorption.

One may say that the effect of multiple scattering on a log intensity ratio is a bluing effect when no ozone is present. Ozone absorption will, for a low sun increase the bluing effect, but when the sun is high the ozone absorption reduces the bluing effect.

The calculated values of $\triangle\mathcal{N}$ are derived by applying an approximate method of calculation. One can not therefore expect this to give more than a qualitative picture of the scattering processes in the atmosphere. When theoretical results are qualitatively confirmed by observations, this supports the validity of the approximation. The method may therefore be applied further, for other directions of observation.

A comparison between the quantitative results obtained by observation, will be valuable in a way, in that one gets an impression of the magnitude of multiple scattering effects relative to secondary scattering effects. But, before this comparison is made, one has to consider the accuracy of the observations.

12. Possible errors in measurements. The log intensity ratio for primary scatered light when the direction of observation is defined by $\theta = z$, is given by the simple relation:

$$\mathcal{N}_p = \mathcal{N}_{sun} - \log s/s'$$

or

$$\log R'/R - \log I_0'/I_0 = \log I'/I - \log I_0'/I_0 - \log s/s'$$

where $\log I_0'/I_0$ is the extraterrestrial constant characteristic for the instrument. The measured value of N depends on the extraterrestrial constant, but will not affect $\triangle N$ which is defined by

$$\triangle N = N_{Sun} - \log s/s' - N_{Sky}$$

where the extraterrestrial constant goes out.

The log intensity ratio of sunlight is the basic reference value for the instrument and is used for calibration. The instrument is calibrated with a ground quartz plate over the inlet window. The ground quartz plate is slightly "coloured" and will be part of the extraterrestrial or instrumental constant. The ground quartz plate will, however, reduce the intensity of light entering the instrument, and for a low sun we take it away and a focussed image of the sun (or sky, for a sky contour), is thrown on the entrance slit of the instrument. This means that the instrument has changed, and it is not even the same for sky and sun as will be shown later.

The ground quartz plate is, for a direct sun measurement, illuminated not only by the sun, but also by light scattered from the sky within the cone into which the instrument looks, the scattered light being richer in shorter wavelengths than sunlight. When the sun is high, the intensity of this forward scattered light will be negligible compared with that of sunlight, and no appreciable error will occur, but when the sun is low this added sky-light may cause serious error in the observed log intensity ratio.

If a focussed image of the sun is thrown on the inlet slit of the instrument, the intensity of the sunlight will be greatly increased, while that of the sky will be reduced because the instrument now is looking into a narrower cone.

Series of direct sun measurements have been carried out during a winter and spring season in Oxford for different wavelength pairs of different ozone absorption, using a focussed image on the entrance slit and a ground quartz plate alternately. The N values obtained have been plotted in a diagram against time, and smoothed curve values are used for estimating a focussed image correction for N to make it equal to the ground quartz plate value, for which the instrument is calibrated. Further, an estimate of the limit at which the ground quartz plate can safely be used for a so called normal sun measurement, is made. As result a steady increase is found in the difference between the log intensity ratio of sun focus and normal sun measurement above $\sec z = 3$ for all wavelength pairs. This indicates that for observations with a ground quartz plate, the forward scattered light starts to cause appreciable error in the measured log intensity ratio of sunlight for $\sec z > 3$, and normal sun measurement should not be used beyond this value of $\sec z$.

When a focussed image of the sun is thrown on the entrance slit of the instrument, the sunlight will be very strong compared with the intensity of scattered light from that part of the atmosphere which is still seen by the slit, so that this added forward scattered light probably does not affect the measured intensity ratio of light from sun disk.

Within the instrument there will be some straylight due to sunlight scattered from optical surfaces in spite of the great care taken to prevent it. When the sun is sufficiently low this internal scattered light will be comparable with the light of short wavelength coming through slit s_2 normally and may cause an appreciable error.

Measurements were made to find out when this internal scattered light begins to affect the measurements of the sun for the focussed image condition. Several series of direct sun measurements with a focussed image were carried out continuing the observations until the sun was very low. O_3 values (X values) from the series are plotted against sec z using the formula for calculating ozone values:

$$X = \frac{N_{sun}}{(\alpha - \alpha')\mu} - \frac{(\beta - \beta')}{(\alpha - \alpha')}\frac{m}{\mu}$$

Here α denotes the decadic absorption coefficient and β the decadic scattering coefficient. m and μ are functions of z giving the equivalent path-length of sunlight through the atmosphere and ozone layer respectively. X denotes the ozone amount, usually given in cm thicknes of ozone layer at *NPT*.

Assuming X constant throughout the runs, a well marked fall in the $X/sec\ z$ curve indicates where the measurements break down. As a result, from several series taken in Oxford, the following mean values of sec z are given as safe upper limits for focussed image sun measurements for different wavelength pairs.

Table 4 *Safe upper limit for focussed image sun measurements.*

Wavelength pair		*Limit* (*sec z*)
3055/3254	A $\lambda\lambda$ ..	3.5
3114/3324	C $\lambda\lambda$ ..	6.0
3176/3398	D $\lambda\lambda$ ..	8.0

Observations taken at sec z values beyond she safe upper limit will be difficult to correct. For our purpose it is not necessary to use measurements beyond this limit.

When the ground quartz plate is used, the full length of the entrance slit is illuminated. But when a focussed image of the sun is thrown on the slit, only part of it is illuminated by sunlight. When the focussed image is moved along the slit the value of the log intensity ratio changes. Hence it is of great importance that the focussed image of the sun is held on a well marked position on the entrance slit for every observation.

Although great effort has been made to explain this effect, it is still not quite clear why this occurs. It does not appear to be due to any effect in the photomultiplier. Presumaly it is due to lens faults and to the shape of the image of the entrance slit on s_2 and s_3 slits. Whatever the cause, the effect is observed, and has to be taken into account.

When sky-light is entering the instrument, the full length of the entrance slit is illuminated whether one has a focussed image adjustment or not.

If the ground quartz plate is used for both sun and sky, contour measurements, the two N values are directly comparable. When a focussed image is used for both sun and sky contour measurement, which is the usual technique of observation, one has to correct back to the ground-quartzplate value for both sun and sky measurements.

For the instrument in Tromsö it is found by observation that

$$\underset{Focus}{N_{sky}} + 0.04 = \underset{G.q.p.}{N_{sky}}$$

where the correction is due to the colour of the ground quartz plate. Further we have

$$\underset{Focus}{N_{sun}} - 0.04 = \underset{G.q.p.}{N_{sun}}$$

where the correction is due to the colour of the ground quartz plate and the fact that focussed sunlight illuminates part of the entrance slit. Hence we get

$$N_{sun} - \log s/s' - N_{sky} - 0.08 = \triangle N$$

when the focussed image adjustment is used for both the sun and the sky contour. In Tromsø measurements were made with the ground quartz plate and with the focussed image adjustment in turn throughout runs of sun-sky measurements. As result these measurements gave an average value of 0.10 log units for the correction, or

$$\underset{Focus}{\triangle N} - \underset{G.q.p.}{\triangle N} = 0.10 \log unit$$

So 0.09 log unit is used as the focussed image correction for sun-sky contour measurements, in fact the maesurement which estimates the observed value of $\triangle N$.

The correction 0.09 is a consequence of the fact that the focussed image of the sun illuminates one part of the entrance slit, while for the sky measurement the full length of the slit is illuminated. As this correction depends on which part is illuminated by the focussed sunlight, it is, as pointed out earlier, very important to adjust the position of the image of the sun disk on the slit carefully. In Oxford a mask over the entrance slit was used, and no focussed image correction applied.

13. Comparison between calculated values of $\triangle N$ and those obtained by observation. Observed values obtained in Oxford and Tromsø of $\triangle N$, the primary scattering correction, for different wavelength pairs are shown in Fig. 6. In the same diagram numerical values of $\triangle N$ based on secondary scattering obtained from the approximate method of calculation, are plotted. The observational results from Oxford and Tromsö do not quite agree. It may be that a mask on the entrance slit is not sufficient for making N-sun and N-sky comparable. The results which are obtained by

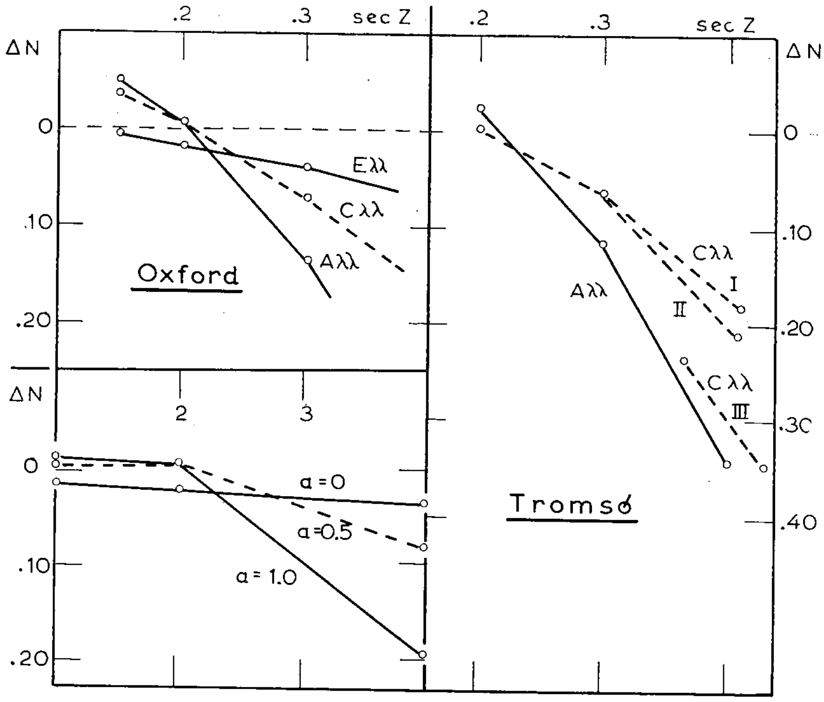

Fig. 6. Observed and calculated deviation from The primary scattering value of $\mathcal{N}$ where ozone absorption is considered.
I, II: small ozone amount. III: large ozone amount.

applying a correction to the observed value, are probably more reliable, and the dotted line at $\triangle\mathcal{N} = +0.03$ is used as the zero line for the Oxford measurements by making $\triangle\mathcal{N}$ for Oxford equal to that for Tromsö at sec $z = 2$ for $C\ \lambda\lambda$ (3114—3324).

Numerical values of $\triangle\mathcal{N}$, observed and calculated, are given in table 5 for quantitative comparison.

Table 5. *Observed abd calculated values of* $\triangle\mathcal{N}$.
s : scattering coefficient.
a : absorption coefficient where a = àX (X is ozone amount).

Observation							*Calculation*				
sec z	$\triangle\mathcal{N}$	$\lambda\lambda$	s	s'	$(\grave{a}X)$ a	$(\grave{a}'X)$ a'	$\triangle\mathcal{N}$	s	s'	a	a
2	.03	E	.93	.69	.12	0	.021	1.0	.8	0	0
4	.09	E					.036	1.0	.8	0	.0
2	.0	C	1.06	.80	.56	.04	.003	1.0	.8	.5	0
4	.19	C			.56	.04	.081	1.0	.8	.5	0
4	.21	C			.64	.05					
4	.28	C			.92	.07	.196	1.0	.8	1.0	0

Mostly due to the focussed image correction one may assume the standard error for a single observation of $\triangle N$ to be about .01. It is seen that the observed $\triangle N$ is consistently higher than the calculated one. This difference is presumably due to the fact that in the calculations secondary scattering only is concerned while actually all orders of scattering occurs. Remembering the formula for $\triangle N$ due to secondary scattering, we take the analogous formula for multiple scattering to be

$$\triangle N = \log \frac{1 + \frac{R_M}{R_1}(\lambda)}{1 + \frac{R_M}{R_1}(\lambda')}$$

Table 2 (page 14) shows how the ratio R_2/R_1 changes with sec z, and the ratio R_M/R_1 will appear with higher values than the analogous ratio R_2/R_1 especially at shorter wavelengths. This will be in accordance with difference between observed and calculated values of $\triangle N$. The progressive ozone absorption presumably attenuates the primary scattered light more than the multiple scattered light beyond a certain zenith distance of the sun, which increases the scattering correction $\triangle N$.

The calculation is based on the characteristics: $s = 1.0$ and $a = .5$ and 1.0 for the shorter wavelength, and $s' = .8$ and $a' = 0$ for the longer wavelength. This corresponds very nearly to wavelength pair C with ozone amount $X = .180$ cm and .355 cm respectively.

As result of this comparison we can say that the calculated effect of secondary scattering is about 2/3 of the observed multiple scattering effect when observations are made with $C\lambda\lambda$ at Z about 76°, and with ozone values from 0.280 to 0.300 cm which gives a quantitative expression of the effect of multiple scattering relative to the effect of secondary scattering.

III. PRIMARY AND SECONDARY SCATTERED LIGHT FROM THE ZENITH

14. Estimation of the primary scattering correction $\triangle N$ for zenith light. Numerical results obtained by applying the approximate method of calculation, have been confirmed qualitatively by sky contour measurements, which support the validity of the approximation, and the method is applied further.

When observations are made of an intensity ratio of scattered zenith light for a wavelength pair where light of the shorter wavelength is absorbed by ozone, and light of the longer wavelength is not absorbed, then the log ratio log R'_1/R_1 first increases and then decreases as the sun sets. This effect, the well known Umkehr effect, is due to a change in pathlength through the ozone layer for the primary scattered light as the mean or effective scattering level for each wavelength ascents through and above the ozone in the atmosphere. By making use of these considerations, GÖTS, MEETHAM and DOBSON were able to deduce the vertical distribution of ozone [5]. Their method of calculation considers primary scattering only, and it may be of interest to apply the approximate method of calculation, which is confirmed qualitatively by observation, to the estimate of $\triangle N$ for zenith light where

$$\triangle N = N_p - N_{p+s}$$

Adding $\triangle N$ to the observed value of N we get

$$\triangle N + N_{\text{observed}} = N_{\text{corrected}}$$

where $N_{\text{corrected}}$ is nearer the value of N_p than the observed uncorrected value of N
If $\triangle N_T$ includes corrections for multiple molecular and non-molecular scattering, we have

$$\triangle N_T + N_{\text{observed}} = N_p$$

Table 6. *Calculated primary and secondary scattered light from zenith.*

Wave-length	*s*	*a*	sec *z*	*cm* O_3	R_1/Ks	R_2/Ks^2	R_2/R_1
λ	.8	0	1	0	.899	.309	.275
			2		.397	.237	.490
			4		.181	.137	.605
			5		.140	.110	.625
			6		.113	.089	.628
λ	1.0	0	1	0	.736	.231	.314
			2		.291	.159	.546
			4		.124	.083	.665
			5				
			6		.075	.051	.686
λ	1.0	0.5	1	.180	.446	.119	.267
			2		.122	.055	.451
			4		.039	.021	.538
			6		.026	.0135	.520
			8		.021	.0109	.512
			1	.360	.271	.070	.258
			2		.054	.024	.442
			4		.019	.0093	.479

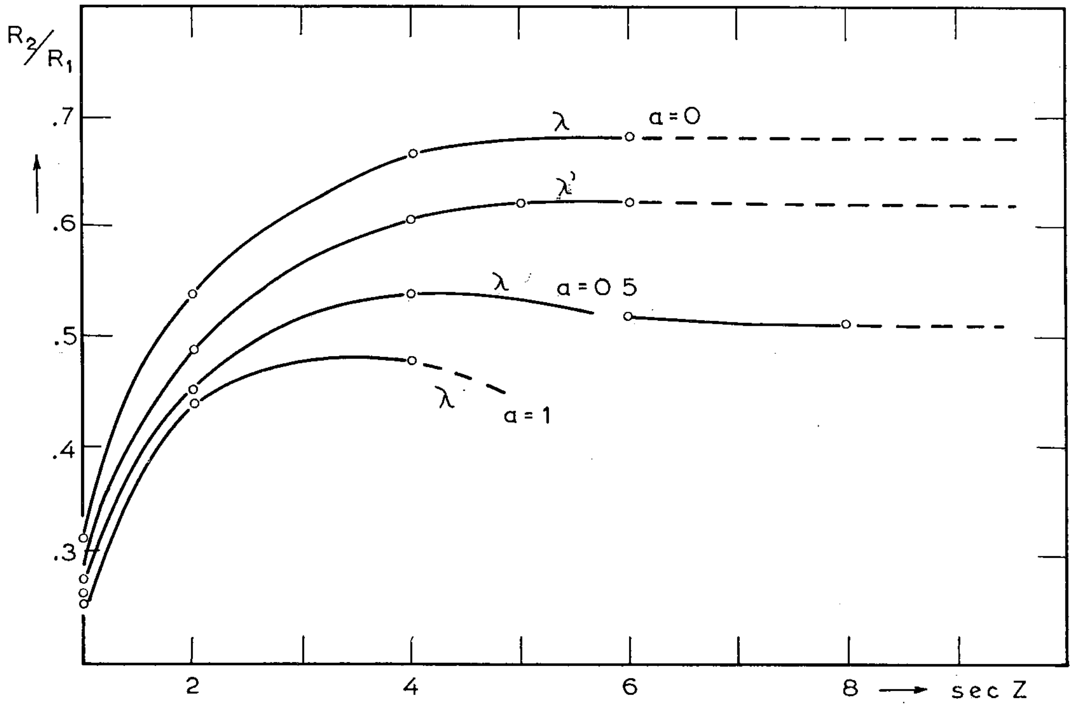

Fig. 7. Calculated values of R_2/R_1, the intensity ratio of secondary and primary scattered light.

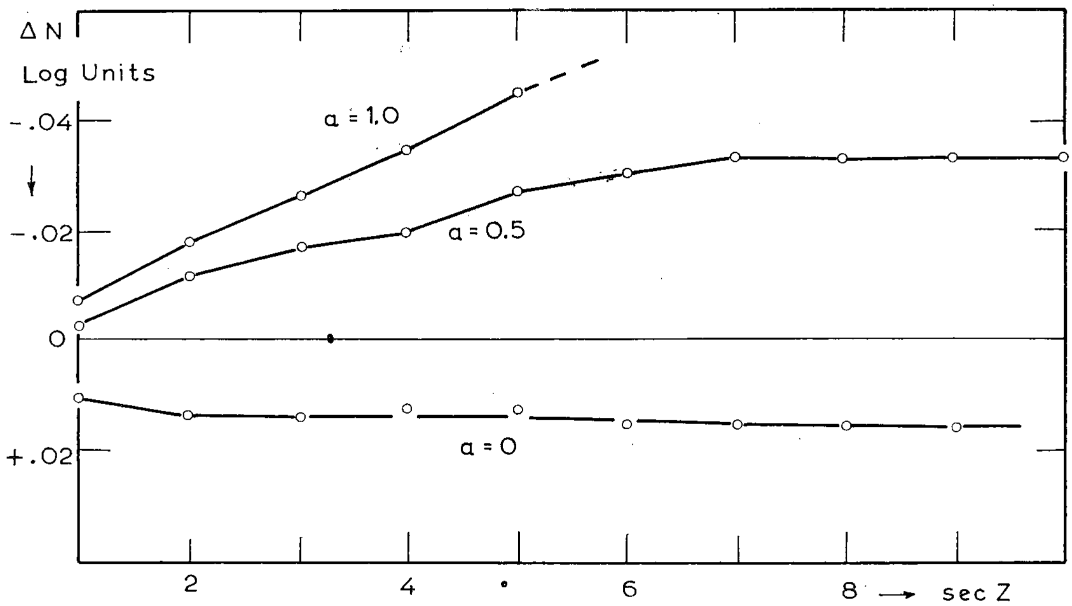

Fig. 8. Calculated values of $\triangle N = N_p - N_s$, the primary scattering correction, for different ozone absorption (a).

For zenith light one must be aware that the vertical distribution of the ozone will affect the intensities of both secondary and primary scattered light of the shorter wavelength. For contour measurements primary scattered lights is independent of the vertical distribution of the ozone.

Values of R_1/Ks, R_2/Ks^2 and R_2/R_1 derived by the approximate method are given in table 6, where R_1 and R_2 are the intensity of primary and secondary scattered light respectively, received at the ground from the zenith. The calculation is carried out for two different wavelengths and for different zenith distances of sun. A thin ozone layer has been put at a depth $\bar{m}$: .150.

Table 6 shows how the ratios R_2/R_1 of λ and λ' vary with sec z, and how the ozone absorption affects it. These calculated values of R_2/R_1 are plotted against sec z, and smoothed curves have been drawn as shown in Fig. 7. From the smoothed curve values of R_2/R_1, $\triangle \mathcal{N}$ has been estimated, and Table 7 gives the numerical values of the secondary scattering correction $\triangle \mathcal{N}$ to the primary scattering process derived on the basis of the approximate method of calculation. In Fig. 8 the estimated values of $\triangle \mathcal{N}$ are plotted in a diagram, showing the variation with sec z for different ozone absorptions.

Table 7. $\triangle$ $\mathcal{N}$, *the primary scattering correction in log unit, zenith light*

sec z			1	2	3	4	5	6	6	8	9	10
s	s'	a										
1.0	.8	0	+.014	+.014	+.013	+.013	+.013	+.016	+.016	+.016	+.016	+.016
1.0	.8	5	−.003	−.012	−.017	− 19	−.027	−0.30	−.033	−.033	−.033	−.033
1.0	.8	1.0	−.007	−.018	−.026	−.034	−.045					

When an observation is made with $C\lambda\lambda$, Table 8 below provides an average correction for secondary scattering. Z^* denotes sun's zenith distance for which $m = f(z^*)$, Bemporades expression for air path of sunlight through an atmosphere over a curved earth, has the same values as our sec z.

Table 8. *Average primary scattering correction* $\triangle \mathcal{N}$ *for* $c\lambda\lambda$, *zenith light.* (Log unit).

Z^*	60°	70°	75°	80°	82°	86°
$\triangle$ $\mathcal{N}$	−.015	−.020	−.025	−.045	−.050	−.050

It is seen from the tables and the diagram how $\triangle \mathcal{N}$ defined by

$$\triangle \mathcal{N} = \mathcal{N}_p - \mathcal{N}_{p+s}$$

is positive and nearly constant with sec z when there is no ozone absorption. The intensity ratio has become "bluer" by secondary scattering.

This bluing effect is due to an increase in the ratio R_2/R_1 with preference to the shorter wavelength. Hence, for no ozone absorption one has a similar secondary scattering effect in zenith light as in light scattered from sky contours, it is just more pronounced and more highly dependent on the sun's zenith distance in the sky contours.

The ozone absorption affects the secondary scattering in zenith light, but here the deviation from the primary value of the log intensity ratio changes from a positive value to a negative value with increasing ozone absorption when the sun is low. The effect found in light scattered from sky contours when the sun is low, is the reverse.

For zenith light we may assume that for all solar elevations, the mean pathlength through the ozone layer is longer for the secondary than for the primary scattered light which will give preference to the ratio R_2/R_1 for the longer wavelength, (decrease it for the shorter).

When $\triangle N$ is negative, the value of N_{p+s} has a higher value than N_p. This means, as will be shown later, that if secondary and higher orders of scattering are neglected in the Umkehr method, the mean height obtained for the atmospheric ozone will be too high. By adding the multiple scattering correction $\triangle N$ to the observed values of N, one gets corrected observed values of the log intensity ratio to be used in the Umkehr method for calculating vertical distribution of atmospheric ozone.

A correction including multiple scattering will presumably exceed the correction due to secondary scattering alone. Before making any supposition however, some comparisons with observations will be made.

15. Comparison with the observations. The E wavelength pair represents, very nearly, the case of no ozone absorption, and the ozone layer will affect the scattering processes only slightly. Hence, for $E\lambda\lambda$, the calculated intensities of the primary scattered light is very accurate.

Having calculated the primary scattering value of N for zenith light, then

$$\underset{calculated}{N_p} - \underset{observed}{N} = \triangle N$$

where $\underset{\text{obs}}{N}$ is the value which the instrument actually reads. Hence N_p values for zenith light are needed in connection with observations, and a curve chart of N_p zenith values for $E\lambda\lambda$ has been worked out. To get over the difficulties with the extraterrestrial constant, one takes the log intensity ratio of sun as base. We have

$$\underset{\text{observed}}{\{N_{Sun} - N_{zenith}\}} - \underset{\text{calculated}}{\{N_{Sun} - N_{zenith}\}} = \triangle N$$

where

$$\triangle N = \{\underset{\text{calcul.}}{N_p} - \underset{\text{obs. zenith}}{N}\}$$

Hence differences

$$N_{sun} - N_{zenith}$$

obtained by calculation and by observation, have to be compared.

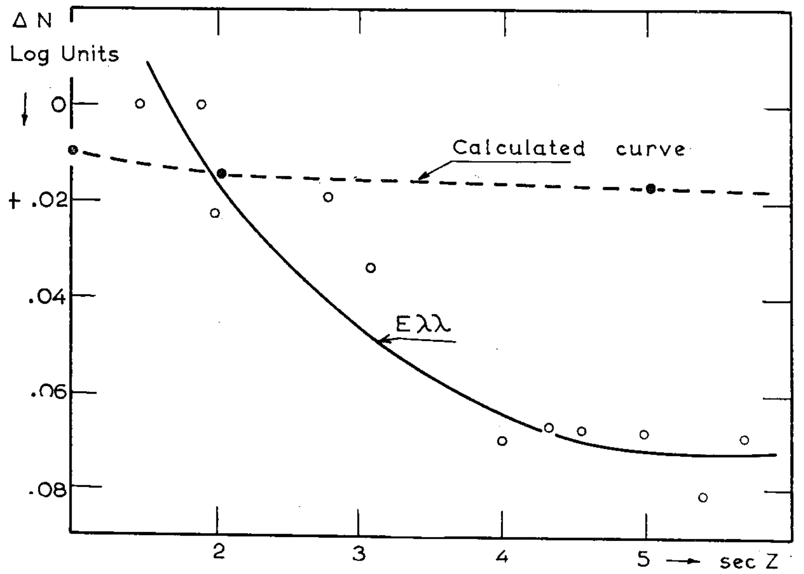

Fig. 9. Theoretical and observed values of $\triangle\mathcal{N}$ in zenith light with no ozone absorption ($E\lambda\lambda$).

To calculate the actual value of the sun's log intensity ratio for $E\lambda\lambda$, we must know the ozone amount present during the observation even though the ozone absorption is small. The actual ozone amount is estimated by an $(A - D)\lambda\lambda$ combination or a $C\lambda\lambda$ sun observation before and after the $E\lambda\lambda$ measurements. Then we will have

$$\mathcal{N}_{Sun}\,(E\,\lambda\lambda) = X(\alpha - \alpha')\,\mu + (\beta - \beta')\,m$$

where X is the ozone amount. The values of β. β' for $E\lambda\lambda$ are extrapolated values from a $(\log\lambda - \log\beta)$ diagram. The value of α is a weighted mean over 18 $\mathring{A}U$ since the slit in the instrument is approximately 9 $\mathring{A}U$ wide. The center position is assumed to be 3216 $\mathring{A}U$. We have found $\alpha = .26$ and α' approx. .01, based on values determined by Ze Ny Tsi and Choong Shin Piaw [6].

The same instrument must be used for the sun measurement as for the zenith measurement. Such sun and zenith observations have been carried out in Oxford, and the result derived is shown in the diagram in Fig. 9. In this diagram the theoretical values of $\triangle\mathcal{N}$ are shown together with the observed ones. The variability in atmospheric conditions will be a source of error, and probably be responsible for the wide range in the $\triangle\mathcal{N}$ values. It seems clear however, that observations with $E\lambda\lambda$ have confirmed the theoretical results so far, that when the ozone absorption is negligible, the deviation from the primary scattering value of $\mathcal{N}$ is positive. Observed deviations tend to be greater than the calculated, presumably due to the fact that the calculated $\triangle\mathcal{N}$ is based on secondary, while the observed is due to all orders of scattering.

As seen from the numerical calculations, the ozone layer has an appreciable influence upon the secondary scattering in zenith light. What we are able to confirm by observation is that the qualitative change in the multiple scattering effect is in agreement, for increasing ozone absorption, with the effect calculated for secondary scattering.

With large ozone absorption the vertical distribution of the ozone in the atmosphere will be an important factor, which governs the primary scattering value of N, but not before the sun is fairly low ($z > 60°$). When the sun is high we can assume the total amount of ozone alone to be the important governing factor, and not the distribution, since the distribution then has little influence on the value of N due to primary scattering. For a high sun one goes through exactly the same procedure for $A\lambda\lambda$ and $D\lambda\lambda$ as for $E\lambda\lambda$. $A\lambda\lambda$ represents very large ozone absorption and $D\lambda\lambda$ small absorption.

Having obtained observed N values of sun and zenith light for A and $D\lambda\lambda$, one estimates theoretically, for the same wavelength pairs, the sun's N values and the primary scattering N values of zenith light. We then have

$$\underset{\text{observed}}{\{N_{Sun} - N_{zenith}\}} - \underset{\text{calculated}}{\{N_{Sun} - N_{zenith}\}} = \triangle N$$

where

$$\triangle N = N_p - N_{p+m}$$

for A and $D\lambda\lambda$.

In Oxford such sun-zenith observations for a high sun and clear sky have been carried out combined with the numerical calculation which is required. The results are given in Table 9 below.

Table 9. *Sun-zenith observations.*

$\lambda\lambda$	z	Sec z	O_3	*Observed*			*Calculated*			$\triangle N$
				N_{sun}	N_{zen}	$\triangle_1$	N_{sun}	N_{zen}	$\triangle_2$	
A	48.1	1.497	.266	1.144	.973	.171	1.138	.958	.180	—.009
D	48.0	1.459		.380	.182	.208	.365	.210	.155	+.053
A	47.8	1.489		1.136	.963	.173	1.131	.953	.178	—.005

It is seen from Table 9 that $\triangle N$ has changed by 0.06 log unit from small to large ozone absorption in qualitative agreement with the result obtained by calculation which gave a change in $\triangle N$ about 0.03 log unit in same direction.

These observations were carefully carried out with the standard instrument (No 2) at Oxford. The ground quartz plate was left on the whole time, and for zenith observations a tube was placed over the inlet window. The observations are adopted as a qualitative confirmation of the theoretically estimated influence of an increasing ozone absorption upon secondary order of scattering in zenith light.

16. Calculated and observed zenith curves. In this section two examples of numerical calculations are given to show how the log intensity ratio of zenith light depends on the vertical distribution of the ozone, and a comparison with actual observation is made.

The author has calculated primary scattering N values of zenith light for A, C and $D\lambda\lambda$ for $0_3 = 0.266$ cm, using an atmospheric model resting on a curved earth where the ozone is put into two thin layers at depts $\overline{m} = 0.050$ and $\overline{m} = 0.200$, and giving a constant mixing ratio above $\overline{m} = 0.025$ when contribution of light from this region is considered. Two extreme distributions are selected, designated by No 4 and No 2, and where the ozone has been distributed in the atmospheric model as follows:

For distribution No. 4:

Above	$\overline{m} = 0.025$,	$0_3 = 0.200$ cm
at	$\overline{m} = 0.050$,	$0_3 = 0.050$ cm
at	$\overline{m} = 0.200$,	$0_3 = 0.016$ cm

For distribution No. 2:

Above	$\overline{m} = 0.025$,	$0_3 = 0.100$ cm
at	$\overline{m} = 0.050$,	$0_3 = 0.066$ cm
at	$\overline{m} = 0.200$,	$0_3 = 0.100$ cm

Distribution No 4 with the center of pressure at 31 mb's, represents the case with ozone high up in the atmosphere. Distribution No 2, with the center of pressure at 101 mb's, represents the case with ozone very low down in the atmosphere. These two distributions will give zenith curves of primary scattering for A,C and $D\lambda\lambda$ as shown in Fig. 10. On the same diagram the observed N curves for $0_3 = 0.266$ cm are shown. The observations were carried out in Oxford by the author.

The diagram in Fig. 10 shows that distribution No 4 with much ozone high up, gives higher N values than those derived from distribution No 2, and the difference between them increases with decreasing height of the sun. The diagram show further that the observed curve for $D\lambda\lambda$ lies below the theoretical ones until the sun is very low. A gradual change is taking place through D and $C\lambda\lambda$, and for A nearly the whole curve obtained by observations lies above the theoretical one for ozone distribution No 2 (low ozone). This feature corresponds to what is found theoretically for the change in the secondary scattering effect. And we may say that this characteristic shift is created by the change in the multiple scattering effect due to the change in ozone absorption from D to $A\lambda\lambda$.

17. Conclusion. Comparison with observation has shown that the observed multiple scattering effect is greater than the calculated secondary scattering effect. For sky contour measurements this is quite clear, and an effect approximately 2 or

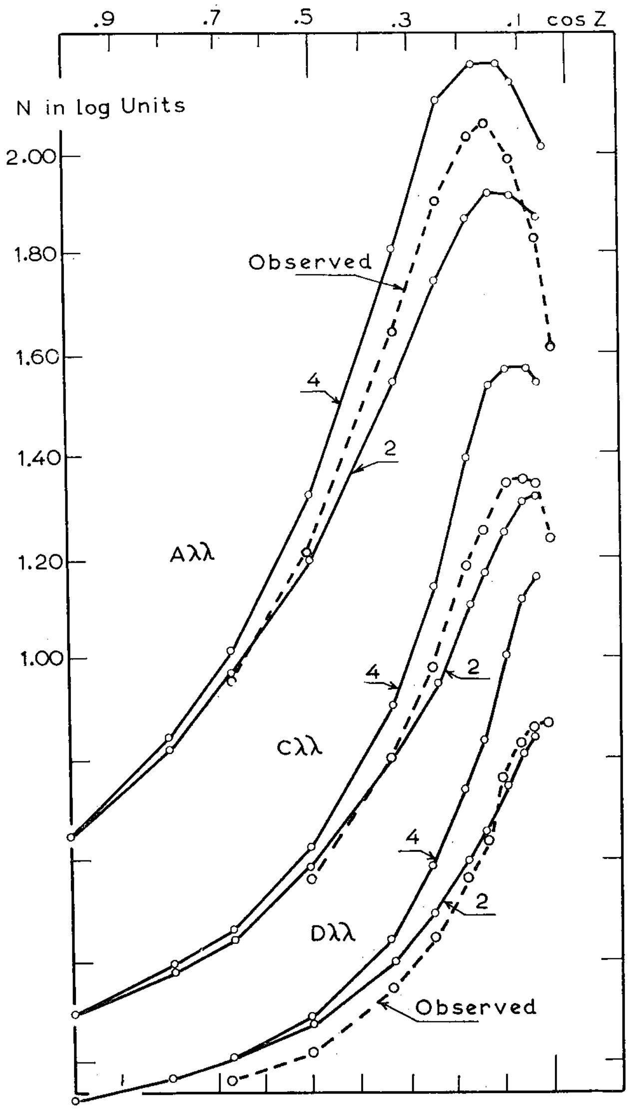

Fig. 10. Observed and calculated N values of scattered light from zenith. 2: The ozone low down in the atmosphere. 4: The ozone high up in the atmosphere.

3/2 times the calculated effect is found to exist. In zenith light the multiple scattering should analogously provide an effect above twice or 3/2 times the calculated secondary scattering effect. For a high sun this was confirmed by observation in the change in the multiple scattering effect from small to large ozone absorption. For low sun one had to consider light with negligible ozone absorption for comparison between observed and calculated effects. Although the observational result in this case was not so good, depending on a more uncertain estimation of N_p, it is clear that multiple scattering provides an effect greatly exceeding the calculated one.

Taking into account the relation which is found between the calculated secondary scattering effect and the observed effect, which is due to multiple scattering, it is believed that the following table provides a reasonable correction for multiple scattering with an ozone amount approximately 0.270 cm when the observations are made with $C\lambda\lambda$.

In the approximate method for calculation of secondary scattering, an atmospheric model has been used with an ozone layer at a depth $\overline{m}$: 0.150 or at a height approximately 14 km. In the three layer model used for calculating umkehr curves, the low situated ozone, distribution No 2, has the centre of pressure at approximately 16 km. Our simple model with the ozone layer at 14 km probably represents an ozone distribution with the ozone too low down in the atmosphere. If, on the other hand, the ozone layer is put in above the upper mass scattering point, this would be to ignore any secondary scattering source above the ozone.

Table 10. *Correction due to multiple scattering in zenith light.*

Suns zen. dist.:	60°	70°	75°	80°	86°
Correction to N_{obs}:	−.03	−.04	−0.5	−.10	−.10

As stated earlier, the aim has been to indicate the importance of higher order of scattering by observation, and the quantitative estimation is based on comparison with observation. The physical picture of the scattering processes has been clarified by considering a simplified model of the atmosphere for numerical calculation.

IV. LARGE PARTICLE SCATTERING

18. Introduction. From several sky contour measurements with a Dobson's Spectrophotometer, one has been aware of an effect, clearly detectable, which has to be interpreted as due to large particle scattering. A sky contour measurement is defined by θ = constant where θ is the zenith distance of the direction of observation. When $\theta = z$, we have for the log intensity ratio N, $N_p = N_{sun} - \log s/s'$ for all azimuth angles Φ. Calculations, in qualitative agreement with observations, stated that secondary scattering affected the intensity ratio in light from sky contours so it became "bluer". The deviation from the primary scattering value of N called $\triangle N$, and defined as

$$\triangle N = N_p - N_{p+s}$$

was found to be positive for no ozone present, and for low sun the ozone absorption made the deviation $\triangle N$ still greater. Further calculation shows that the intensity of primary and secondary scattered light do change along a sky contour, and a corresponding change in $\triangle N$ or N_{p+s} occurs. Calculation gave as result the dates given in Table 11.

For primary scattering only, the N value is constant along a sky contour. When secondary scattering is considered the N value varies with Φ, but the curve is very nearly symmetrical about $\Phi = \pi/2$. At $\Phi = \pi/2$ one has a minimum in N, and towards

Table 11. *Primary and secondary scattering along a sky contour.*

sez z = 4		R_1/Ks			R_2/Ks^2			R_2/R_1		
		Φ			Φ			Φ		
s	a	0	$\pi/2$	π	0	$\pi/2$	π	0	$\pi/2$	π
.8	0	.326	.164	.288	.223	.191	.221	.55	.93	.61
1.0	0	.147	.074	.129	.098	.085	.096	.671	.15	.75
1.0	.5	.020	.010	.017	.0157	.0140	.0155	.791	.41	.89
								+		
	.0						$\triangle N$:	.032	.046	.036
	.5						$\triangle N$:	.062	.096	.070

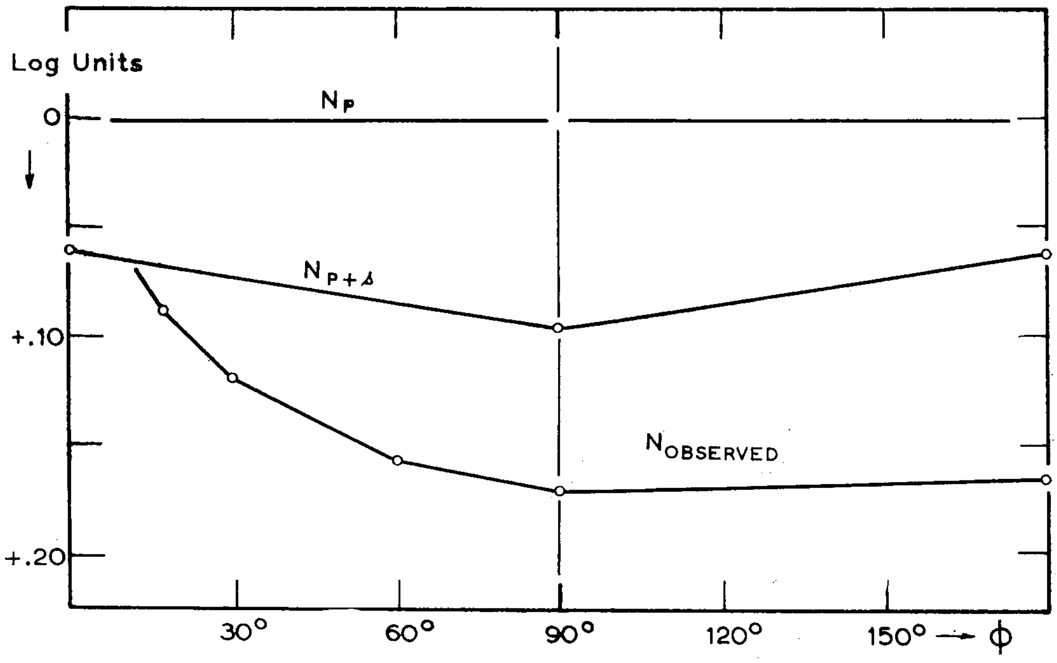

Fig. 11.

$\Phi = \pi$ and $\Phi = 0$, where the bluing effect is less, the N value increases. The N value is slightly higher at $\Phi = 0$ than at $\Phi = \pi$. Ozone absorption will increase the bluing effect of secondary scattering and deepen the minimum value of N.

Fig. 11 shows two calculated curves, one based on primary scattering only, the second based on primary and secondary scattering. Ozone absorption is considered in both cases. Then an observed curve $(C\lambda\lambda)$ is drawn where the difference in N between N_p and $N_{observed}$ at $\Phi = \pi$ is actually observed.

One sees from the figure that both the level and the shape of the observed curve are different from the calculated ones. The assymetric shape of the observed curve, with an increasing "reddening" effect of the log intensity ratio when approaching the sun's vertical plane, is taken to be a consequence of large particle scattering. The deviation from the primary scattering value of the log intensity ratio, $\triangle N$, due to large particle scattering, may be expressed as

$$\triangle N = \log \frac{1 + \frac{A}{R_1}(\lambda)}{1 + \frac{A}{R_1}(\lambda')}$$

where A denotes the intensity of scattered radiation from large sized scattering material, and R_1 denotes the intensity of primary molecular scattering. According to Rayleigh's inverse fourth power low, we will have $\log R_1/R'_1$ proportional to $4 \log \lambda'/\lambda$. For non

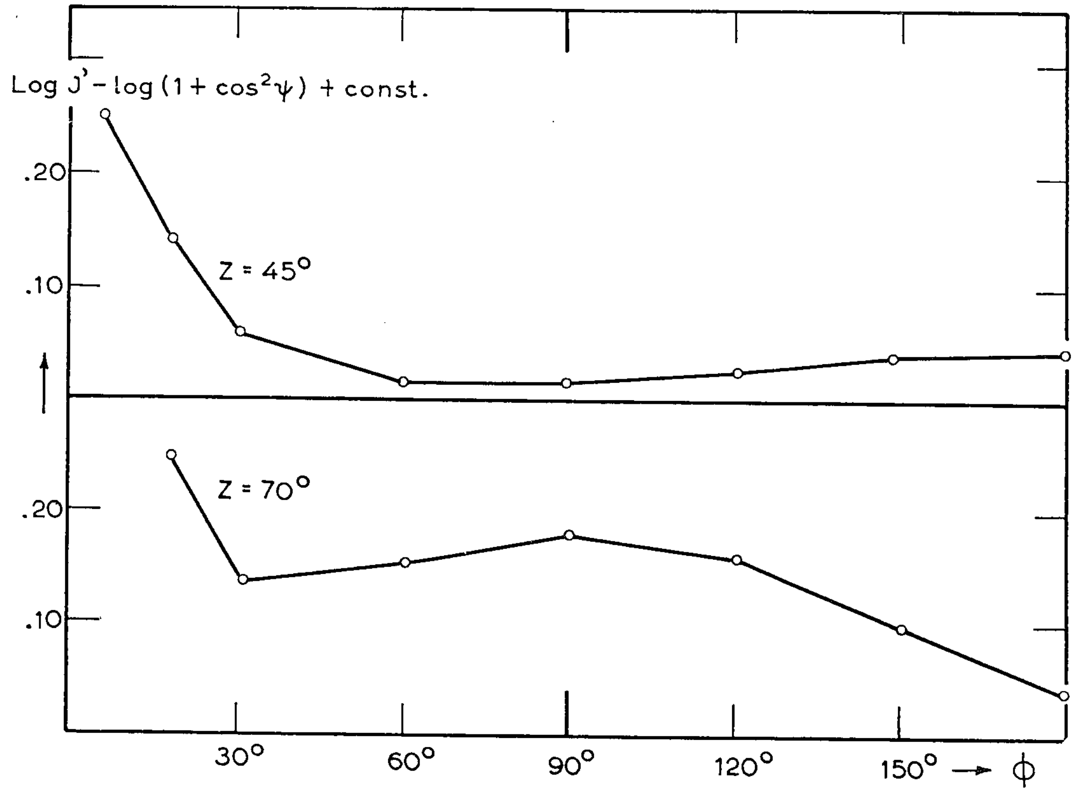

Fig. 12. Log intensity — log $(1 + \cos^2 \psi)$ measurements in sky contours.

molecular or large particle scattering we may write log A/A' proportional to n log λ'/λ where $n < 4$ and $\lambda' > \lambda$. According to this we may say that scattered radiation in the shorter wavelength is predominant in both cases, but at a greater rate for molecular or Rayleigh scattering. This makes $\triangle N$ negative.

Hence the presence of large sized scattering material in the atmosphere would mean an addition of radiation which gives "reddening" of the log intensity ratio. As the direction of observation for contour measurements approaches the forward scattering direction, the large particles scattering will increase in quantity. This makes the logarithmic difference between $(1 + A/R_1)$ for the longer and the shorter wavelength greater, which means an increasing "reddening" of the intensity ratio.

19. Log intensity measurements. To get more information about the non molecular scattering processes in the atmosphere, a new method of observation is introduced. Observations are made with a Dobson's Spectrophotometer, now furnished with a lamp which illuminates the slit which allow light of wavelength about 4500 Å. U. to fall on the photomultiplier. By keeping this light intensity constant with a controlled current through the lamp, one measures the relative change of the log intensity of light of the longer wavelength λ', where $\lambda' = 3324$ Å. U. for $C\lambda\lambda$, for light entering the instrument.

We know that the intensity of primary scattered light will vary along a sky contour. This variation depends merely on the scattering angle. We can therefore put

$$\log R_1 = \log (1 + \cos^2 \psi) + C$$

for θ = constant, where ψ is the scattering angle.

If we observe the log intensity of scattered light along a sky contour and from the instrumental readings subtract the corresponding values of $\log (1 + \cos^2 \psi)$, one should get a constant value if merely primary scattering exists. Numerous log intensity measurements were carried out in Oxford during the spring and summer season 1957. In the autumn, observations of the same type were made at The Auroral Observatory in Tromsø. Typical observational results are shown in Fig. 12.

The observed value of $\log I' - \log (1 + \cos^2 \psi) + C$ is not constant along a sky contour, and the deviation is due to additional radiation of secondary and higher orders of molecular scattering and radiation scattered from large sized particles. Earlier in this paper we have calculated values of R_2/Ks_2 where R^2 is intensity of secondary scattered light. From the comparison made between the calculated and the observed deviations from the primary scattering value of the log intensity ratio, one may assume $R_M = 2\,R_2$ at $\sec z \geq 4$ where R_M denotes the true value of multiple scattering. Refering to the theoretical work of Deirmendjian [7], we assume the intensity of large particle scattering to be equal to the Rayleigh primary scattering at an angular distance of 15° from the sun, say

$$\underset{(\Phi = 15)}{R_1} = \underset{(\Phi = 15)}{A}$$

where A denotes intensity of large particle scattering. R_1 at $\Phi = 15°$ deviates just slightly from R_1 at $\Phi = 0$, and we assume these two intensities to be equal. Further we assume

$$\underset{(\Phi = 0)}{A} = 10\,\underset{(\Phi = 15)}{A}$$

and

$$\underset{(\Phi = 90)}{A} = \underset{(\Phi = 180)}{A} = 1/10\,\underset{(\Phi = 15)}{A}$$

Considering the case, $\sec z = 4$ and $s = 1$, we can now make following summation

Φ:	0°	15°	90°	180°
$1/K\,(R_1 + R_M + A)$:	1.813	0.490	0.259	0.336
$\log (R_1 + R_M + A) + \log C$:	1.258	.690	.413	.526
$\log (1 + \cos^2 \psi)$:	.30	.30	.0	.24
$\text{Log } I - \log f + c$:	.958	.390	.413	.286

where I denotes $(R_1 + R_M + A)$ and f denotes $(1 + \cos^2 \psi)$.

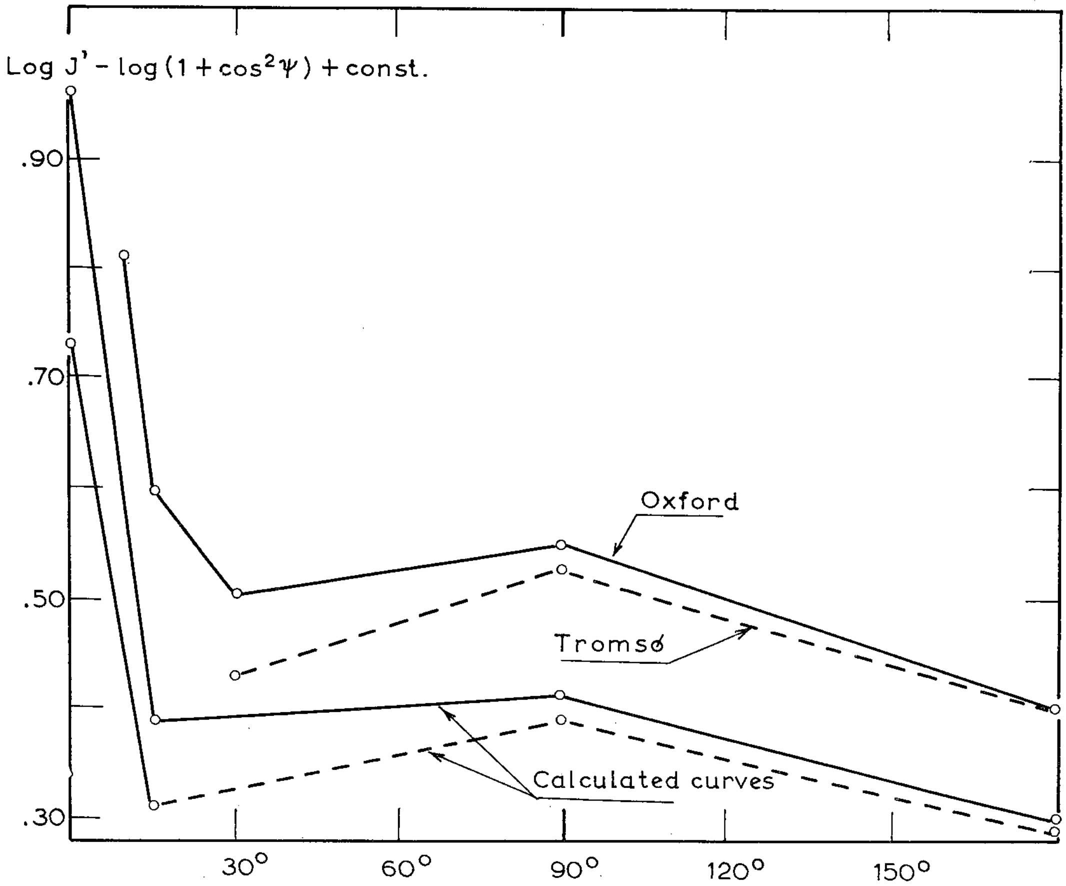

Fig. 13. Observed and calculated values of (log I′ — log f + c.)

If we apply half the amount of radiation from large sized scattering material ($A = 1/2\ R_1$ at $\Phi = 15°$) we get as results

	0°	15°	90°	180°
Log I — log $f + c$;.......	.733	.320	.400	.276

The relative change of (log I — log $f + c$) with Φ is directly comparable with the log intensity measurements. In a diagram (Fig. 13) the calculated values of (log I — log $f + c$) are plotted together with the observed values obtained from log intensity measurements in Oxford and Tromsö.

The diagram shows a fairly good qualitative agreement between calculated and observed values of intensity along a sky contour and seems to justify the assumptions made about large particle scattering, and these will be further applied to estimate its effect on a log intensity ratio as shown in the next section.

20. Estimated effect on a log intensity ratio of large particle scattering. The assumptions made about large particle scattering may be expressed as follows:

$$A_{(\Phi=15)} = R_{1\,(\Phi=15)} = q\lambda^{-4} \text{ or } A_{(\Phi=15)} = 1/2\, R_{1\,(\Phi=15)} = 1/2\, q\lambda^{-4}$$

for a large amount or for a smaller amount of large sized scattering material respectively at an azimuth angle relative to sun's vertical plane of 15°. Further we assumed

$$A_{(\Phi=15)} = A_{(\Phi=0)} \times \frac{1}{10}$$

$$A_{(\Phi=90)} = A_{(\Phi=180)} \quad A_{(\Phi=15)} \times \frac{1}{10}$$

$$R_{1\,(\Phi=0)} = R_{1\,(\Phi=15)}$$

From calculations made earlier in this paper we have

$$R_1/Ks_{(\Phi=90)} = R_1/Ks_{(\Phi=0)} \times 1/2$$

$$R_1/Ks_{(\Phi=180)} = R_1/Ks_{(\Phi=0)} \times \frac{1}{1.11}$$

We assume the large particle scattering to be independent of wavelength, so that

$$A(\lambda')_{(\Phi=15)} = A(\lambda)_{(\Phi=15)} = q\lambda^{-4} \text{ or } 1/2\, q\lambda^{-4}$$

Hence we have, applying the formula for $\triangle N$

$$\triangle N_{(\Phi=15)} = \log \frac{1 + \frac{A}{R_1}(\lambda)}{1 + \frac{A}{R_1}(\lambda')} = \log \frac{1 + \frac{q\,\lambda^{-4}}{q\,\lambda^{-4}}}{1 + \frac{q\,\lambda^{-4}}{q\,(\lambda')^{-4}}} = -.057$$

Using the relations given above we get the following values of $\triangle N$ for different values of Φ.

Φ:	0°	15°	90°	180°	Remarks
$\triangle N$:	−.099	−.057	−.021	−.012	$A = R_1$ at $\Phi = 15°$
$\triangle N$:	−.091	−.039	−.011	−.001	$A = 1/2\, R_1$ at $\Phi = 15°$

These simple calculations show that large particle scattering will make the log intensity ratio "redder". The maximum reddening effect is in the sun's vertical plane, $\Phi = 0$, a consequence of the sun's aureole. Following the contour we see that at $\Phi = 180°$ the effect of large particle scattering has a minimum. At $\Phi = 90°$, the effect is larger again although we have kept A at the same value. As the primary scattering

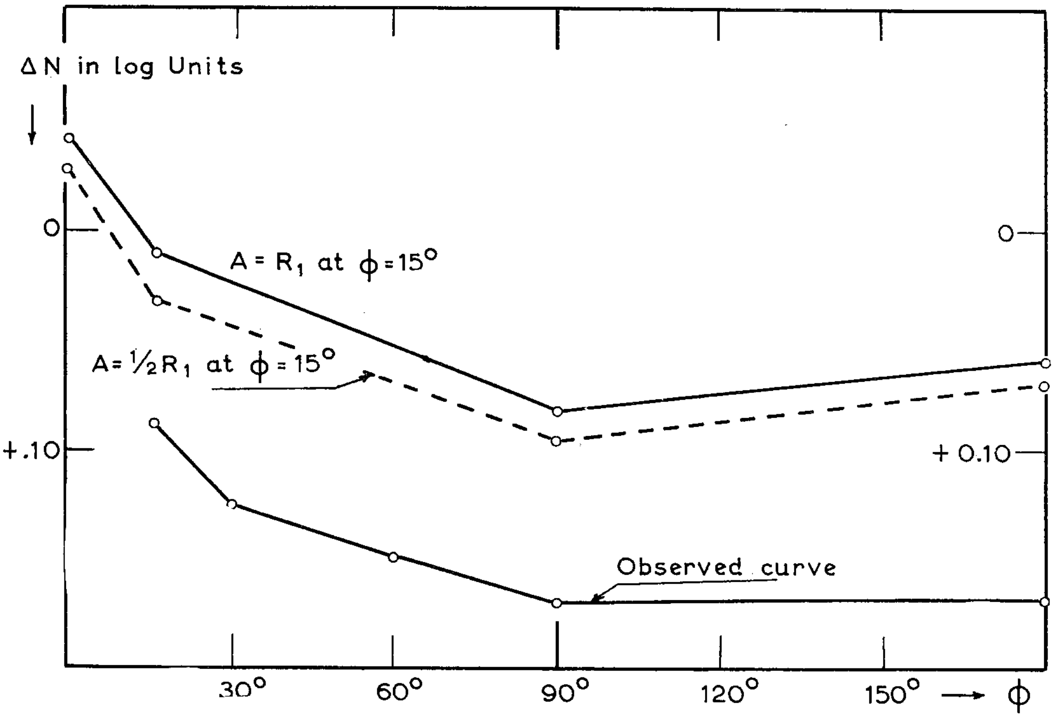

Fig. 14. Observed and calculated sky contour curves.

value of $\mathcal{N}$ is constant along a contour, the sum of $\triangle\mathcal{N}$ for secondary- and large particle scattering gives the shape of the contour curve and the relative position to the primary value of $\mathcal{N}$, which can be directly compared with observations. As results we get

Φ	0	15°	30°	60°	90°	180°	Remarks
$\Sigma \triangle \mathcal{N}$:	−.04	+.01			+.08	+.06	$A = R_1$ at $\Phi = 15°$
$\Sigma \triangle \mathcal{N}$:	−.03	+.03			+.09	+.07	$A = R_1/2$ at $\Phi = 15°$
$\triangle \mathcal{N}$: observed		+.08	+.12	+15.	+.17	+.17	

In Fig. 14 these calculated and observed data are plotted in a diagram for compari-rison.

The difference in position between the observed and the calculated sky contour curves, must be due to multiple scattering which exceeds the calculated secondary scattering. The assymetric shape of the sky contour curve of $\mathcal{N}$, is obtained by calculation, but whether the curveture of the earth may give the curve a different shape or not, is difficult to say. Secondary processes of large particle scattering will certainly count, but are not considered.

As to the first effect of the ozone absorption in contour measurements, this attenuates the direct sunlight of shorter wavelength which is scattered by both large particles and by molecules. In the ratio A/R_1 in the formula for $\triangle N$, both A, the large particle scattering, and R_1, the primary molecular scattering, falls at a rate exp ($-a$ sec z) due to ozone absorption, and the value of $\triangle N$ will not be altered. For secondary molecular scattering, we know that ozone absorption plays an important role, and is considered in the summation of $\triangle N$.

We see then, that the comparison between the observed and the calculated results, shows that the assumptions made about large particle scattering are fairly reasonable, and the next step will be to estimate the effect of large particle scattering on zenith measurements.

21. Large particle scattering effect in zenith measurements. The assumption made about large particle scattering in contour measurements, this being as intense as primary molecular scattering at an azimuth distance of 15° from sun's vertical plane, is valid when considering the case sec $z = 4$. When the direction of observation is towards the zenith (sec $\theta = 1$), we may assume the intensity of large particle scattering contributed from the zenith, to be the same as the light received from $\Phi = 90°$ in the sky contour measurement. Comparing a contour measurement with a zenith measurement, in the latter the direction of observation will look into a much shorter column of large sized scattering material but the attenuation of the scattered radiation will be less, so the assumption may not be too far out. For primary molecular scattering, the intensity will increase slightly when the direction of observation is altered from $\Phi = 90°$, along a sky contour, to the zenith. Making this assumptions we will have

$$\underset{\substack{Zenith\\ Z=4}}{A} = \underset{\substack{Conotur\\ \Phi=15}}{A} \times 1/10 = \underset{\substack{Contour\\ \Phi=15}}{R_1} \times 1/10 = q\lambda^{-4} \times 1/10$$

$$\underset{\substack{\Phi = 15 \text{ or } 0\\ contour}}{R_1/Ks} = 0.147 \text{ where } R_1 = q\lambda^{-4}$$

$$\underset{Zenith}{R_1/Ks} = 0.124 \text{ where } \underset{Zenith}{R_1} = q\lambda^{-4}\,(0.84)$$

For λ' we have

$$\underset{\substack{\Phi = 0\\ contour}}{R'_1/K's'} = 0.326 \text{ where } R'_1 = q\,(\lambda')^{-4}$$

$$\underset{Zenith}{R'_1/K's'} = 0.181 \text{ where } \underset{Zenith}{R'_1} = q(\lambda')^{-4}\,(0.55)$$

Hence we have

$$\underset{\substack{Zenith\\ Z=4}}{\triangle N} = \log \left\{ \frac{1 + \dfrac{q\,\lambda^{-4}\ (\cdot 10)}{q\,\lambda^{-4}\ (\cdot 84)}}{1 + \dfrac{q\,\lambda^{-4}\ (\cdot 10)}{q\,(\lambda')^{-4}\,(\cdot 55)}} \right\} = -\,O \cdot 041$$

Less large sized scattering matter will reduce the intensity of large particle scattering, and we substitute $A = R_1$ with $A = 1/2\ R_1$. This gives

$$\underset{\substack{Zenith \\ Z=4}}{N} = -\ 0.024$$

We have not yet considered any ozone absorption. When an ozone layer is present, the direct sunlight is attenuated by the ozone before reaching the large sized scattering material. Hence, we must substitute A with Ae^{-Za}. The primary molecular scattering from the zenith will not be reduced at the same rate.

We have

$$\underset{\Phi=15}{A}\ e^{-Za} = \underset{\Phi=0}{R_1}\ e^{-Za} = q\,\lambda^{-4}\,e^{-Za}$$

$$\underset{Zenith}{A} = q\,\lambda^{-4}\,e^{-Za}\,\frac{1}{10}$$

Light of the longer wavelength is not affected by the ozone, and we have

$$\underset{Zenith}{A} = q\,\lambda^{-4}\,\frac{1}{10}$$

Further we have

$$\underset{\substack{contour \\ \Phi=0 \\ a=.5}}{R_1/Ks} = 0.0198 \text{ where } R_1 = q\,\lambda^{-4}\,e^{-Za}$$

$$\underset{\substack{Zenith \\ a=0.5}}{R_1/Ks} = 0.039 \text{ where } \underset{Zenith}{R_1} = q\,\lambda^{-4}\,e^{-Za}\,(1.97)$$

For λ' we have as before

$$\underset{Zenith}{R'_1} = q\,(\lambda')^{-4}\,(.55)$$

and we get

$$\underset{\substack{Zenith \\ Z=4 \\ a=.5}}{\triangle N} = \log \frac{1 + \dfrac{q\,\lambda^{-4}\ e^{-Za}}{q\,\lambda^{-4}\ e^{-Za}} \cdot \dfrac{(.10)}{(1.97)}}{1 + \dfrac{q\,\lambda^{-4}}{q\,(\lambda')^{-4}} \cdot \dfrac{(.10)}{(.55)}} = -\ 0.069$$

For less amount of large sized scattering material we get

$$\underset{\substack{Zenith \\ Z=4 \\ a=.5}}{\triangle N} = -\ 0.038$$

We see that for zenith measurements the large particle scattering makes the log intensity ratio "redder" and the reddening effect is larger when ozone absorption is considered. The change in the reddening effect from air with little large sized scattering material to air with large amounts of it, is more pronounced when ozone absorption is considered.

It is of particular interest to try to follow the large particle scattering effect with a setting sun. As the sun gets lower the air mass which the sun rays have to penetrate before reaching regions where the large particle scattering is created, will increase. The large particle scattering will decrease, and we may assume it to decrease at the same rate as molecular scattering, up to a certain value of the sun's zenith distance. If we have very low sun, we may write

$$\underset{\substack{Zenith\\ Z=8}}{A} = \underset{\substack{Zenith\\ Z=4}}{A} (.40) = q\,\lambda^{-4}\,e^{-Za}\,(10)\,(.40)$$

$$\underset{\substack{Zenith\\ Z=8}}{A'} = q\,\lambda^{-4}\,(.10)\,(.50)$$

$$\underset{\substack{\Phi=0\\ Z=4\\ a=.5\ contour}}{R_1/Ks} = 0.0198 \text{ where } R_1 = q\,\lambda^{-4}\,e^{-Za}$$

$$\underset{\substack{Zenith\quad a=.5\\ Z=8}}{R_1/Ks} = 0.021 \text{ where } \underset{Zenith}{R_1} = q\,\lambda^{-4}\,e^{-Za}\,(1.06)$$

For λ' we have

$$\underset{\substack{\Phi=0\\ Z=4\quad contour}}{R'_1/K's'} = 0.326 \text{ where } R'_1 = q\,(\lambda')^{-4}$$

$$\underset{Zenith\quad Z=8}{R'_1/K's'} = 0.081 \text{ where } \underset{Zenith}{R_1} = q\,(\lambda')^{-4}\,(.25)$$

Applying the above relations we get

$$\underset{\substack{Zenith\\ Z=8\\ a=.5}}{\triangle \mathcal{N}} = \log \frac{1 + \dfrac{q\,\lambda^{-4}}{q\,\lambda^{-4}}\,\dfrac{e^{-Za}}{e^{-Za}}\,\dfrac{(.10)\,(.40)}{1.06}}{1 + \dfrac{q\,\lambda^{-4}}{q\,(\lambda')^{-4}}\,\dfrac{(.10)\,(.50)}{(.25)}} = -\,0.083$$

For less large sized scattering material we get

$$\triangle \mathcal{N} = -\,0.044$$

The calculated effects on a log intensity ratio due to large particle scattering in zenith light are summarized below, expressed in terms of $\triangle \mathcal{N}$, (log units).

sec z	$O.$ $\triangle \mathcal{N}$	T $\triangle \mathcal{N}$	$(O.-T.)$ $\triangle(\triangle \mathcal{N})$
4	−.069	−.038	−.031
8	−.083	−.044	−.039

Where in 0.: $A = R_1$ at $\Phi = 15°$, sec z = sec $\theta = 4$.
and in T.: $A = 1/2\ R_1$.

It is found that there is an increase in the reddening effect as the sun sets. This increase may continue until the sun is very low. For an extremely low sun or when the sun is below the horizon, it is reasonable to assume the large particle scattering to decrease rapidly and disappear when direct sunlight, due to the long air path, does not reach the large sized scattering material. In other words, one would expect an in creased reddening effect up to a certain zenith distance of sun and then a decrease and disappearence of it for an extremely low sun or when the sun is below the horizon. The reasoning will, as a consequence, make large particle scattering responsible for part of the umkehr shape of the zenith curve. In connection with this suggestion, an interesting observational result will be shown.

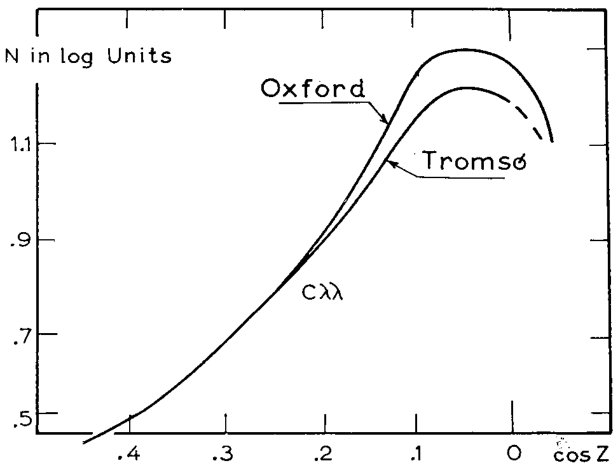

Fig. 15. Umkehr curves observed at Tromsö and in Oxford.

In Fig. 15 is shown typical umkehr observations from Oxford and Tromsö. The atmospheric conditions are different at these two places with a more clear blue coloured sky in Tromsö. It may well be that the marked difference between the umkehr curves from Tromsö and Oxford is caused by different vertical distribution of ozone at the two places, but the assumption made about large particle scattering would require part of this difference as a consequence of different large particle scattering in the atmosphere above Oxford and Tromsö.

One has to be careful when drawing conclusions with respect to large particle scattering on the basis of these simple calculations. It seems, however, as if the "reddening" of the log intensity ratio in contour measurements together with the effects observed in log intensity measurements are reasonably reproduced by calculations and thus justify the assumption made about large particle scattering. And it seems unlikely that an actually observed large particle scattering effect in a contour measurement 90° from the sun should disappear when the direction of observation is altered towards the zenith.

The quantitative result obtained which gives a reddening of the log intensity ratio of the zenith denoted as

$$\triangle N = -\,.069 \text{ log unit for sec } z = 4$$
$$\triangle N = -\,.083 \text{ log unit for sec } z = 8.$$

for "Oxford conditions", may be altered considerably with a more elaborate method of calculation. For this purpose thorough knowledge is required about the scattering processes from large sized scattering material and about the vertical distribution of the particles themselves. If the mean difference in shape of umkehr curves which actually is observed between Oxford and Tromsö, is partly due to differences in non molecular scattering, then non molecular scattering is not negligible. The primary scattering correction due to multiple molecular scattering should be supported by a correction for large particle scattering. The consequence would be a primary zenith curve requiring an ozone distribution with a centre of pressure still lower down.

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