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## THE ATMOSPHERIC SCATTERING OF LIGHT

By FREDERICK E. FOWLE

Rayleigh has indicated how the amount of energy scattered from a beam of light within a gaseous medium may be used to determine the number of molecules in that medium. It will be shown in what follows that, whereas the application of the process to the enumeration of the number of molecules in dry air leads to normal results, its application to atmospheric aqueous vapor leads to an anomaly. Further, this anomaly, like the aurora and certain atmospheric optical phenomena, seems to be related to certain phases of solar activity.

In the process of determining the intensity of the sun's radiation as it reaches the outside of the earth's atmosphere, certain so-called atmospheric transmission coefficients are obtained.<sup>1</sup> These coefficients express the fractional amounts of the sun's energy incident at the outer limits of the atmosphere which would reach an observer at the earth's surface with the sun in the zenith. They are determined at some 40 different wave-lengths between 0.35 and 2.5  $\mu$ . In the following discussion only those values will be considered which belong to the region from 0.35 to 0.57  $\mu$  practically free from any complication due to selective or banded absorptions.

These, which for the moment may be called "crude" transmission coefficients,  $a_\lambda$ , will be subjected to several "refining" processes. It will first be assumed that the composition of dry atmospheric air remains in general practically unchanged from day to day above an altitude like that of Mount Wilson (1,730 meters) where the air is nearly free from dust contamination. The amount of aqueous vapor, however, changes many-fold. Let the coefficient  $a_\lambda$  for wave-length  $\lambda$  be assumed composed of two parts,  $a_{a\lambda}$ , proper to dry air; and  $a_{w\lambda}^w$  due to an amount of aqueous vapor above the station, which, if precipitated, would form a layer of water  $w$  centimeters thick. Then

$$a_\lambda = a_{a\lambda} a_{w\lambda}^w,$$

or taking logarithms,

$$\log a_\lambda = \log a_{a\lambda} + w \log a_{w\lambda}.$$

If the logarithms of the observed transmission coefficients,  $\log a_\lambda$ , are plotted as abscissae against the precipitable water,  $w$ , as ordinates,

<sup>1</sup> Annals of the Astrophysical Observatory of the Smithsonian Institution, vol. 2, p. 13 *et seq.*, 1908.

the points will be found to lie nearly on straight lines. The tangent which the straight line best representing the points for the wave-length  $\lambda$  makes with the axis of abscissae gives  $\log a_{w\lambda}$  and its intercept on the axis of ordinates gives  $\log a_{a\lambda}$ .

The observations taken each year at Mount Wilson (generally during the months from June to November, inclusive) have been subjected, year by year, to this refining process. They yield the results given in tables 1 and 2. The process is described in more detail and

TABLE 1.—Yearly Mean Dry-air Transmission Coefficients,  $a_{a\lambda}$   
Obtained at Mount Wilson, altitude 1,730 m., barometer 62.3 cm.

Wave-length, $\mu$	.350	.360	.371	.384	.397	.413	.431	.452	.475	.503	.535	.574
$a_{a\lambda}$ , year 1910.	.654	.668	.690	.724	.751	.782	.807	.837	.864	.885	.898	.905
1911.	.674	.672	.679	.707	.752	.783	.810	.842	.863	.885	.898	.904
1913.	.614	.637	.667	.689	.738	.763	.792	.816	.836	.859	.873	.877
1914.	.607	.646	.661	.693	.758	.780	.804	.831	.852	.874	.886	.892
1915.	.631	.650	.681	.706	.764	.775	.805	.829	.851	.885	.897	.903
1916.	.637	.651	.670	.693	.742	.767	.792	.821	.845	.869	.887	.888
Dry dustless air.	(.630)	(.655)	(.686)	.714	.752	.783	.808	.840	.863	.885	.898	.905

TABLE 2.—Yearly Mean Atmospheric Aqueous-Vapor Transmission Coefficients,  $a_{w\lambda}$

Obtained at Mount Wilson. 1 cm., precipitable water.

Wave-length, $\mu$	.350	.360	.371	.384	.397	.413	.431	.452	.475	.503	.535	.574
$a_{w\lambda}$ , year 1910. . . . .	.945	.951	.964	.952	.963	.970	.975	.975	.974	.979	.980	.977
1911. . . . .	.898	.934	.954	.962	.961	.962	.962	.962	.973	.974	.980	.976
1913. . . . .	.933	.948	.923	.929	.962	.938	.944	.955	.951	.957	.964	.966
1914. . . . .	.974	.971	.971	.972	.968	.967	.973	.973	.974	.980	.982	.981
1915. . . . .	.958	.963	.962	.953	.968	.971	.971	.978	.975	.976	.980	.979
1916. . . . .	.963	.967	.969	.972	.974	.975	.979	.979	.980	.980	.980	.982

plots shown in the *Astrophysical Journal*, 38, p. 392, 1913, and 40, p. 435, 1914. Improved apparatus and methods have led to greater accuracy in plots like those of figure 1 of the first of these communications. Because of the presence in the upper atmosphere during 1912 of a great amount of volcanic dust and the considerable variation of its amount from day to day, the observations of that year were not adapted to the present investigation and are omitted.

The coefficients  $a_{a\lambda}$  and  $a_{w\lambda}$  were then subjected to a second refining process. Following the lead of Rayleigh, Schuster and L. V. King,  $a_{a\lambda}$  may be placed equal to  $e^{-k}$  where  $e$  is the base of the natural logarithms. Then

$$k = \frac{32}{3} \left\{ \pi^3 (n-1)^2 \frac{H}{N_0 \lambda^4} + bH \right\} \frac{p}{p_0} + D$$

where  $n$  is the index of refraction of air;  $H$ , the height of a "homogeneous atmosphere" in cm. when the pressure  $p_0$  is 76 cm.  $H$  equals  $7.99 \times 10^5$ ;  $p$ , the observed atmospheric pressure;  $\lambda$ , the wave-length in cm.;  $N_0$ , the number of molecules per cm.<sup>3</sup> at 76 cm. pressure and 0° C;  $b$ , a factor to represent the amount of energy absorbed and changed into heat and which approximates zero in the region considered (no selective absorption);  $D$ , a coefficient of transmission suitable to whatever dust may be present. This dust is presumed to be composed of particles so large that  $D$  is invariable with the wave-length.

Treating  $N_0$  and  $D$  as the unknowns, least-square solutions were made by Miss F. A. Graves from the values of  $a_{a\lambda}$  grouped year by year. Table 3 contains the results.

TABLE 3

$N_0$ , the number of molecules per cm. <sup>3</sup> , 76 cm. pressure, 0° C. $D$ , the value of $K$ for dry atmospheric dust.			
1910-11..	$N_0 = (2.73 \pm 0.02) 10^{19}$	$D = 0.005 \pm 0.002$	Weight 18
1913.....	$(2.69 \pm 0.03) 10^{19}$	$0.026 \pm 0.003$	6
1914.....	$(2.66 \pm 0.05) 10^{19}$	$0.010 \pm 0.006$	3
1915.....	$(2.74 \pm 0.05) 10^{19}$	$0.010 \pm 0.005$	3
1916.....	$(2.89 \pm 0.08) 10^{19}$	$0.032 \pm 0.007$	1
Weighted mean $(2.72 \pm 0.01) 10^{19}$			

(The separate values were weighted inversely as the squares of their probable errors.)

First to be noted is the close agreement of the mean value of the number of molecules per cm.<sup>3</sup> with what is probably the best value<sup>1</sup> obtained from other methods  $(2.705 \pm 0.003) 10^{19}$ . The corresponding value of Avogadro's constant is  $6.09 \times 10^{23}$ . Next to be noted are the dust-transmission values. Remembering that  $a_d = e^{-D}$ , during 1910 to 1911  $a_d$  equals 0.995. That is, only about 0.5 per cent of the in-

<sup>1</sup> Millikan, Philosophical Magazine, 34, p. 3, 1917. See also "The Physical Properties of Colloidal Solutions," Burton, p. 38, 1916, for table of determinations of these constants by various methods.

coming energy from the sun was scattered by this dust or what may be called "dry haziness" in distinction from a somewhat similar condition to be discussed later but associated with water vapor and therefore denoted "wet haziness." During 1912<sup>1</sup> owing to volcanic dust, this scattering by dust particles increased to about 25 per cent on the haziest days. It had decreased, on the average, to 2.6 per cent during 1913, and 1 per cent during 1914 and 1915. During 1916 it increased again to an average value of 3.2 per cent producing a marked streakiness in the sky as seen at dawn at Mount Wilson.

Between wave-lengths 0.35 and 0.57  $\mu$  nearly all the loss of light from a beam passing through dry, dust-free air is seen to be due to scattering by the molecules of the air. As has been just noted, during 1910-11 the air was nearly dust free. In the last line of table 1 are given the means of the dry-air coefficients for these two years. They are closely in accord with the values to be expected from Rayleigh's theory. For the first three values, in brackets, theoretical values have been substituted since at these wave-lengths the accuracy of the observed ones is vitiated by field light.

The water-vapor coefficients will next be analysed. Because of the more normal results, the formula will first be applied to a group of transmission coefficients for liquid water obtained by Kreuzler,<sup>2</sup> Ewan,<sup>3</sup> and Aschkinass.<sup>4</sup>

TABLE 4.—Number of Molecules  $N_0$  derived from Liquid Water Transparency

Wave-length in $\mu$	.200	.210	.220	.230	.240	.260	.300
$(1 - \mu) 10^3$ .....	.321	.311	.304	.298	.292	.283	.273
$k$ .....	.00901	.00607	.00568	.00339	.00314	.00253	.00149
$N_0 \times 10^{-19}$ .....	2.85	3.26	2.76	3.70	3.26	2.75	2.44
Wave-length in $\mu$	.415	.430	.450	.475	.487	.500	
$(1 - \mu) 10^3$ .....	.261	.260	.258	.257	.256	.256	
$k$ .....	.00035	.00023	.00020	.00020	.00014	.00020	
$N_0 \times 10^{-19}$ .....	2.63	2.84	3.25	2.59	3.32	2.09	

The data of the above table were somewhat differently treated in the *Astrophysical Journal* (38, p. 401, 1913). There the values were graphically reduced using a uniform value of the index of refraction for all wave-lengths. Here  $n - 1$  is assumed to have the same fractional variation from wave-length to wave-length that liquid water has. However, the observed value of  $n$  even for wave-length 0.589  $\mu$  must be held very doubtful.

<sup>1</sup> Annals of the Astrophysical Observatory of the Smithsonian Institution, vol. 3, p. 216, 1913.

<sup>2</sup> Annalen der Physik, 6, p. 412, 1901.

<sup>3</sup> Proceedings of the Royal Society, 57, p. 117, 1894.

<sup>4</sup> Annalen der Physik und Chemie, 55, p. 401, 1895.

For the range of wave-lengths utilized in table 4, 0.2 to 0.5  $\mu$ , the mean value of  $N_0$  obtained from the liquid-water data is  $2.90 \times 10^{19}$  which though large is of the right order of magnitude and quite as accurate as the accuracy of the data warrants. For these wave-lengths therefore liquid water scatters transmitted radiation just as would the same amount of water in gaseous state according to Rayleigh's theory.<sup>1</sup>

Values of  $N$  of quite a different order of magnitude are obtained when based on the transmission coefficients for atmospheric aqueous vapor. A graphical rather than a least-squares method has been resorted to in the present case.  $N_{tp}$ , the number of molecules per cm.<sup>3</sup> at the pressure  $p$  and the temperature  $t$ , may be derived from the expression<sup>2</sup>

$$k = \frac{32}{3} \left\{ \pi^3 \left( \frac{(n-1)p}{(1+at)760} \right)^2 \frac{(1+at)760 \times 10^3}{(0.81)p} \frac{1}{N_{tp} \lambda^4} \right\} + D$$

Here  $\frac{0.81p \times 10^{-3}}{(1+at)760}$  is approximately the weight of aqueous vapor in grams per cm.<sup>3</sup>, or in other words the reciprocal of the height of a column 1 cm.<sup>2</sup> containing 1 cm. precipitable water at the temperature  $t$  and the pressure  $p$ . Plotting the observations with  $(n-1)^2/\lambda^4$  and  $k$  as variables and calling  $M$  the tangent made by the best representative right line with the  $X$  axis, then  $N_{tp}$  may be obtained through the equation

$$N_{tp} = \frac{32\pi^3}{3} \cdot \frac{p \times 10^3}{0.81(1+at)760} \cdot \frac{1}{M}$$

Figure 1 shows the graphical steps and the following table the resulting values:

TABLE 5.—Number of Molecules  $N_{tp}$  derived from the Transparency of Atmospheric Aqueous Vapor

Year	$M \times 10^{12}$	$N_{tp} \frac{(1+at)760}{p} \times 10^{-17}$	Grade	$D$
1910	0.88	4.7	Good.	0.015
1911	.98	4.2	Good.	.015
1913	1.52	2.7	Excellent.	.025
1914	.70	5.9	Poor.	.014
1915	.52	7.9	Excellent.	.018
1916	.49	8.4	Excellent.	.013

<sup>1</sup> For shorter wave-lengths greatly decreased transmission is found as the great metallic reflection band at 0.115  $\mu$  is approached (Martens, *Annalen der Physik*, 6, p. 603, 1901), and for wave-lengths greater than 0.50  $\mu$  as a region of selective absorption is approached. For metallic reflection and selective absorption the molecular formula would not hold.

<sup>2</sup> *Astrophysical Journal*, 38, p. 400, 1913.

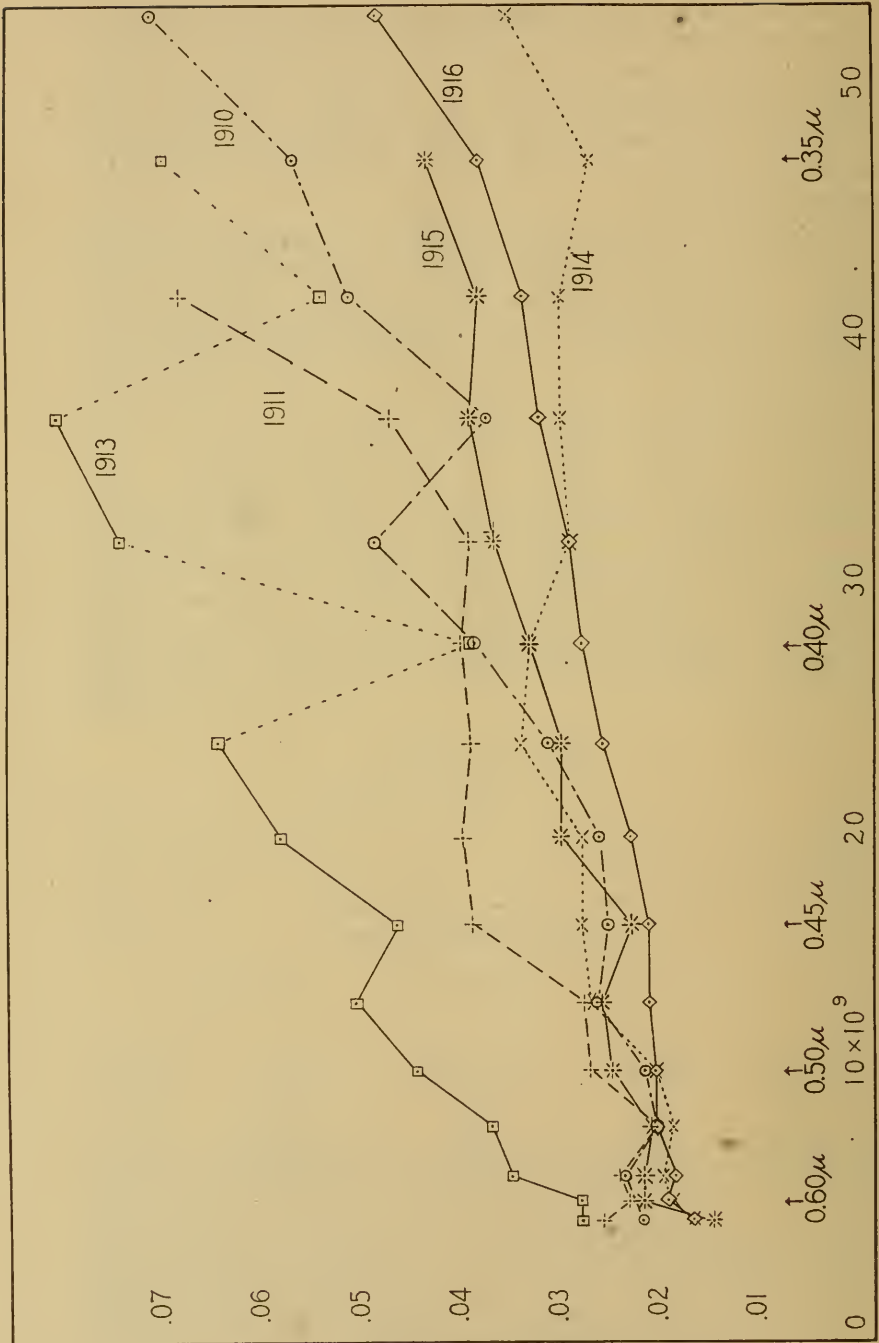


FIG. 1.

Abscissae are  $(n-1)^2/\lambda^2$ . Ordinates are  $K = -\log a$ .



Over the region plotted  $k$  may be considered equal to  $1 - a_{10}\lambda$ , that is the scale of ordinates of figure 1 represents approximately the fractional absorption of energy by 1 cm. of precipitable water in the form of atmospheric vapor. The data for wave-lengths to the right of the region shown (wave-length less than  $0.35 \mu$ ) and to the left (greater than  $0.60 \mu$ ) are very inaccurate, the first because of spectroscopic field-light and very small measurable quantities, and the second because of selective absorption. The accuracy with which the observations fall on a straight line is beyond expectation. Within the wave-length limits just named the average departures from a straight line for the different years correspond in absorption as follows:

Year	1913	1915	1916
Per cent departure.....	0.2	0.2	0.1

(1913, omitting poor points.)

The mean value of  $N_{tp}$  obtained from the atmospheric aqueous water vapor is about

$$5 \times 10^{-17} \left\{ \frac{p}{(1+at)760} \right\},$$

whereas assuming Avogadro's law applicable to water vapor, a value of

$$2.7 \times 10^{19} \left\{ \frac{p}{(1+at)760} \right\}$$

or about 50 times as great would be expected. This anomalous result, already noted in an earlier communication,<sup>1</sup> is therefore confirmed by the results of subsequent years.

There appears to be associated with water vapor what has elsewhere been denoted a "wet haziness" producing a uniform absorption over all the wave-lengths considered and giving a value for  $D$  averaging about 0.017 which corresponds to a 2 per cent loss.

There is an apparent peculiarity of the formula for  $N_{tp}$  in that the more opaque the vapor, that is the greater  $k$ , the smaller the number of molecules per cm.<sup>3</sup> This formula is based upon Rayleigh's

$$k = \frac{32\pi^3}{3N} (n-1)/\lambda^4, \quad (1)$$

<sup>1</sup> Astrophysical Journal, 38, p. 392, 1913.

which is derived from

$$k = \frac{8\pi^3 N}{3} \frac{(D' - D)^2}{D^2} \frac{T^2}{\lambda_1^4}, \quad (2)$$

by substituting from

$$n - 1 = \frac{NT}{2} \left( \frac{D' - D}{D} \right)^2, \quad (3)$$

where  $D$  and  $D'$  are now the original and the altered densities of the medium and  $T$  the volume of the disturbing particle. That is  $n$ , the index of refraction, is a function of  $N$ , the number of molecules per cm.<sup>3</sup> In the present case the value of  $n$  cannot be observed. A preliminary use of the formula for  $N_{tp}$  leads to the suspicion of something abnormal in the condition of atmospheric aqueous vapor. For instance, is it in some colloidal state resulting from some form of ionization of the air? Wilson,<sup>1</sup> for instance, has shown that under the influence of ultra-violet light, in moist dust-free air, nuclei are formed and may grow "till they become large enough to scatter ordinary light." By careful laboratory researches he has shown that oxygen and water vapor alone are necessary for their production; that water vapor is necessary; that saturated vapor is not necessary; that these nuclei persist for some time after their formation; that they are different from ions since they carry no electric charge; that they are probably due to some combination,  $H_2O_2$ , which by decreasing the vapor pressure allows drops of water containing one of them to form and grow where pure water drops would evaporate. Bieber<sup>2</sup> has since shown that  $H_2O_2$  is formed by the action of ultra-violet light. Although the ultra-violet energy in sunlight is too weak at the surface of the earth to be very efficient in the formation of these nuclei, in the clear air above Mount Wilson it may well be very active. In such nuclei, dependent directly upon the presence of water vapor, there seems a possible explanation of the increased absorption. Or, is it possibly due to some emanation from the sun producing some change in the condition of the water vapor?

Reverting now to formula (2) it is to be noted that if the molecules cluster together because of some ionization phenomena or otherwise and in such state each cluster acts as a whole in scattering light as ordinarily a single molecule does, then, neglecting for the moment the effect of the factor  $(D' - D)^2/D^2$ , the intensity of the scattering

<sup>1</sup> Philosophical Transactions of the Royal Society, 192, p. 403, 1899.

<sup>2</sup> Annalen der Physik, 39, p. 1313, 1912.

would vary directly as the sixth power of the diameter of the scattering unit and the first power of  $N$ , so that diminishing  $N$  by  $\frac{1}{2}$ , for instance, may increase the  $T^2$  factor by 4-fold thus doubling the scattering. In table 6 formula (2) has been used to avoid introducing the unknown index of refraction for atmospheric water vapor.

TABLE 6.—*The Variation of the Transparency of Atmospheric Water Vapor compared with Solar Phenomena*

Date	$M \times 10^9$	$N_{tp} \frac{(D' - D)^2}{D^2} \cdot T^2 \cdot \frac{(1 + at) 760}{p}$	Grade	Sun-spot No.	Intensity of solar radiation. Cal./cm. <sup>2</sup> /m.
1910	0.60	$0.61 \times 10^{-17}$	Good.	18.6	1.921
1911	.67	$.68 \times 10^{-17}$	Good.	5.7	1.923
1913	1.03	$1.05 \times 10^{-17}$	Excellent.	1.4	1.907
1914	.47	$.48 \times 10^{-17}$	Poor.	9.7	1.948
1915	.35	$.36 \times 10^{-17}$	Excellent.	46.0	1.949
1916	.33	$.34 \times 10^{-17}$	Excellent.	60.	1.955

Arranging the figures of the 3d, 5th and 6th columns in order of the increasing intensity of solar radiation the apparent correlation of the three quantities is easily seen.

TABLE 7.—*Solar Phenomena and Atmospheric Water-Vapor Transparency*

Solar radiation...	1.907	1.921	1.923	1.948	1.949	1.955
$N_{tp} \left\{ \dots \right\} \dots \dots$	1.05	0.61	0.68	0.48	0.36	0.34
Sun-spot number .	1.4	18.6	5.7	9.7	46.	60.

The relationship between the solar constant of radiation, the sun-spot numbers and the values of  $N_{tp} (D' - D)^2 T^2 / D^2$  is better shown in figure 2, especially in the curves *a*, *b*, and *c*. Additional years of observations will be required to thoroughly establish the relationship.

#### SUMMARY

The atmospheric transmission coefficients obtained at Mount Wilson in the years 1910 to 1916 for the region free from selective absorptions between wave-lengths 0.35 and 0.50  $\mu$  have been analyzed and have yielded the following data and results.

The transmission coefficients for dry air ( $a_{a\lambda}$ ) vary with the inverse fourth power of the wave-length. They are apparently wholly due to molecular scattering since the number of molecules in a cm.<sup>3</sup> of air at 76 cm. pressure and 0° C. corresponding to them,  $(2.72 \pm 0.01) \times 10^{19}$ , is in excellent agreement with the best value,  $(2.705 \pm 0.003) \times 10^{19}$  (Millikan), determined by other methods.

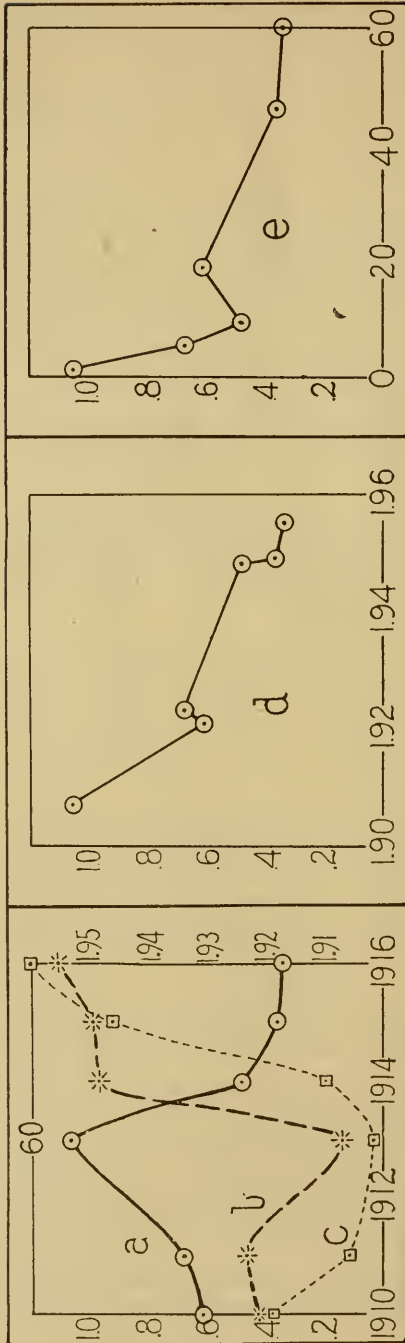


FIG. 2.

Curve *a*, abscissae are years, ordinate  $N_{th} \left( \frac{D'-D}{D} \right)^2 T^2 \times 10^{17}$  varies as  $K\lambda^4$

Curve *b*, abscissae are years, ordinates mean yearly solar radiation, cal. cm.<sup>2</sup> m.

Curve *c*, abscissae are years, ordinates sun-spot numbers.

Curve *d*, abscissae are solar radiations, ordinates same as curve *a*.

Curve *e*, abscissae are sun-spot numbers, ordinates same as curve *a*.

As has been stated in former communications, this strongly confirms the accuracy of our estimations of the atmospheric losses affecting the radiation reaching us from the sun.

There is to be expected above the altitude of Mount Wilson (11,730 meters) a certain amount of what has been called "dry haziness" to distinguish it from a similar haziness associated with aqueous vapor. Before the Mount Katmai eruption of 1912, during 1910 and 1911, this caused a loss of only about  $\frac{1}{2}$  of one per cent from the incoming solar radiation when the sun was in the zenith. The mean of the coefficients for these two years (table 1), given in the lower line of that table, may be taken as a close approximation to the transparency of dry, dust-free air. During 1913, this loss due to dry haziness decreased from its enormous value of 25 per cent just subsequent to the Mount Katmai eruption to about 3 per cent and during 1914-15 to about 1 per cent, but it increased again to 3 per cent during 1916.

Within the same spectrum region, the transmission coefficients for atmospheric aqueous vapor ( $a_{w\lambda}$ ) also apparently vary with the inverse fourth power of the wave-length. The scattering of radiation when passing through liquid water is shown to be the same as would be expected from the number of ( $H_2O$ ) molecules present if the same quantity of water existed in a gaseous state. But the same amount of water in the form of *atmospheric* water vapor should give 50-fold less absorption than that observed. This may be due to some combination ( $H_2O$ )<sub>x</sub> of a portion, at least, of the vapor. Increasing the effective diameter of the scattering particle may be far more effective in scattering the radiation than is compensated by the resultant decrease in their number; for the scattering varies with the sixth power of the diameter and only directly with the number. This peculiar molecular condition might be supposed connected with some ionization phenomenon, and possibly, like the aurora (Störmer), in some way might be dependent on charged particles coming from the sun. As shown in figure 2 there does seem to be a connection between this phenomenon, curve *a*, the solar radiation intensity, curve *b*, and the sun-spot numbers, curve *c*. This amounts to saying that the smaller the average solar radiation or the sun-spot number, the greater is the absorptive power of atmospheric water vapor. This result requires further testing. It is, however, con-

