$\Delta T$ 's at which the critical heat inputs were observed were quite large (0.018° at 1.7°K), dropping to 0.005° at 2.1°K.

These critical heat inputs for the heat transport are proportional to the well-known transfer rate of the saturated film, as already reported by BBM (reference 1); however, the limiting initial heating rate (for which

no  $\Delta T$  was observed) was dependent on the amount of excess liquid in the cell. Further, the critical heat input observed was very high; at 1.7°K it was twenty-five times greater than that observed for the thickest film of Fig. 2. The experiments were not continued, since adequate interpretation seems difficult in view of the absence of a reliable estimate of the film thickness.

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# **Resonance Absorption of Sunlight in Twilight Layers**

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Solar radiation must pass at least once through the absorbing layer to reach the twilight zone of a layer of atoms scattering resonance radiation. The attenuation of the solar beam is calculated for resonance absorption and the resulting scattered intensity compared with the transparent layer model intensity for the same thickness of material. It is shown that in the case of sodium, the reduction in intensity for layers thicker than 10<sup>9</sup> atoms/cm<sup>2</sup> is too serious to permit the deduction of layer thickness from a simple theory which neglects imprisonment of resonance radiation.

### INTRODUCTION

ROM measurements of the time variation in intensity of the sodium D lines at twilight and at dawn the location, distribution, and vertical thickness of the scattering layer of sodium atoms has been deduced.<sup>1-4</sup> The basic assumption that the light observed is scattered sunlight is supported by strong evidence.5-7 Careful account has been taken of such important factors in the interpretation of the observations as refraction and attenuation by the gases of the lower atmosphere which the incident sunlight must traverse.<sup>3,4</sup> Unfortunately, an uncertainty in the intensity incident at the bottom of the Fraunhofer lines makes for an uncertainty as large as an order of magnitude in the deduced sodium thickness. Values given range from  $2 \times 10^9$  atoms/cm<sup>2</sup> to  $2 \times 10^{10}$  atoms/cm<sup>2</sup>. The layer appears to be located somewhere between 70 and 115 km above the earth's surface.

With the correction mentioned for general atmospheric extinction—which is of course independent of the sodium layer thickness-the flux incident in the twilight scattering layer is taken in these calculations to be uniform throughout the region. This assumption, however, neglects the fact that the sunlight incident on the sodium layer after sunset must pass once completely

57 (1954).

through the layer and, in general, partly through it again. It is the purpose of this note to give the results of a calculation of the consequent attenuation of the incident light by resonance absorption for layer thicknesses in the range from  $2 \times 10^9$  atoms/cm<sup>2</sup> to  $2 \times 10^{10}$ atoms/cm<sup>2</sup>. Appreciable attenuation under these conditions would not only force a revision upward of the layer thickness, but, because this in turn would imply further attenuation, would seem to suggest an altogether different treatment of the problem of twilight excitation. This is particularly true since this treatment neglects reradiated resonance photons. Under such conditions these should contribute a non-negligible component to the density of excited atoms in twilight.8

The importance of an accurate knowledge of the sodium layer thickness for the determination of the altitude of the nightglow D line emission has been pointed out in connection with a calculation of the effect of resonance absorption on the variation with zenith distance of the radiation from an airglow layer.9



FIG. 1. Path of a photon through the absorbing layer to reach the point  $(r,\theta)$ .  $r_0$  is the radius of the earth.

<sup>&</sup>lt;sup>1</sup> D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) A187, 261 (1946).

A. Kastler, Compt. rend. 210, 530 (1940). <sup>6</sup> J. Bricard and A. Kastler, Ann. Geophys. 1, 53 (1944); 6, 286 (1950).

<sup>&</sup>lt;sup>7</sup> Bricard, Kastler, and Robley, Compt. rend. 228, 1601 (1949).

<sup>&</sup>lt;sup>8</sup> A. Foderaro and T. M. Donahue, Phys. Rev. 91, 1561 (1953). <sup>9</sup> T. M. Donahue and A. Foderaro, J. Geophys. Research 60, 75 (1955).

#### ABSORPTION OF INCIDENT SUNLIGHT IN SODIUM LAYER

Consider sodium atoms distributed in a layer between  $r_1$  and  $r_2$  as in Fig. 1, where r is the distance from the center of the earth. Let the density of atoms be

$$N(r) = N_0 \exp[-\alpha(r-r_0)].$$
(1)

The thickness of sodium traversed by a photon which reaches a point  $(r,\theta)$  in the sodium layer is

$$L(\mathbf{r},\theta) = \int_{x(r_2)}^{x(r_1)} N(\mathbf{r}') dx' + \int_{x(r_1)}^{x(r)} N(\mathbf{r}') dx', \qquad (2)$$

where

$$\begin{aligned} x' &= (r_2^2 - p^2)^{\frac{1}{2}} - (r'^2 - p^2)^{\frac{1}{2}}, \\ p &= r \cos\theta, \end{aligned}$$
 (3)

and  $\theta$  is measured from "sunset." For  $r_0 , this becomes$ 

$$L(\mathbf{r},\boldsymbol{\theta}) \cong N_0(\pi p/2\alpha)^{\frac{1}{2}} \times (\operatorname{erf} w_2 + \operatorname{erf} w - 2 \operatorname{erf} w_1) \exp[\alpha(\mathbf{r}_0 - p)], \quad (4)$$

subject to the condition

$$(r'^2 - p^2)^{\frac{1}{2}} \ll p$$
 (6)

for all r' along the path of the photon, and where

w

$$= \left[ \alpha (r^2 - p^2) / 2p \right]^{\frac{1}{2}}, \tag{7}$$

 $w_2$  being the value of w at  $r=r_2$  and  $w_1$  its value at  $r=r_1$ . For  $r_2 > p > r_1$ , similarly,

$$L(\mathbf{r},\boldsymbol{\theta}) \cong N_0(\pi p/2\alpha)^{\frac{1}{2}}(\mathrm{erf}w_2 + \mathrm{erf}w) \exp[\alpha(\mathbf{r}_0 - p)]. \quad (8)$$

And for all values of  $\theta$  in the fourth quadrant (before sunset),

$$L(\mathbf{r},\theta) \cong N_0(\pi p/2\alpha)^{\frac{1}{2}}(\operatorname{erf} w_2 - \operatorname{erf} w) \exp[\alpha(\mathbf{r}_0 - p)]. \quad (9)$$



FIG. 2. Attenuation at the center of the sodium  $D_2$  line  $({}^{2}S_{\frac{1}{2}} - {}^{2}P_{\frac{1}{2}})$  for solar radiation reaching points in the twilight layer defined by  $(r, \theta)$ , where r is the distance from the center of the earth and  $r_{\theta}\theta$  is the distance on the surface from sunset. Vertical thickness of the sodium layer here is assumed to be  $1.84 \times 10^{9}$  atoms/cm<sup>2</sup> column.



FIG. 3. Attenuation at the center of the sodium  $D_2$  line  ${}^{2}S_{\frac{1}{2}}-{}^{2}P_{\frac{1}{2}})$  for solar radiation reaching points in the twilight layer defined by  $(r,\theta)$ , where r is the distance from the center of the earth and  $r_{\theta}\theta$  is the distance on the surface from sunset. Vertical thickness of the sodium layer here is assumed to be  $1.84 \times 10^{10}$  atoms/cm<sup>2</sup> column.

## THE SCATTERED INTENSITY

If the intensity per unit frequency of the light incident on the earth in the neighborhood of the Fraunhofer Dlines is taken to be  $J_0$ , independent of frequency, then

$$J_0 \exp[-\sigma(\nu)L]d\nu \tag{10}$$

will be the intensity incident between  $\nu$  and  $\nu + d\nu$  at the point  $(r,\theta)$ .  $\sigma(\nu)$  is the cross section for absorption at frequency  $\nu$ . The scattered intensity then, apart from small geometrical factors, would be

$$I(\theta) \propto \int_{r_1}^{r_2} \int \sigma(\nu) J_0 N(r) \exp[-\sigma(\nu) L(r,\theta)] d\nu dr.$$
 (11)

# COMPUTATION FOR MODEL SODIUM LAYERS

 $L(r,\theta)$  has been computed under the assumption that sodium is distributed between 70 and 100 km according to

$$N(r) = \begin{cases} 0, & r < 6.47, \\ N_0 \exp[-127(r-6.40)], & 6.47 < r < 6.50, \\ 0, & r > 6.50, \end{cases}$$
(12)

where distances are measured in thousands of km. Two values of  $N_0$  have been assumed,  $2.17 \times 10^8$  cm<sup>-3</sup> and



FIG. 4. Predicted intensity of radiation scattered from the zenith as a function of angle measured from sunset for the nonabsorbing sodium layers and the absorbing sodium layers of the same thicknesses.  $L_0$  is the vertical thickness assumed. Curves are for the center of the  $D_2$  component. The lower of each pair of curves is for an absorbing layer.

 $2.17 \times 10^7$  cm<sup>-3</sup>. The first corresponds to a vertical thickness of  $1.84 \times 10^{10}$  sodium atoms/cm<sup>2</sup>, the second to  $1.84 \times 10^9$  per cm<sup>2</sup>. Curves are drawn in Fig. 2 and Fig. 3 showing exp( $-\sigma_0 L$ ), where  $\sigma_0$  is the absorption cross section at the center of the  $D_1$  component and is here taken, for a Doppler line at 240°, to be  $10^{-11}$  cm<sup>2</sup>.

Traversal of even the less thick layer results in great attenuation, particularly in the time just after sunset. Furthermore, the incident flux of radiation in the region where twilight observations are usually made can be seen to vary appreciably with time  $(\theta)$  and with altitude for fixed  $\theta$  as well as to have suffered an over-all attenuation.

Integration at selected fixed values of  $\theta$  of the product function of r,

$$N_0 \exp[-\alpha(r-r_0)] \exp[-\sigma_0 L(r,\theta)], \qquad (13)$$

gives a measure of the intensity scattered radially

TABLE I. Relative intensities for the two sodium layers of Fig. 4 at  $\theta = 0.1464$  and  $\theta = 0.1570$  radian. Here the intensities are all compared to that of the  $1.84 \times 10^{10}$  cm<sup>-2</sup> layer normalized to 10 in arbitrary units.

	$r(\theta) = 70 \text{ km}$	$r(\theta) = 80 \text{ km}$
Thick layer—no attenuation Thick layer—attenuated	10.00 1.07	10.00 0.60
Thin layer—no attenuation Thin layer—attenuated	1.00 0.73	$\begin{array}{c} 1.00\\ 0.74\end{array}$

(zenith observation). This may be compared with

$$N_0 \int_{r(\theta)}^{r_2} \exp[-\alpha(r'-r_0)] dr', \qquad (14)$$

which would be the measure of the scattered intensity for the case of no resonance attenuation (see Fig. 4). The lower limit of integration  $r(\theta)$  is the lowest illuminated point in the sodium layer at the angle  $\theta$ . The logarithmic scale of intensity used in the figure obscures the very large effects calculated even for the thinner layer. The reduction in intensity is by a factor larger than 10 for the thicker layer and larger than 4/3 for the thinner layer throughout the twilight region. The relative intensities at two values of  $r(\theta)$  the lower limit of illumination in the layer, are given in Table I.

## DISCUSSION

No other model sodium atmospheres have been considered here. It seems clear that no simple alteration in layer height or in the distribution would affect seriously the sizeable attenuation or lead to a qualitatively different shape of intensity curve. Neither has the full contribution of the doublet been computed as it would be given from (11). While it is true that the attenuation is most severe for the case selected, the other frequencies have a correspondingly lower probability of being scattered and observed. In fact, when absorption but not imprisonment is taken into account, as in this paper,

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the scattered radiation should be strongly self reversed whenever the important part of the incident sunlight must travel through a thickness of sodium so great that  $\sigma_0 L \gg 1$ . For both of the examples treated here, this is the case. The fact that the actual twilight radiation is not self-reversed may perhaps be explained on the basis of replenishment of photons near the center of the line by imprisonment. It seems scarcely profitable to pursue all such refinements as these separately. Calculations are being made of the intensity of radiation which would be received near twilight in various zenith directions for several model sodium atmospheres in which the transport of imprisoned resonance radiation is accounted for.

It would appear from these results that unless the observed zenith intensity in twilight is consistent with a vertical thickness of less than 10<sup>9</sup> atoms/cm<sup>2</sup>, it is unsafe to conclude much about the distribution of sodium atoms without a careful account of the history of the resonance photons before they reach the scattering region. The inclusion of sodium layer absorption in the present simple theory of the twilight effect leads in fact to a very large "predicted" variation during early twilight for which there is no observational evidence. Such effects are expected to vanish when the contribution of the imprisoned resonance radiation to the density of excited atoms is properly accounted for.

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# Statistical Analog of the Second Law

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In recent papers Landsberg and the writer have used two different propositions to represent the statistical analog of the second law of thermodynamics. The difference is discussed and the writer's viewpoint presented. There is also included a necessary addition to a proof given in the author's previous analysis.

ANDSBERG<sup>1</sup> has recently given an extension and generalization of an analysis<sup>2</sup> by the writer. This analysis involved the logical relations among the second law of thermodynamics and certain propositions in statistical mechanics when the transition probabilities are assumed independent of time. Landsberg obtains analogous results except that the statistical implications of the second law appear to be different in the two analyses. These exceptions arise from the fact, clearly pointed out by Landsberg, that his proposition (H) is not completely analogous to the proposition (S) used by the writer. It seems desirable to clarify this difference.

The second law asserts that, aside from statistical fluctuations, the entropy of an isolated system will never decrease, whatever initial values may be assigned to the macroscopic variable. The statistical form of this law would seem to require that the statistical analog of entropy must never decrease, whatever initial values may be assigned to the probabilities. (The objection may be raised that certain initial distributions could be set up only by a Maxwell demon. In any event there are a very large variety of permissible distributions.) (S) is intended to meet precisely the above requirement. However, a system is said to obey Landsberg's (H) at a time T if the entropy is constant or increasing at the instant T—even though at a different time, or with different initial probabilities, the entropy may decrease. For instance, in Landsberg's example (iii) the entropy will decrease if one takes  $P_1 = \frac{1}{6} + \epsilon$ ,  $P_2 = \frac{1}{3}$ , and  $P_3 = \frac{1}{2} - \epsilon$ . This decrease may be verified by a simple calculation; qualitatively it means that the system tends to the equilibrium distribution and that this distribution is less random than the initial one. Thus (S) implies (H)but is a far stronger restrictive condition. Consequently it is possible to deduce certain statistical propositions from the second law alone if it is taken in the form (S), but not if it is taken as (H).

Dr. Landsberg<sup>3</sup> takes the view that (H) is too weak to represent the H-theorem, but that (S) is too strong. He feels that the connection of these propositions with the second law may require further investigation.

It should be noted that Lemma 4 in Landsberg's paper is really needed to complete the writer's<sup>2</sup> proof of Theorem 2 by showing that S is a minimum. As a counterexample, consider  $f(x,y) = (x-y)^2 - x^4$ , which has a saddle-point at the origin but appears to have a minimum if only second-order terms are considered. This flaw in the proof was pointed out by Fröman.<sup>4</sup>

<sup>&</sup>lt;sup>1</sup> P. T. Landsberg, Phys. Rev. **96**, 1420 (1954). <sup>2</sup> J. S. Thomsen, Phys. Rev. **91**, 1263 (1953).

<sup>&</sup>lt;sup>3</sup> P. T. Landsberg (private communication). <sup>4</sup> P. O. Fröman, University Institute for Theoretical Physics, Copenhagen (private communication).