

Sodium dayglow: Observation and interpretation of a large diurnal variation

Jacques Emile Blamont, T. M. Donahue

▶ **To cite this version:**

Jacques Emile Blamont, T. M. Donahue. Sodium dayglow: Observation and interpretation of a large diurnal variation. Journal of Geophysical Research, 1964, 69 (19), pp.4093-4127. 10.1029/JZ069i019p04093 . insu-03636083

HAL Id: insu-03636083

https://insu.hal.science/insu-03636083

Submitted on 10 Apr 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Copyright

Sodium Dayglow: Observation and Interpretation of a Large Diurnal Variation

J. E. BLAMONT

Service d'Aéronomie, Réduit de Verrières
Verrières, Seine-et-Oise, France

T. M. DONAHUE

University of Pittsburgh, Pittsburgh, Pennsylvania

Abstract. Analysis of the dayglow of the sodium D lines since September 1960 and the twilight glow since 1954 at Haute Provence Observatory shows a large seasonal maximum of 30 kR for the dayglow in June. The ratio of daytime to twilight abundance then is about 7 to 1. The ratio becomes 2 to 1 in December. Evidence presented for the reality of this effect includes actual line profiles showing an emission peak above Rayleigh-scattered background, observation of the dayglow from a high-altitude airplane, and observation of the dayglow with a rocket-borne photometer. The seasonal maximum is accompanied by a seasonal decrease of 5 km in twilight layer altitude in midsummer. The effect is interpreted as being caused by a diurnal variation in atomic oxygen and ozone enhanced by turbulent diffusion of the sodium and its compounds. Other possible interpretations such as photochemical excitation are rejected. A seasonal variation is also found in the ratio of morning to evening sodium abundance in twilight. The maximum ratio is 1.4 at the equinoxes. At Tromsø, Norway, the dayglow intensity is about 15 kR and shows no seasonal variation.

INTRODUCTION

In this paper the results obtained from observations of the sodium twilight airglow between 1954 and 1964 at the Observatoire de Haute Provence and the sodium dayglow between 1960 and 1964 will be presented. The instrument used in all the work was a magnetic scanning resonance cell photometer. The validity of the method used to measure the dayglow intensity has been tested in many ways. It has been demonstrated that the photometer observes intense and distinct emission lines at the bottom of the Rayleigh-scattered Fraunhofer lines and that the presumed sodium emission is not attributable to a continuum or some other distortion of the Fraunhofer lines or to the effect of water vapor absorption. Furthermore, results obtained at 13-km altitude when the photometer was used for dayglow observations in a jet aircraft were the same as those obtained for the dayglow intensity on the ground. Finally, a resonance cell photometer mounted in a rocket saw an overhead sky intensity which descended to a plateau at 23 km. The plateau intensity was identical with the component of the sky light which was attributed to the sodium dayglow on the ground.

The dayglow is much stronger, particularly in the summer, than would be expected from the twilight glow if the dayglow is to be attributed entirely to resonance scattering and if the abundance of free sodium does not undergo a systematic diurnal variation. On the assumption that the dayglow is entirely resonance scattering, it has been determined that the ratio of free sodium in daytime to that in twilight varies from 7 to 1 in June to 2 to 1 in December. The dayglow zenithal intensity reaches a maximum of about 28 kR in June and a minimum of about 12 kR in December. The morning twilight glow has a sharp maximum of 3.9 kR in early November; the evening twilight glow maximum of 3.2 kR occurs in late December. The minimum is reached in April and June at 1.2 kR. There are secondary maximums in March and August–September. The daytime abundance seasonal variation is from 13×10^9 atoms/cm^2 to 32 atoms/cm^2. In part the twilight summer minimum is a result of absorption of sunlight in the day layer. The abundance variation is only

from 4×10^9 atoms/cm^2 in June to 10×10^9 atoms/cm^2 (morning in November) and 7.25×10^9 atoms/cm^2 in the evening. The abundance in the morning is about 1.4 times as high as the abundance in the evening during February and November. The ratio of morning to evening abundance has a seasonal variation somewhat like that predicted by *Hunten* [1954] on the basis of photoionization and nocturnal recombination.

The altitude of the twilight layer varies from 87 km in June to 92 km in March. There is a distinct indication of a strong relationship between the low altitude of the summer twilight, the high daytime abundance, and the large day to twilight ratios.

In Tromsø, Norway, the average dayglow emission rate is about 15 kR with no seasonal variation. The twilight glow varies between about 1 kR in summer and 3 kR in December.

An attempt has been made to show that a diurnal variation in sodium abundance could be a consequence of a diurnal variation in O and O_3. The ratio of sodium to its oxides is determined in part by the ratio of the reducing rates controlled by O and the oxidizing rates controlled by O_2 (three-body) and O_3 (two-body). However, turbulent diffusion is also important in altering chemical distributions that vary too rapidly with altitude. Recent measurements which have given higher values for the rate of ozone formation from O and O_2 bring the region of significant diurnal variation in atomic oxygen up to almost 90 km. Turbulent diffusion is also important in determining the vertical distribution of O and O_3 as a function of time and should cause the ozone density to be rather higher at night in the 90-km region than has been supposed. Thus the large summertime abundance of atomic oxygen below 90 km in the day will permit a large daytime build-up of sodium which will rapidly become oxidized when, as the sun sets, the O disappears and the O_3 builds up. Turbulent transport of sodium downward and its oxides upward will enhance this effect. The dayglow layer should extend below the twilight layer, and both in summer are some 5 km lower than they are in winter when the atomic oxygen abundance is smaller.

This analysis depends on a reevaluation of sodium three-body oxidation rates which indicates that the heretofore measured values are based on a faulty technique and are orders of magnitude too high. This restores the Chapman reaction involving ozone to important status once more in this problem.

Other mechanisms for exciting the dayglow involving photodissociation or chemical reduction followed by rapid oxidation have been examined and found unattractive. All impose as a condition that the oxides be orders of magnitude more abundant than the free sodium even at 90 km. It then becomes apparently impossible to explain the twilight layer with a peak at 90 km and a rapidly decreasing density above.

The Observations

Since 1954 the twilight sodium airglow has been observed in a routine program at the Observatoire de Haute Provence [*Blamont,* 1956; *Donahue and Blamont,* 1961]. The instrument used has been a magnetic scanning resonance cell photometer; the apparatus has been described in several papers [*Blamont,* 1956; *Donahue and Blamont,* 1961]. The principal element of the photometer is a cell of hot sodium vapor on which sky light is focused. The sodium atoms in the cell scatter light within their bandwidth (about 0.045 A) to a photomultiplier. Since this light contains a white-light component arising from Rayleigh scattering it is necessary to subtract this contribution to obtain the portion of the detected radiation attributable to sodium emission. The basis for this subtraction is laid by periodically shifting the Zeeman components of the resonantly scattered light from the cell some 0.08 A with a magnetic field of 4000 oersteds. Under these conditions a very small part of the narrow emission lines (0.03 A wide) from the upper atmosphere contributes to the light received by the photomultiplier tube.

The method. Since September 1960 this apparatus has also been used to observe the sodium dayglow emission. A report of the results obtained during the first two months of operation has already been published [*Blamont and Donahue,* 1961], in which a complete discussion of the method of separating the Rayleigh-scattered white light from the sodium dayglow emission was presented. The technique involves observing sky light, varying the magnetic field to a spectral region about 0.16 A wide at the bottom of the Fraunhofer lines, and comparing this spectrum

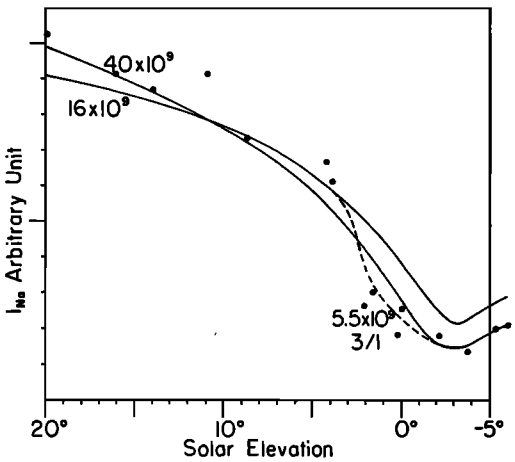


Fig. 1. Sodium day and twilight glow, May 10, 1962, Tromsø, Norway. Theoretical curves are for 40×10^9 atoms/cm^2 and for 16×10^9 atoms/cm^2 in the day followed by 5.5×10^9 atoms/cm^2 in twilight.

with that obtained by similar scanning of direct sunlight. The spectrum of the sky light is fitted to the Fraunhofer line shape in the region far away from the center of the lines. If the Fraunhofer spectrum is reproduced in the Rayleigh-scattered light, and if there is no other source contributing to the observed radiation near the center of the line, the emission from the upper atmosphere can be extracted from this radiation by subtraction of the white-light component.

On many occasions and over a period of about a year the spectrum at the bottom of the Fraunhofer lines was scanned completely in this fashion as a check on the validity of the method. Readings for some 5 to 10 settings of the field from 0 to 5000 oersteds were generally taken during such observations. Since the beginning of 1962, however, the procedure has been simply to compare readings at 0 and 4000 oersteds in the sky light with those made for the same field settings on direct sunlight. If the ratio $I_s(0)/I_s(4000)$ for direct sunlight is called R_F, then

$$I_w = R_F I(4000)$$

is the white-light or Rayleigh-scattered contribution at the center of the line where $I(4000)$ is the photometer reading at 4000 oersteds for sky light. The simple subtraction

$$I_{Na} = I(0) - I_w$$

gives the presumed contribution of the dayglow emission lines.

An instrumental difficulty is associated with the presence of stray light within the bandwidth of the interference filter in front of the photometer. The contribution of this light is measured by periodically cooling the cell and condensing the sodium. Unfortunately, the stray light is not exactly the same from the cold cell as from the hot cell. For this reason it is very important to minimize the amount of stray light as well as to measure the percentage change in stray light that occurs when the cell is heated. The measurement is made by means of a helium lamp (free of sodium) which emits yellow lines within the bandwidth of the interference filter. The presence of a large stray-light component from December 1960 to early August 1961 led to the rejection of data obtained during this period. It was also responsible, apparently, for an erroneous evaluation of R_F during the early work. The value of 0.42 used at first [*Blamont and Donahue*, 1961] has been replaced by a carefully and repeatedly observed value of 0.54.

Several typical runs showing I_{Na} as a function of the angle of solar elevation have been published. In Figures 1–3 are shown a few more such runs, obtained at Tromsø, Norway, during a time when the sun went only to about 7° below the horizon. The change of solar angle with time was so slow that the standard dayglow technique could be employed even in twilight. Almost 48 hours of continuous observation are represented in Figure 2. The data show unmistakably the presence of a minimum at about 2° solar dip angle. This was predicted several years ago [*Donahue and Resnick*, 1955; *Donahue and Stull*, 1959]. It is the consequence of resonance absorption in the long path through the sodium layer which the sunlight must traverse during early twilight. A notable feature of all observations except those made in midwinter is the very large dayglow signal. It is much greater than that expected if the dayglow is produced entirely by resonance scattering and the sodium abundance in daytime is the same as that in twilight. To fit the data in Figure 1, for example, an abundance of 40×10^9 atoms/cm^2 would be necessary. Alternatively, a model with 16×10^9 atoms/cm^2 in the daytime and 5.5×10^9 atoms/cm^2 in twilight would suffice. This point will be discussed fully in a later section.

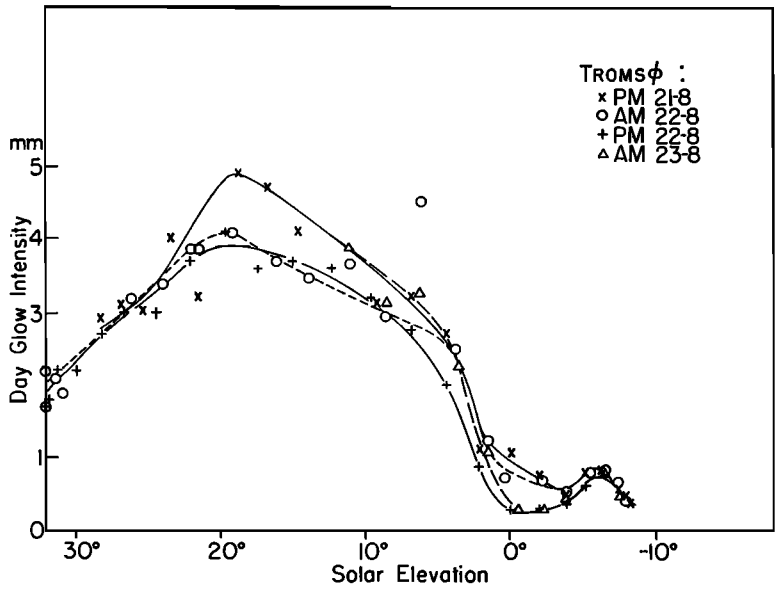


Fig. 2. Sodium day and twilight glow from noon August 21 to noon August 23, 1962, Tromsø, Norway. Units are arbitrary.

A number of tests have been made to check the validity of the method of extracting the contribution of the dayglow emission. Fundamentally the problem is whether the spectrum of the light in the wavelength region scanned by the Zeeman photometer can be uniquely decomposed into a portion having the spectrum of the Fraunhofer lines and a residual component consisting entirely of D-line emission from the upper atmosphere. There are two effects that might vitiate this procedure. One would be a consequence of scanning over atmospheric absorption lines. In particular, if there were such a line in the spectral region observed with 4000 oersteds on the cell it would cause an underestimate of the white-light component at zero field. The other effect is a possible systematic distortion of the line shape of the background scattered sky light. It could occur because of some unsuspected mechanism for frequency shifts in scattering by the lower atmosphere or because of the presence of a continuum in sky light other than sunlight. Such effects would certainly be unexpected, but they need to be considered particularly as a consequence of the observations by *Grainger and Ring* [1962] of a distortion of the H line of calcium in scattered light. Actually a program to establish the presence or absence of such phenomena was undertaken from the beginning of the observational program in 1960.

Atmospheric absorption lines in the neighborhood of the D lines have been catalogued by *McNutt and Mack* [1963]. Contrary to their statement, the only intense line that is a menace, a water vapor line about 400 mK (0.18 A) to the red of the D_2 line, is far beyond the region swept by the magnetic field (about 0.08 A). In fact, only one weak absorption line lies in this region, 0.09 A to the blue of the D_2 line. The observations of McNutt and Mack, indeed, constitute evidence that absorption lines pose no serious threat to the Zeeman photometer.

An extensive survey has been made to determine whether there is any anticorrelation between the presumed sodium intensity I_{Na} and $I(4000)$ or the subtracted white-light component $R_F I(4000)$, as there would be if the supposed emission resulted from an underestimate of I_w caused by systematic reduction of $I(4000)$ by an atmospheric absorption line. No correlation of any sort was found. The data plotted in Figure 4 for the period July through November 1961 are representative. The correlation coefficient of I_{Na} with $I(4000)$ is zero.

On the other hand, there is always a strong correlation between I_{Na} and $I(0)$. It is shown in Figure 5, again for the July–November 1961

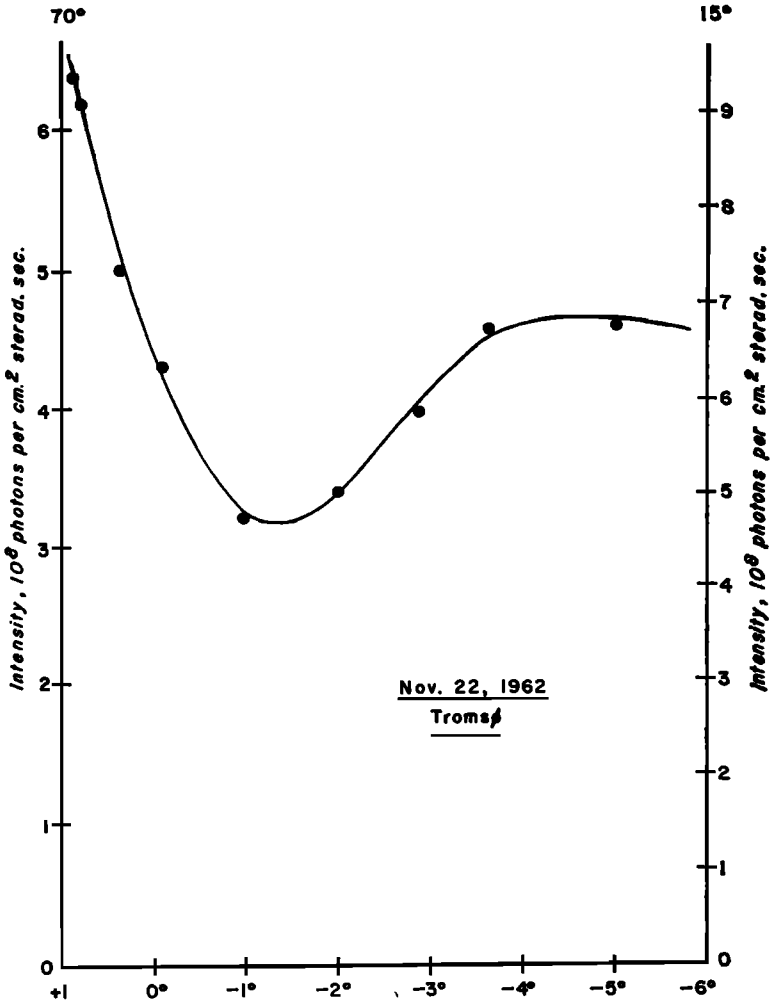


Fig. 3. Sodium twilight glow, November 22, 1962, Tromsø, Norway.

period. The correlation coefficient in this case is 0.7. Of course, some scatter is sure to occur because I_w also contributes to $I(0)$, is highly variable, and, as was just pointed out, is uncorrelated with I_{Na}. These results, which hold equally well for all data from 1960 through 1963, show that a change in I_{Na} occurs because of a change at the center of the line, not because of a variation in the wings.

Extensive data were also obtained for a magnetic field value of 2000 oersteds, about 0.025 A from the line center. At this field setting the σ Zeeman components will still overlap part of the upper atmosphere emission line but certainly do not suffer from interference by any atmospheric absorption lines. The white-light contribution at 2000 oersteds is subtracted from $I(2000)$, using $I(4000)$ and the ratio of intensities at 2000 and 4000 oersteds in the solar line to derive $I_w(2000)$ and thence the sodium emission contribution $I_{Na}(2000)$. It is always found that $I_{Na}(2000)$ is about 0.5 $I_{Na}(0)$ and strongly correlated (Figure 6).

Alternatively, if the sky light intensities at 2000 oersteds are used instead of those at 4000 oersteds to derive the white-light component at the center of the line the resulting sodium intensities $I_{Na}^*(0)$ are directly proportional to those obtained when $I(4000)$ is used to yield the white-light correction (Figure 7). Of course,

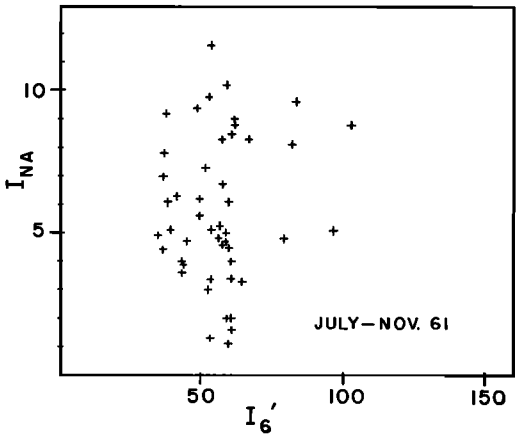


Fig. 4. Sodium dayglow signal plotted against total photometer response at 4000 oersteds July–November 1961, Haute Provence.

$I_{Na}^*(0)$ turns out to be smaller than $I_{Na}(0)$ because $I(2000)$ contains an appreciable contribution from sodium emission. These tests show that what is being observed is a narrow emission feature at the center of the D lines and that I_{Na} cannot be an artifact of an absorption line affecting the high field intensity.

This is also graphically demonstrated whenever the spectral region studied is scanned in several steps. Three examples are presented in Figures 8, 9, and 10 for August 16 and September 22, 1961, and December 1, 1960. The magnetic field was increased and decreased in steps for a large number of solar elevation angles. In these figures it is apparent that the phenomenon observed is a narrow emission feature. A pronounced increase in intensity is present near the line center, not a mere flattening of the Fraunhofer-line profile except at the very highest sun angles in autumn and winter. In midsummer when the dayglow is strongest the maximum persists even when the Rayleigh-scattered light has become very intense. Even if the white-light signal at zero field is presumed to be given by the minimum intensity observed in each scan, which usually occurs near 2000 oersteds, there remains a very strong dayglow residue compared with the twilight intensity. It will be shown that even this minimum dayglow intensity is considerably larger than expected.

Experiments designed to determine more precisely the shape and width of the emission line are still in progress. It cannot yet be said with complete confidence that there is not an underlying continuum which would reduce somewhat the contribution of the narrow emission line, nor is it possible to assert that the sodium line is narrow enough to exclude the possibility of a contribution to the emission from excitation processes other than resonance scattering.

On July 20 and 21, 1963, a new version of the Zeeman photometer was carried in an aircraft to 13 km during experiments relating to the

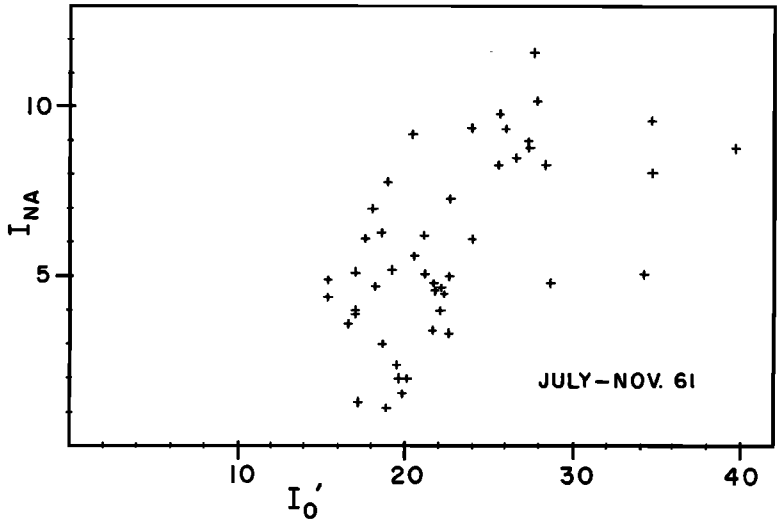


Fig. 5. Sodium dayglow signal plotted against photometer response at zero field, July–November 1961.

total solar eclipse. These experiments will be discussed in detail in a subsequent paper. It is relevant to this discussion, however, to remark that I_{Na} observed at a level above 90% of the atmospheric water vapor was as large as it was on the ground even though I_w was very appreciably reduced. (Of course, this was not true during the eclipse itself.)

Furthermore, on the same occasion simplified versions of the photometer were prepared to be flown in Aerobee 110 sounding rockets launched from Fort Churchill. The flight photometers consisted of two parallel optical systems which looked through holes in the rocket skin just below the ogival section of the nose cone. One system contained a heated sodium cell on which sky light was focused. The light scattered from the cell was gathered by a photomultiplier. The other system contained a similar cell without sodium. This system was designed to monitor the stray light and was calibrated against the (cold) cell in the other channel on the ground. No magnetic scanning was incorporated. However, the photometer was used on the ground to observe the sky signal and compared with the Zeeman system. Thus it was known what fraction of the output of the sodium channel (less stray light) should be I_{Na} and what should be I_w.

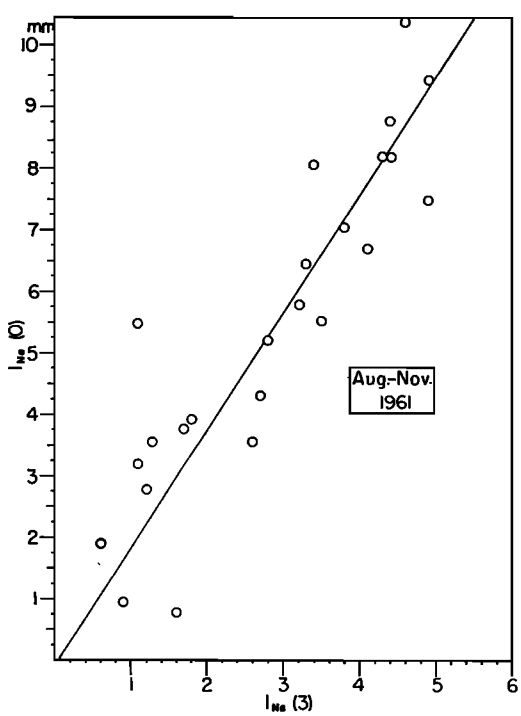


Fig. 6. Sodium dayglow signal at zero field plotted against sodium dayglow signal at 2000 oersteds.

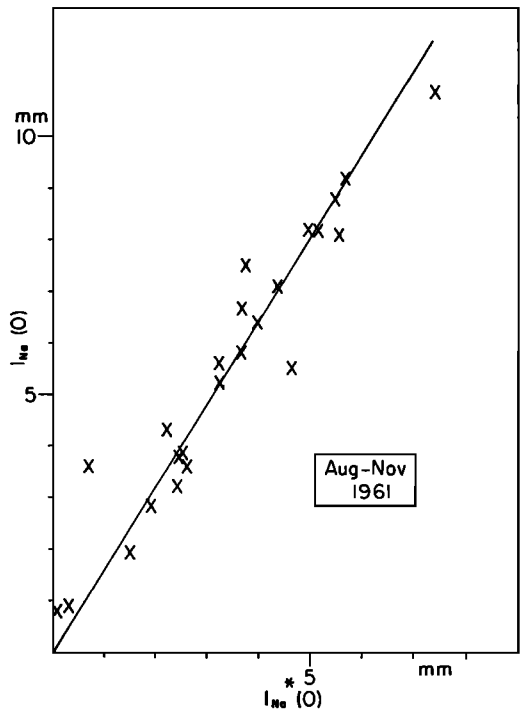


Fig. 7. Sodium dayglow signal at zero field obtained by using sky light signal at 4000 oersteds to determine the white-light signal at zero field compared with sodium dayglow signal at zero field obtained by using sky light signal at 2000 oersteds to determine the white-light component. Sky light at 2000 oersteds certainly has no water vapor contamination, but the evidence here is that it does contain a sodium emission component.

Unfortunately, rocket failure prevented the photometer from reaching peak altitude, and telemetry was lost at about 34 km. The photometer did obtain data up to that altitude (Figure 11). Once each roll cycle it looked into the sky toward the west at a zenith angle of 70°. At low altitude the telemetered signal of 1.35 volts above stray light should have consisted of 0.27 volt sodium emission and 1.08 volts white light according to the Zeeman photometer decomposition. The photometer reading decreased with altitude to a plateau of 0.28 volt, which set in at about 23 km and persisted until the last reading was telemetered at 33.5 km. The white-

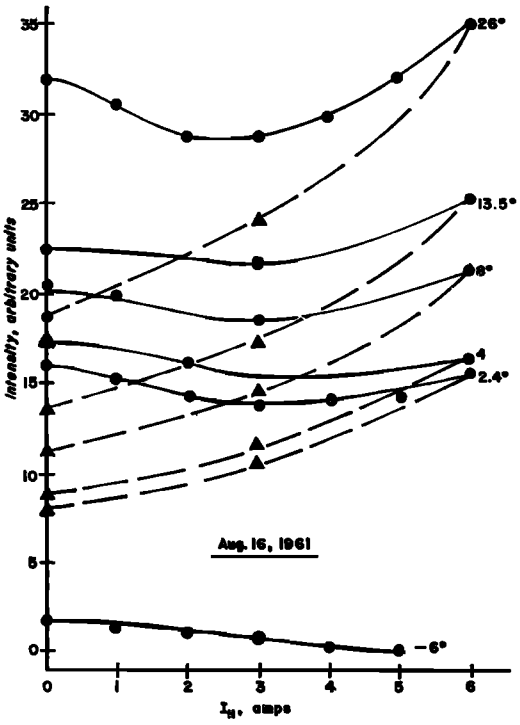


Fig. 8. Magnetic scans of Zeeman photometer from 0 to 4000 oersteds for various angles of solar elevation, August 16, 1961. Fraunhofer-line components in sky light fitted at 4000 oersteds are dashed lines.

light signal above 0.28 volt decreased exponentially with a decrement corresponding to the scale height of the troposphere. Between 23 and 33.5 km the photometer saw a steady signal from above which corresponded exactly to the presumed sodium emission as deduced at ground level from an application of the standard dayglow observational technique. The conclusion is reached that a high degree of reliability has been demonstrated for the validity of this technique.

Other indications that I_{Na} is indeed closely related to the sodium in the upper atmosphere will be discussed more fully in their proper place. They include the correlations between I_{Na} in the day and the twilight intensity for the same day and the anticorrelation between the seasonal variation of the dayglow intensity and the altitude of the twilight layer.

Results. The twilight 'plateau' intensities observed 15° above the horizon from 1960 through 1963 are plotted in Figures 12*a*, *b*, and *c*. The units on the left of the figures are arbitrary. Conversion of these to absolute intensities will be discussed farther on. Although there does appear to be structure superimposed on the general annual variation, the scatter of points is too large to permit a very confident evaluation of it. All the twilight data from 1954 through 1963 obtained at Haute Provence have been averaged for semimonthly intervals. The results for morning and evening data averaged separately are plotted in Figure 13. Each average represents some fifty data points. There is a sharp rise in late October, with a maximum about November 10 in morning twilight, followed by a slow decline through February, with a weak secondary maximum in March. This maximum is obviously not a consistent one from year to year, as the 1960–1963 data will readily show. In 1962 it was certainly not present, and the intensity more or less smoothly decayed after mid-January to a minimum in April. In 1962 there was a maximum in early February rather than in March.

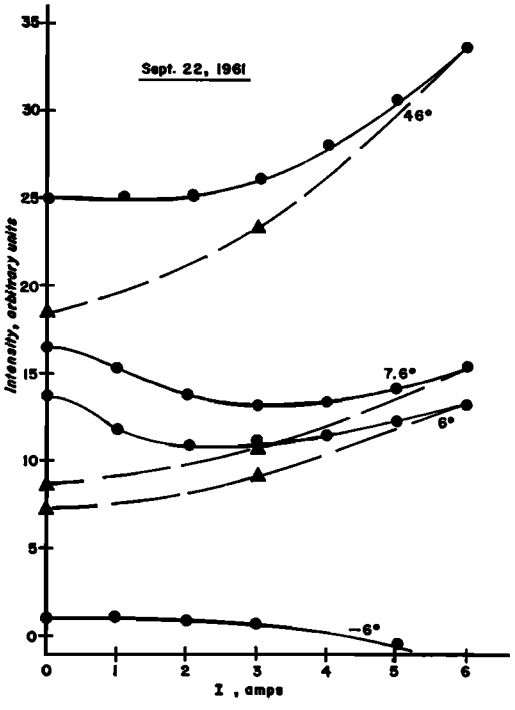


Fig. 9. Magnetic scans of Zeeman photometer from 0 to 4000 oersteds for various angles of solar elevation, September 22, 1961. Fraunhofer-line components in sky light fitted at 4000 oersteds are dashed lines.

On the other hand, a secondary maximum in late August and early September seems to be quite real and recurs every year. In 1963 it was particularly spectacular. The evening twilight intensities are consistently weaker than those in the morning. The late summer maximum is weaker in the evening; it occurs earlier, and the November peak is definitely absent.

Dayglow intensities observed in the direction of the pole, 43° above the horizon for solar elevation angles of 30°, are plotted also in Figures 12. The units to the left are the same as twilight units without any correction for the different zenith angles of observation. The data for November, December, and January are for 20° solar elevation angle. Semimonthly averages are plotted in Figure 14. There is a seasonal variation with a maximum near the summer solstice. The dayglow then is about twice as intense as it is at the winter solstice. Two other features may be statistically significant: secondary maximums near November 20 and in late February or early March. Except for the detailed structural features the annual pattern of the dayglow is just inverse to that of the twilight glow. The slow recovery of twilight intensity after the late June minimum is reflected in slow decline in the dayglow. Similarly the dayglow begins to recover just after the beginning of January at the time the twilight intensity begins to slide down from its maximum. The sharp increase in dayglow begins in early April, when the twilight glow on the average is experiencing its period of steepest decline.

If the major part of the dayglow intensity is produced by resonance scattering, the radically different seasonal variations must mean that there is considerably more free sodium in the upper atmosphere during daytime in midsummer than there is in twilight. It also must mean that at least twice as much free sodium is present during the daytime in midsummer than in midwinter. In this case it is not possible, without resort to the results of a calculation based on radiative transport in the telluric sodium layer, to say even qualitatively from the twilight intensity variation what is the annual variation of twilight abundance. The twilight intensity is strongly controlled by the daytime abundance, since the sunlight has to pass through the daytime layer to reach the twilight layer. The theory of these effects was discussed in the

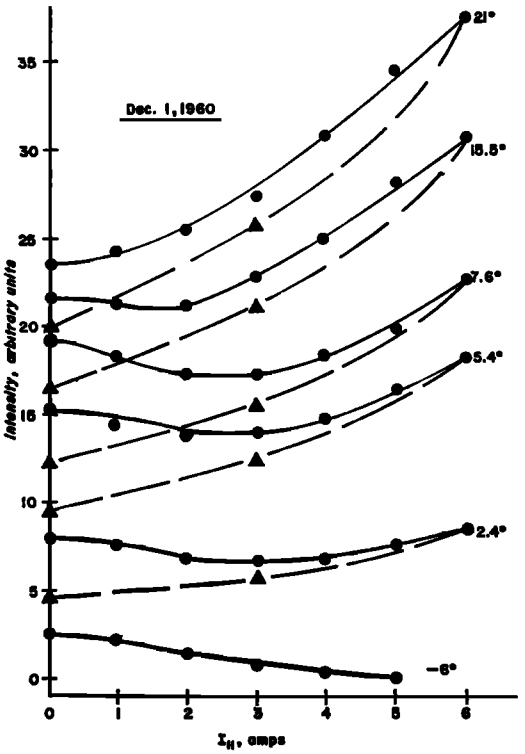


Fig. 10. Magnetic scans of Zeeman photometer from 0 to 4000 oersteds for various angles of solar elevation, December 1, 1960. Fraunhofer-line components in sky light fitted at 4000 oersteds are dashed lines.

first dayglow paper [*Blamont and Donahue*, 1961] and has been more carefully developed by *Sherby* [1961].

The theory of radiative transfer for resonance radiation in the earth's sodium layer and the excitation of the dayglow and twilight glow have been discussed thoroughly in the literature [*Donahue*, 1956; *Chamberlain et al.*, 1958; *Donahue and Stull*, 1959; *Brandt and Chamberlain*, 1958]. Sherby has evaluated the effect of an asymmetry between the daytime and nighttime sodium layer for ratios ranging from 1/1 to 6/1 between the day (+6°) and night (−6°) abundance. (Note in Figure 1 that the abundance change occurs within 5° of sunset.) Multiple scattering, absorption by ozone, scattering and refraction in the lower atmosphere, and reflection are all taken into account. In Figure 15 are presented his results for the twilight intensity as a function of twilight abundance for various day to night ratios. In Figure 16 are

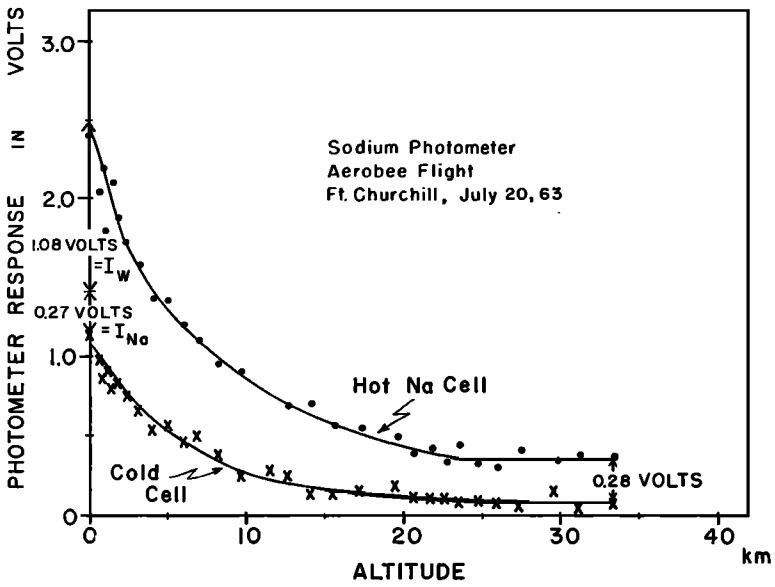


Fig. 11. Data from rocket sodium photometer flight, Fort Churchill, July 1963. Units are telemetered electrometer output signals. The ground-level decomposition into sodium emission I_{Na}, and white light I_w, is indicated along the ordinate scale.

the predicted D_2/D_1 ratios in twilight. For the dayglow intensities the results of previous calculations may be used [*Donahue,* 1956; *Brandt and Chamberlain,* 1958; *Blamont and Donahue,* 1961]. When the dayglow intensity observed in the direction of the pole for a solar elevation angle of 30° is plotted against the twilight intensity observed at 15° above the horizon for a solar elevation angle of −6° the result is uniquely a function of the day to twilight abundance ratio.

A family of curves for the various ratios ranging up to 6 to 1 is plotted in Figure 17.

If the photometer had an absolute calibration the abundance in the day could immediately be determined from theory [*Blamont and Donahue,* 1961, Figure 9] and the day to twilight ratio from Figure 17. Since it does not, it is necessary to use Figure 17 to obtain the calibration. If the ratio remains fixed over a sufficiently long interval, the photometer readings in day and twilight can be plotted against each other and then one of the curves of Figure 17 can be fitted to the data. In fact, there is a great deal of scatter. However, as can be seen from Figure 16, it is possible to fit the observations fairly well with theoretical curves, which indicate an average ratio ranging from about 2/1 in midwinter to about 7/1 in summer. There is a systematic tendency for the data belonging to low intensities in twilight during any limited period to associate themselves with dayglow intensities indicating higher ratios than those given by the high-intensity twilights. This may indicate that abnormally low twilight intensities are generally a consequence of a physical situation leading to high day-night ratios. In any event the fit to theory is not so spectacular as to be compelling. It is strongly suggestive, however, and perhaps as good as can be expected for such a highly erratic phenomenon as the airglow.

The photometer sensitivity resulting from this calibration is 4×10^8 photons/cm^2 sec ster, or 5 kR in the direction of observations per millimeter recorder deflection. On this basis the run of the twilight intensities observed at Haute Provence becomes almost the same as that obtained at Saskatoon by Hunten and his coworkers [*Chamberlain et al.,* 1958; *Scrimger and Hunten,* 1955; *Bullock and Hunten,* 1962].

In Figure 13 the twilight abundances at Christchurch, New Zealand (latitude 43°S), recently reported by *Hunten et al.* [1964], have also been plotted. The time axis has been shifted by 6 months. There is a clear correlation be-

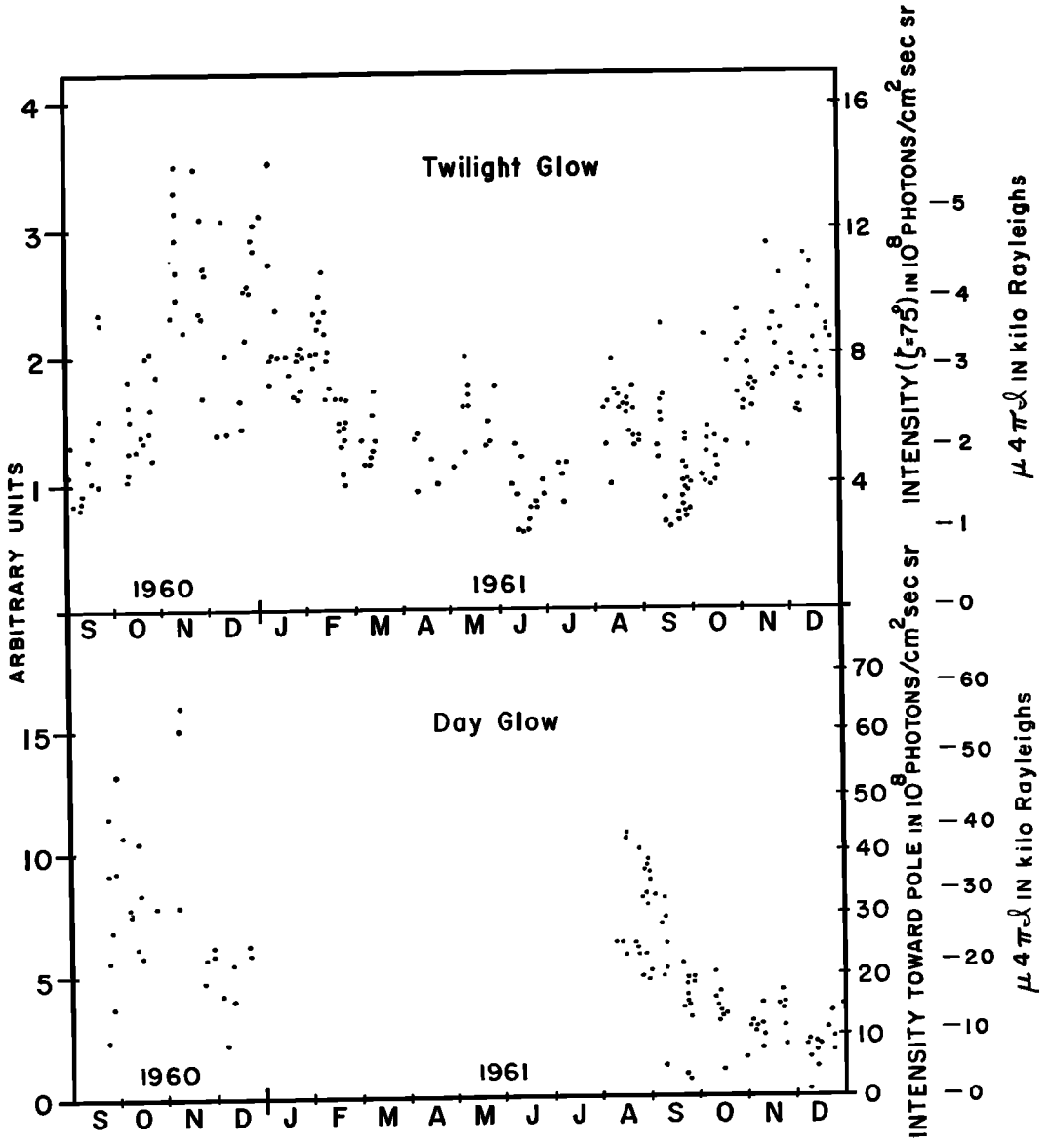


Fig. 12*a*. Sodium twilight-glow and dayglow intensities 1960, 1961, Haute Provence. Emission rate scale in kilorayleighs applies to zenith. Dayglow data are for a solar elevation angle of 30° except for November, December, and January, when they are for 20°.

tween the structure in both annual variations even in very fine details. The high intensities reported from New Zealand are probably the result of difficulties with the calibration, according to the authors. At Haute Provence the winter intensities are close to those reported from Saskatoon. The intensities previously reported from Tamanrasset [*Donahue and Blamont,* 1961] are also about the same in summer as at other northern hemisphere stations (1.2 kR) but in winter rise only to at most 1.8 kR compared with 3 kR farther north.

The dayglow gets up to some 28 kR (reduced to the zenith) on the average in midsummer, with a variation between 17.5 and 42 kR; in midwinter it decreases to about 13 kR with a

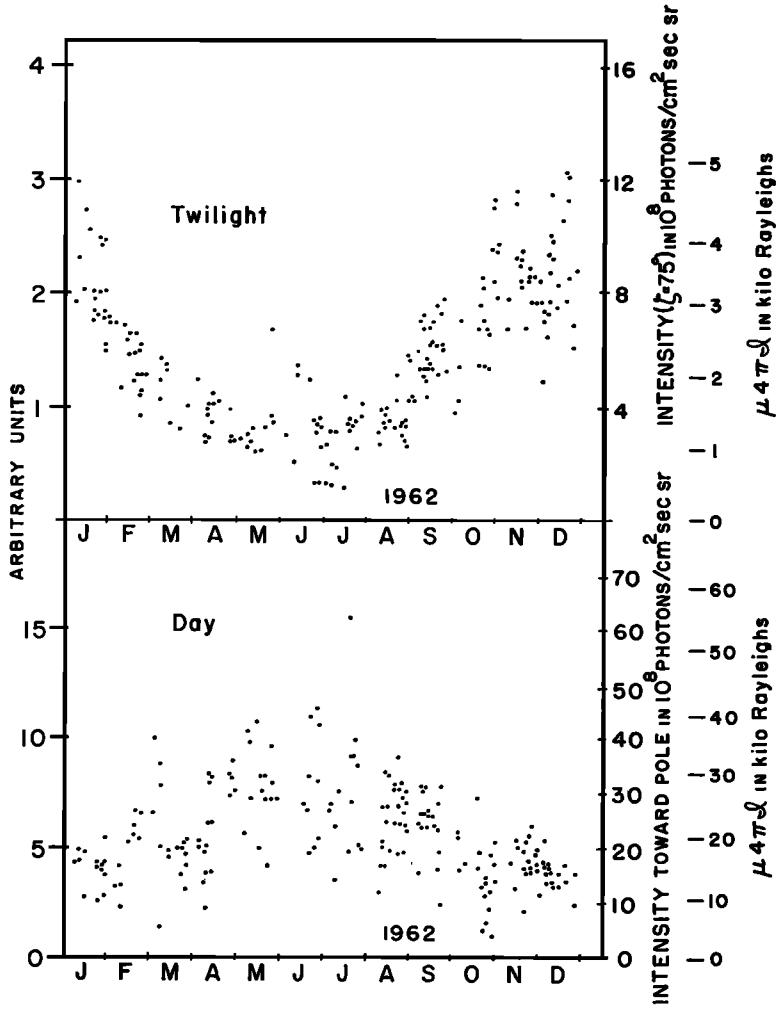


Fig. 12*b*. Sodium twilight-glow and dayglow intensities 1962, Haute Provence. Emission rate scale in kilorayleighs applies to zenith. Dayglow data are for a solar elevation angle of 30° except for November, December, and January, when they are for 20°.

variation from about 3.5 to 17.5 kR. From the dayglow average intensity (Figure 14) the average abundance of sodium has been computed throughout the year (Figure 14). It ranges from about 12 × 10^9 atoms/cm^3 in midwinter to 32 × 10^9 atoms/cm^3 in midsummer. The average day to twilight ratio is also computed from the daytime and twilight average intensities (Figures 13 and 14) and the theoretical curves in Figure 17. Then from the daytime abundance and the ratio the twilight abundance is obtained and plotted through the year (Figure 18). The variation is from 4.5 × 10^9 atoms/cm^3 near the summer solstice to about 7 × 10^9 atoms/cm^3 in December and January with a sharp peak to about 8.5 × 10^9 atoms/cm^3 in November. Much of the seasonal variation in twilight brightness is an effect of absorption in the daytime layer and is not reflected in the abundance. Through most of the year, from late February through October, it remains close to 5 × 10^9 atoms/cm^3.

It is interesting that even if it is assumed that the Fraunhofer lines are not reproduced in the white light and the profile observed between 4000 and 2000 oersteds is extrapolated smoothly to zero field the resulting minimum emission

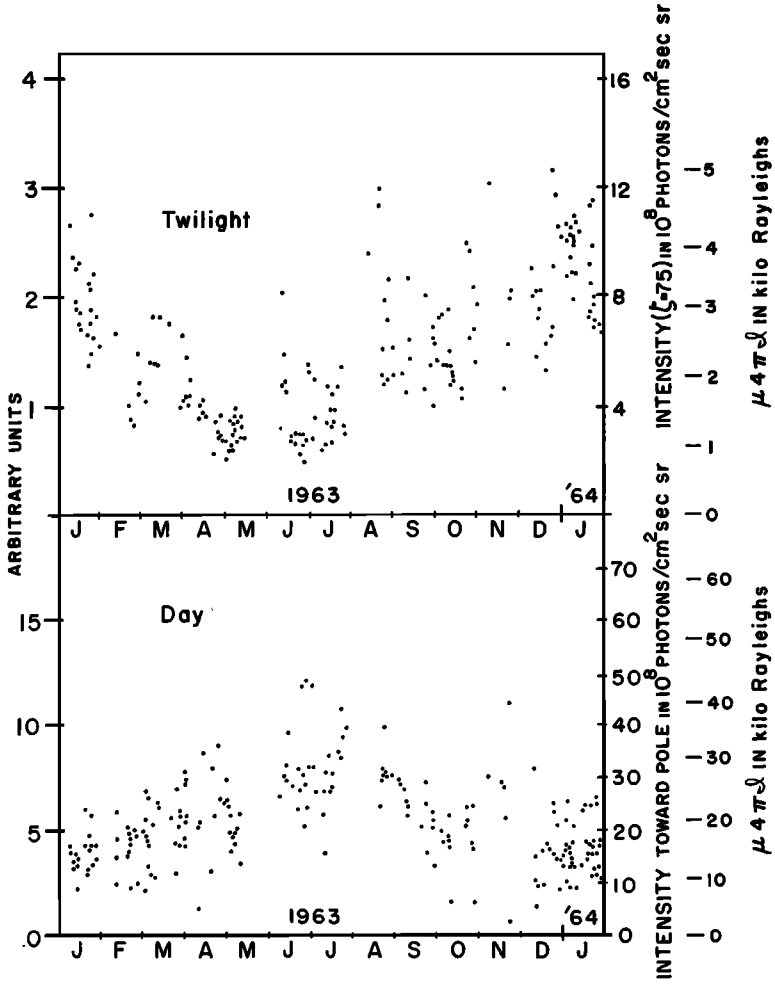


Fig. 12c. Sodium twilight-glow and dayglow intensities 1963, Haute Provence. Emission rate scale in kilorayleighs applies to zenith. Dayglow data are for a solar elevation angle of 30° except for November, December, and January, when they are for 20°.

feature is far too large in summer to be compatible with a 1 to 1 ratio of day to twilight abundance. For example, in the data for August 16, 1961 (Figure 8), the minimum value of the emission feature observed in the direction of the pole is 4.5 in arbitrary units while the twilight signal was 1.8 at 75° zenith angle in the same units. The theoretical curves of Figure 17 show that this ratio of intensities would be possible for a 1 to 1 abundance ratio only if the twilight intensity were to be 17.2 × 10^8 photons/cm^2 sec ster and the dayglow intensity 35 × 10^8 photons/cm^2 sec ster. This would mean 35 × 10^9 atoms/cm^2 in August. Actually the data for the minimum signal versus solar elevation would be fitted by the theoretical dayglow curve for 20 × 10^9 atoms/cm^2, which would call for 22 × 10^8 photons/cm^2 sec ster at 26° solar elevation. The photometer sensitivity would then be 5 × 10^8 photons/cm^2 sec ster per mm. This would mean that the twilight intensity was 9 × 10^8 photons/cm^2 sec ster, or 3.5 kR reduced to the zenith. A 2.2 to 1 day to twilight abundance ratio would then result, but the twilight intensity would be somewhat too high to be consistent with the results of other observers in general. (See, however, the results from New Zealand of *Hunten et al.* [1964].) In fact, the intensity was rather large in twilight on this particular day. In other midsummer data, using

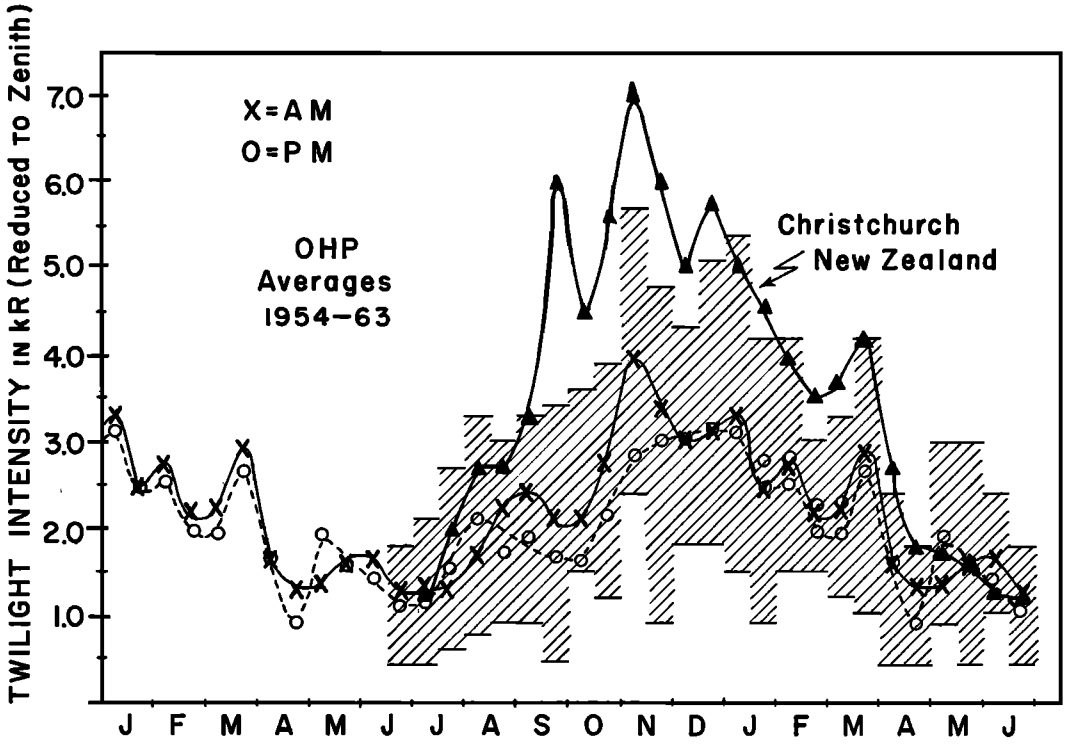


Fig. 13. Sodium twilight glow intensity at Haute Provence averaged from 1954 through 1963. Cross hatching indicates range of values observed. New Zealand data of *Hunten et al.* [1964] are plotted for comparison.

minimum emission intensities the day to twilight abundance ratio is found to run to about 3.5 to 1.

Tromsø. During 1962 and 1963 observations were carried out at Tromsø, Norway (latitude 70°N). The results are plotted in Figure 19. The dayglow that can be observed only from April to October shows no discernible seasonal variation. The general level is well below that found at Haute Provence. The average intensity reduced to the zenith is 16 kR compared with the 30-kR average in June at Haute Provence and 20 kR there in April and September. About half the observations fall below the lowest values observed at Haute Provence at corresponding times.

The twilight data from Norway are too sparse to warrant very detailed analysis. There appears to be a seasonal variation with the summer minimum a little below that in France (1 kR reduced to the zenith compared with about 1.2 kR). The winter maximum is about the same, but the suggestion is that it occurs in December rather than early November. The average ratio of daytime to twilight sodium abundance through the period of April to September is about 6 to 1.

Vertical distribution. By standard techniques [*Donahue and Blamont,* 1961; *Bullock and Hunten,* 1961; *Hunten,* 1962] the altitude of the twilight layer can be determined. Previously the altitudes determined at Haute Provence have been given for three directions of observation, in azimuth 0°, 90°, and 180° with the direction of the sun. Altitudes deduced from observations in the last two directions, particularly those away from the sun, showed extremely erratic behavior, frequently indicating a very high layer in August. It seems most probable that these large values are a consequence of scattering in the lower atmosphere. This is accentuated in horizon observations. In early twilight much of the sodium overhead is still strongly illuminated. Under conditions of excessive scattering at low altitudes light from this glowing layer can get into the photometer long after the light

coming from the sodium layer itself in the direction of observation has died out. Therefore, it has been decided to abandon altitude measurements for directions of observation other than those toward the sun. Only a thin region up to 20° above the horizon is then illuminated. The altitude data in this direction have been averaged for semimonthly intervals for the entire period 1954–1963. Morning and evening altitudes have been averaged separately (Figure 20), and the average of mornings and evenings lumped together has also been computed (Figure 21). The standard deviations are indicated by error bars. In general there is a seasonal variation with an amplitude of about 5 km. A rapid decrease in average altitude takes place between the middle of April and the end of June. After that there is a fairly rapid recovery followed by a slow increase from August to the end of March. *Bullock and Hunten* [1961] have presented altitude data averaged over 3-month intervals. Their values when corrected [*Hunten*, 1962] coincide very closely with these except during the autumn months where they find their minimum of 85.5 km. Their layer is almost 4 km below the twilight layer at Haute Provence during this period. Although their range of altitudes was much larger, the general shape of the annual variation found by *Cronin and Noelcke* [1955] in 1954–1955 in Maryland was identical with that reported here. The latitude was also the same.

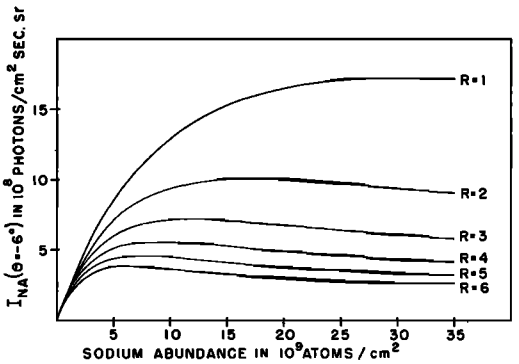


Fig. 15. Twilight glow intensity at 6° solar depression as a function of the twilight abundance for various ratios of day to twilight abundance.

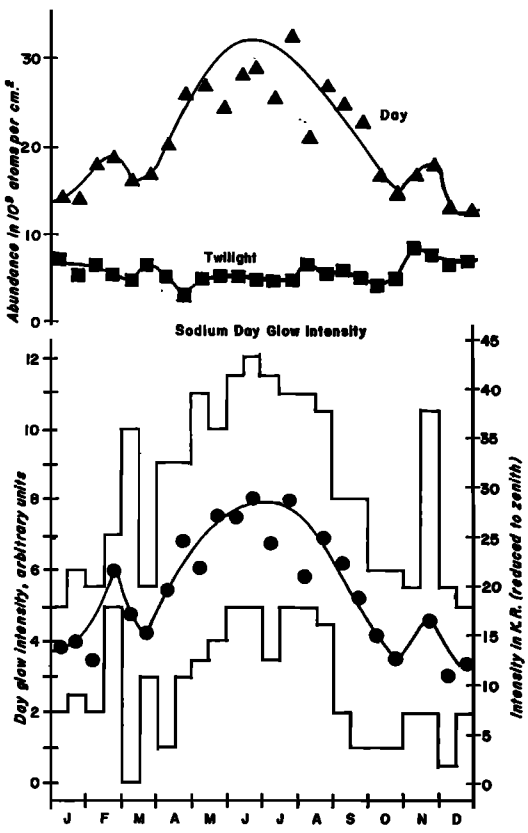


Fig. 14. Sodium dayglow intensity at Haute Provence for a solar elevation angle of 30° (20° November–February). Extreme readings are indicated as well as averages from August 1961 to January 1964. The daytime and twilight abundances are plotted at the top of the figure.

A very strong anticorrelation between the altitude of the twilight layer and the daytime abundance is apparent (Figures 14 and 21); it is shown in Figure 22. Conversely, the twilight abundance and the twilight altitude appear to show a direct correlation. As the altitude of the layer in twilight comes down in late spring the ratio of daytime to twilight sodium increases. Most of this increase occurs because of an increase in the total amount of free daytime sodium. During the period of minimum altitude the ratio is a maximum, and then as the layer slowly goes to greater heights in late summer and autumn the ratio and the daytime abundance decrease. This effect appears to be so definite that it can scarcely be accidental. The changes in altitude, abundance, and diurnal variation appear to have a strong interrelationship, which should be accounted for in any explanation of the seasonal variation of the so-

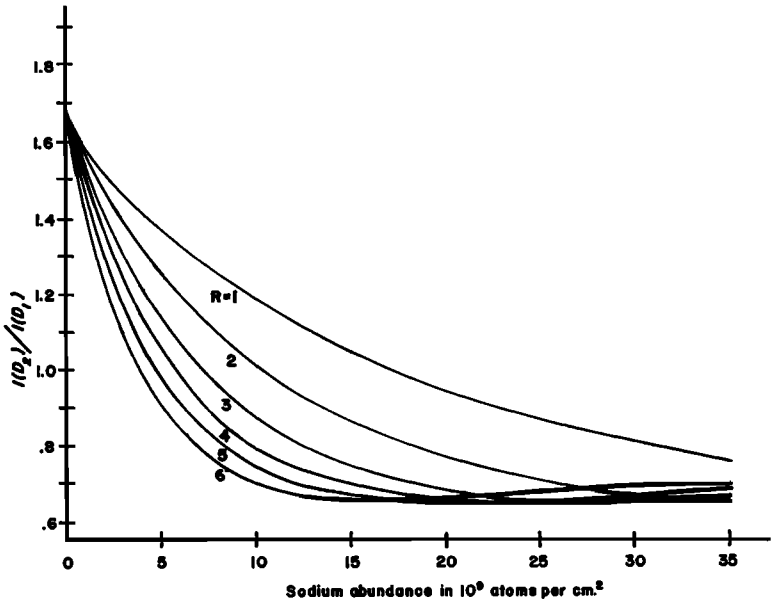


Fig. 16. The ratio of the fine structure component intensities in twilight as a function of twilight abundance for various ratios of day to twilight abundance.

dium layers and may be an important clue to the explanation.

The half-width of the layer in twilight is obtained from the shape of the intensity curve in late twilight by methods that have previously been outlined [*Blamont, Donahue, and Weber,* 1958; *Donahue and Blamont,* 1961]. The average widths by months, for morning and evening, are given in Table 1. These again are for the entire period 1954–1963. There appears to be a slight seasonal variation, the layer being about 1.5 km less wide in winter at its maximum altitude. There may also be a morning to evening variation with an increase by about 1 km in the evening. These are full widths at half maxi-

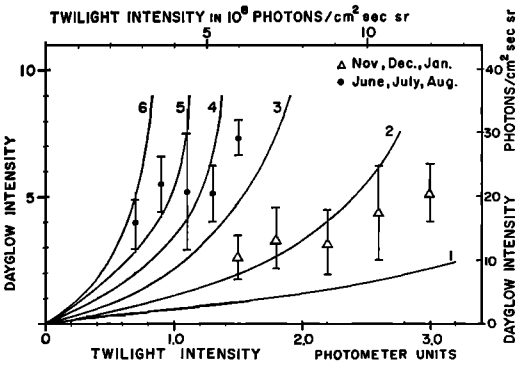


Fig. 17. The dayglow signal at 30° solar elevation toward the pole plotted against the twilight signal at −6° solar elevation for observation 15° above the horizon. Averaged data for June, July, and August 1961–1963 are plotted. Theoretical curves to which the scales on the top and to the right apply are labeled with numbers representing the day to twilight abundance ratio.

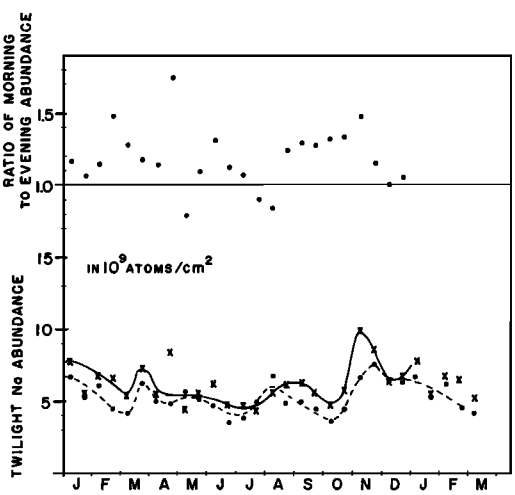


Fig. 18. Abundance of sodium in twilight at Haute Provence morning and evening. Ratio of morning to evening abundance is plotted at the top.

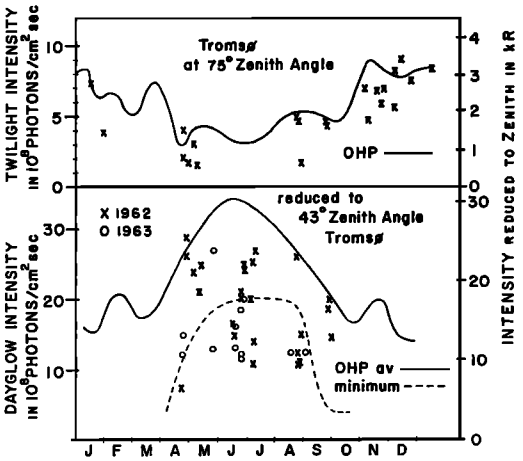


Fig. 19. Sodium twilight and dayglow intensities at Tromsø for 1962 and 1963 compared with the averages (solid lines) and minimum dayglow intensities at Haute Provence (dashed line).

mum and are narrower than those found at Saskatoon [*Bullock and Hunten*, 1961; *Sullivan and Hunten*, 1964].

Morning-evening effects. In the average twilight intensity data of Figure 13 there is present an obvious tendency for greater values to appear during morning twilight. These data need to be corrected for variation of the wavelength of the portion of the solar Fraunhofer lines which provide the excitation because of the rotation and orbital motion of the earth [*Donahue and Stull*, 1959]. When this correction has been applied the morning-evening intensity ratio varies from a little less than unity to as much as 1.4. The values are reproduced in Table 2. To obtain the abundance variation it is necessary to obtain the day-twilight abundance ratio separately for morning and evening. This was done, and the results are also presented in Table 2 and, graphically, in Figure 18. The abundance ratio appears to have maximums in late winter and early autumn, when it rises to values close to 1.4. In July and December it falls close to unity. The magnitude and seasonal variation for this effect is very close to that predicted long ago by Hunten for the effect of photoionization of Na and neutralization of Na^+.

Theory

The chemical reactions presumed to be of possible importance in the formation of the daytime and nighttime sodium layers are as follows:

Oxidation

$$Na + O_2 + M \rightarrow NaO_2 + M \qquad k_1 \qquad (1)$$

$$Na + O + M \rightarrow NaO + M \qquad k_2 \qquad (2)$$

$$Na + O_3 \rightarrow NaO + O_2 \qquad k_3 \qquad (3)$$

Reduction

$$NaO_2 + O \rightarrow NaO + O_2 \qquad k_4 \qquad (4)$$

$$NaO_2 + H \rightarrow NaH + O_2 \qquad k_5 \qquad (5)$$

followed by

$$NaO + O \rightarrow Na + O_2 \qquad k_6 \qquad (6)$$

$$NaH + O \rightarrow Na + OH \qquad k_7 \qquad (7)$$

Photodissociation

$$NaO_2 + h\nu \rightarrow Na + O_2 \qquad J_8 \qquad (8)$$

$$NaO + h\nu \rightarrow Na + O \qquad J_9 \qquad (9)$$

Ionization

$$Na + h\nu \rightarrow Na^+ + e \qquad J_{10} \qquad (10)$$

Recombination or neutralization

$$Na^+ + X^- \rightarrow Na + X \qquad \alpha \qquad (11)$$

$$Na + X + M \rightarrow NaX^+ + M \qquad k_{12} \qquad (12)$$

$$Na^+ + XY \rightarrow NaX^+ + Y \qquad k_{13} \qquad (13)$$

followed by

$$NaX^+ + e \rightarrow Na + X \qquad \alpha_2 \qquad (14)$$

The classical treatment of the sodium layer formation by *Chapman* [1939] made use of reactions 2, 3, and 6. This was developed further by *Hunten* [1954]. Since the discussion of the sodium problem by *Omholt* [1957], however, the three-body reactions, (1) and (2), have been taken to be the predominant oxidation reactions. The accepted mode of formation of the sodium 'layer' has invoked a higher rate for the two-body reduction reactions, (4) and (6), involving atomic oxygen, than the oxidizing three-body reactions, (1) and (2), at high altitudes down to about 90 km. Here the increasing ratio of O_2 to O finally causes the recombination to NaO_2 by (1) to prevail, and the sodium goes over predominantly to the oxidized form. Of course, only the ratio of reaction rates and reactants is critical in such an analysis. However, the choice of (1) over (3), the ozone reaction, as the important oxidizing reaction at the base

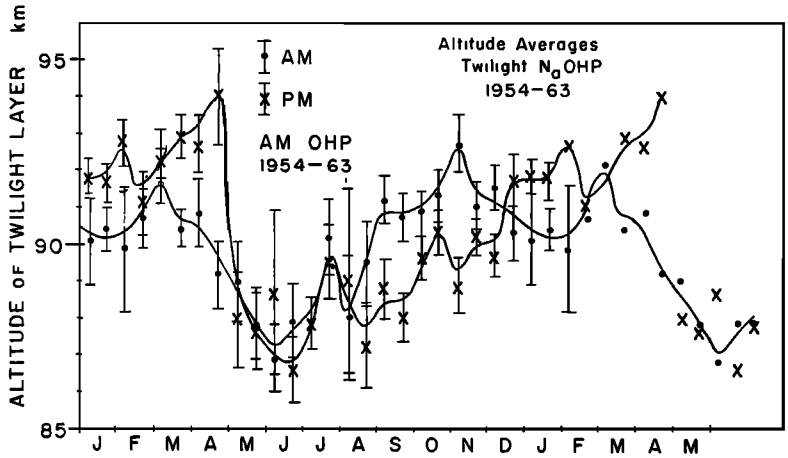


Fig. 20. Average altitude of twilight layer at Haute Provence 1954–1963, morning and evening. Standard deviations are indicated.

of the layer has been made as a consequence of a measurement of the rate of (1) by *Bawn and Evans* [1937] which gave for this reaction the extraordinarily high rate coefficient

$$k_1 = 5 \times 10^{-30} \text{ cm}^6/\text{sec at } 250^\circ \text{K}$$

according to *Bates* [1954]. This very large reaction rate forces acceptance of correspondingly high rate coefficients for the reduction reactions, (4) and (6), so as to permit the sodium to become free above 90 km [*Potter and Del Ducca*, 1961; *Vallance Jones*, 1961; *Ballif and Venkateswaran*, 1962]. It is notable that all these rate coefficients involving sodium need to be orders of magnitude higher than their counterparts involving hydrogen. Many of the hydrogen rates have actually been measured. For example,

$$H + O_2 + M \rightarrow HO_2 + M \quad (15)$$

has a rate coefficient of only 2×10^{-32} cm^6/sec at room temperature, according to *Clyne and Thrush* [1963]. Since these high rates for reactions 1, 4, and 6 tend to overwhelm all other processes that might be considered in the sodium

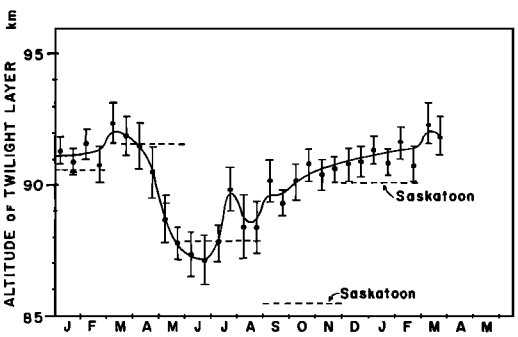


Fig. 21. Average altitude of twilight layer at Haute Provence 1954–1963, morning and evening data lumped. Results of Bullock and Hunten at Saskatoon are shown for comparison.

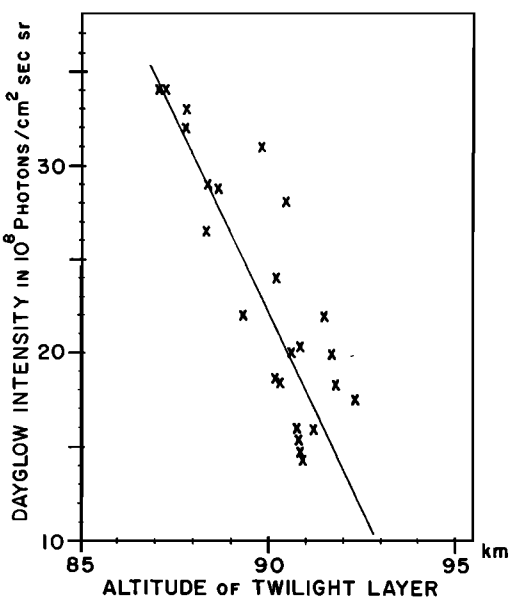


Fig. 22. Anticorrelation of dayglow intensity with altitude of twilight layer. Points are taken from semimonthly averages.

TABLE 1. Average Width of the Sodium Twilight Layer, 1954–1963

Month	Morning km	Evening km
January	7.5	8
February	9.0	10.5
March	9.0	9.8
April	8.5	11
May	8.8	9
June	8.9	10
July	10.2	12
August	9.3	11
September	10.1	10.2
October	9.7	10.1
November	7.2	8.4
December	7.3	8.8

problem, and indeed appear to be unreasonably great, it is important to examine carefully the procedure by which k_1 was deduced.

Measurement of k_1. The technique employed, called the diffusion flame method, has been used extensively in measurements of alkali atom reaction rates [*Polanyi*, 1962]. In the experiment under consideration, N_2, after passing over sodium metal at 300°C, emerged along with the sodium vapor through an orifice into a tube in which O_2 was flowing. The partial pressures of N_2 and O_2 were known from flow rates, and the pressure of Na was taken to be that of the saturated vapor in N_2 at the mouth of the orifice. Beyond this nozzle as it diffused through the N_2-O_2 mixture the sodium was oxidized by (1). Knowledge of the diffusion coefficient of the sodium and the value to which the density of sodium had fallen somewhere else in the flow tube would permit an evaluation of the reaction rate. This density was measured by illuminating the reaction region with the light from a sodium vapor electrodeless discharge. The visible radius of the D-line glow was measured. In a previous experiment the smallest density of sodium vapor that could be seen in reasonantly scattered light

TABLE 2. Ratio of Abundances between Morning and Evening Twilights

Ratio of brightness, corrected for Fraunhofer-Doppler effect, is in the second column. Brightness is in units of 10^8 photons/cm^2 sec ster at 75° zenith angle. Abundance is in 10^9 atoms/cm^2.

Month	I_m/I_e	I_e	I_m	Day/Twilight Abundance Ratios e	Day/Twilight Abundance Ratios m	Abundance Day	Abundance Twilight e	Abundance Twilight m	Twilight Abundance Ratio m/e
Jan.	1.09	8.1	8.8	2.1	1.8	14.2	6.75	7.9	1.17
	1.05	6.2	6.6	2.7	2.5	14	5.2	5.6	1.07
Feb.	1.15	6.3	7.3	3	2.6	18	6	6.9	1.15
	1.24	4.8	6.0	4.1	2.8	18.6	4.5	6.7	1.49
Mar.	1.25	4.8	6.0	3.9	3.0	16	4.1	5.4	1.29
	1.18	6.8	7.9	2.7	2.3	16.8	6.2	7.3	1.18
April	1.12	5.1	5.7	4	3.5	20	5	5.7	1.14
	1.68	4	6.8	5.4	3.1	26	4.8	8.4	1.75
May	0.77	4.7	3.6	4.7	6.0	26.8	5.7	4.5	0.79
	1.10	3.9	4.3	5.3	5.9	30	5.1	5.6	1.10
June	1.23	3.5	4.3	6.8	5.2	32	4.7	6.15	1.30
	1.30	2.6	3.4	8	6.7	32	4	4.8	1.31
July	1.26	2.8	3.6	7.5	6.5	31	4.1	4.8	1.08
	0.90	3.8	3.4	5.9	6.6	29	4.9	4.4	0.90
Aug.	0.85	5.4	4.6	4	4.8	27	6.75	5.6	0.83
	1.35	4.3	5.8	5	3.7	24.5	4.9	6.1	1.25
Sept.	1.27	4.8	6.0	4.5	3.5	22	4.9	6.3	1.29
	1.31	4.4	5.7	4.6	3.6	20	4.35	5.55	1.28
Oct.	1.27	4.1	5.3	4.7	3.6	17	3.6	4.7	1.31
	1.25	5.6	7.0	3.3	2.5	14.4	4.4	5.8	1.32
Nov.	1.39	7.4	10.3	2.5	1.7	16.8	6.7	9.9	1.48
	1.12	7.8	8.8	2.4	2.1	18	7.5	8.6	1.15
Dec.	1.01	7.8	7.8	2.1	2.1	13.2	6.3	6.3	1.00
	1 03	7.9	8.1	2	1.9	12.8	6.4	6.75	1.06

originating from the same source had been measured. This was taken to be the density of sodium at the edge of the glow in the experiment. Actually the two-body reaction rate Na + O_2 was found not to vary linearly with N_2 pressure between 2 and 25 torr, and this was taken to mean that the reaction went over to a two-body-like process at high pressure. From the low-pressure data the dependence of the reaction rate on N_2 pressure can be determined, although Bawn and Evans do not publish a value. The rate thus obtained from the data published appears to be closer to 2×10^{-30} cm^6/sec at 200°K than the value normally accepted. The temperature in the reaction zone was 260°C rather than 250°K. Much more serious, however, is the assumption that the density of sodium was known at the edge of the visible glow. Over the entire range of N_2 and O_2 pressures used, quenching of the resonance radiation and pressure broadening are very serious. It is certain that the actual Na density at the edge of the visible glow was seriously underestimated. Probably the data obtained have as much to do with the pressure dependence of quenching and line strength and width of the D lines as they do with the oxidation reaction rate. The most recent measurements of the cross section for the quenching of the ^2P state of sodium by N_2 [*Demtröder*, 1962] give a value of 4.3×10^{-25} cm^2, or

$$\langle \sigma_0 v \rangle = 2.6 \times 10^{-10} \quad \text{cm}^3/\text{sec}$$

at 250°C. At a nitrogen pressure of 1 torr the lifetime against quenching is 1.27×10^{-8} second compared with the natural lifetime against radiation of 1.59×10^{-8} second also measured by Demtröder. At 1 torr, therefore, the density of sodium was underestimated by a factor of 1.25. At 10 torrs it was underestimated by a factor of 3.5; at 25 torrs, by 4.1. An upper limit to the reaction rate measured by Bawn and Evans, using these correction factors, is 1.3×10^{-30} cm^6/sec at 250°C. The value could be as low as 8×10^{-31} at 250°C, or 5×10^{-31} at 200°K, if, as suggested by the authors, physiological factors associated with the presence of the bright central glow made the location of the edge so difficult as to introduce another factor-of-2 uncertainty in the sodium density. This method of measuring reaction rates appears to be of questionable reliability. Measurements based on some other method of determining the sodium-density variation are needed. Optical absorption measurements along a flow tube, for example, would escape the objections raised here. In view of these difficulties it seems that the hydrogen reaction rates corrected for collision frequency provide the best guide to choosing analogous sodium rates, or else the entire question should be considered open until some valid measurements become available.

The analogous (uncorrected) reaction rates for oxygen and hydrogen at 300°K [*Kaufmann*, 1964] are

$$k_1 = 2 \times 10^{-32} \quad \text{cm}^6/\text{sec}$$

$$k_2 = 2 \times 10^{-32} \quad \text{cm}^6/\text{sec (estimate)}$$

$$k_3 = 2.6 \pm 0.5 \times 10^{-11} \quad \text{cm}^3/\text{sec}$$

$$k_4 \geq 10^{-11} \quad \text{cm}^3/\text{sec}$$

$$k_5 \geq 3 \times 10^{-12} \quad \text{cm}^3/\text{sec}$$

$$k_6 = 5 \pm 2 \times 10^{-11} \quad \text{cm}^3/\text{sec}$$

$$k_7 = 2 \times 10^{-11} \exp[-9.2/RT] \quad \text{cm}^3/\text{sec}$$

Formation of the sodium layer. The assumption will be made for the time being that photodissociation rates are slow at all altitudes of interest in comparison with the chemical rates so as to determine whether it is possible to account for the diurnal and annual variations in sodium without invoking photodissociation. Furthermore, sodium and its compounds will be assumed to be present in amounts small compared with the principal atmospheric constituents. Thus sodium will behave only as a tracer. Ionization and recombination will be ignored. To avoid cumbersome notation the chemical symbol X is used to denote the density $n(\text{X})$, and the density product $n(\text{X})n(\text{Y})$ is written X·Y to distinguish it from the molecule XY. With these assumptions the steady-state abundances of the various forms of sodium become

$$\text{NaO}_2 = \frac{k_1\ \text{Na}\cdot\text{O}_2\cdot\text{M}}{k_4\ \text{O} + k_5\ \text{H}} \tag{16}$$

$$\text{NaO} = \frac{k_3\ \text{Na}\cdot\text{O}_3}{k_6\ \text{O}} + \frac{k_2\ \text{Na}\cdot\text{M}}{k_6} + \frac{k_4\ \text{NaO}_2}{k_6} \tag{17}$$

$$\text{NaH} = \frac{k_5\ \text{NaO}_2\cdot\text{H}}{k_7\ \text{O}} \tag{18}$$

Writing

$$N = \mathrm{Na} + \mathrm{NaO_2} + \mathrm{NaH} \qquad (19)$$

we obtain

$$\mathrm{Na} = \frac{N}{1 + \dfrac{k_1\,\mathrm{O_2}\cdot\mathrm{M}}{k_5\,\mathrm{O} + k_5\,\mathrm{H}}\left(1 + \dfrac{k_4}{k_6} + \dfrac{k_5\,\mathrm{H}}{k_7\,\mathrm{O}}\right) + \dfrac{k_3\,\mathrm{O_3}}{k_6\,\mathrm{O}} + \dfrac{k_2\,\mathrm{M}}{k_6}} \qquad (20)$$

The probable importance of the terms in the denominator may be assessed as follows:

$(k_2\,\mathrm{M})/k_6 \ll 1$ even at 75 km unless $k_2/k_6 > 10^{-15}$, which is highly unlikely. $(k_3\,\mathrm{O_3})/(k_6\,\mathrm{O}) \ll 1$ for $k_3/k_6 = 30$ unless $\mathrm{O_3}$ densities get within 10^{-2} times those of O. This is likely to happen only toward the bottom of the layer at night. For the present this term will be neglected, but its possible role will be discussed later. In general, the problem is to choose between the rates $k_3\,\mathrm{O_3}$ and $k_1\,\mathrm{O_2}\cdot\mathrm{M}$. If k_1/k_3 is really as small as 10^{-19} the $\mathrm{O_3}/\mathrm{O_2}$ ratio need only get above 10^{-5} to make the ozone oxidation important.

$(k_5\,\mathrm{H})/(k_7\,\mathrm{O}) < 1$ for $\mathrm{H/O} < 0.1$ unless k_5 is considerably larger than k_7. In view of the fact that around 90 km H is almost surely more than two orders of magnitude less dense than O this term also will be neglected. $(k_5\,\mathrm{H})/(k_4\,\mathrm{O}) < 1$ will also be assumed for the same reason.

Thus the usual equilibrium relationship is obtained

$$\mathrm{Na} = \frac{N}{1 + \dfrac{k_1\,\mathrm{O_2}\cdot\mathrm{M}}{k_4\,\mathrm{O}}\left(1 + \dfrac{k_4}{k_6}\right)} \qquad (21)$$

which may also be written

$$\mathrm{Na} = \frac{N}{1 + \dfrac{2k_1\,\mathrm{O_2}\cdot\mathrm{M}}{k_4\,\mathrm{O}}} \qquad (22)$$

since there is no a priori reason to assume that k_4 and k_6 are different.

Assuming that N follows the atmospheric altitude variation means that (22) will give an Na distribution in which $\mathrm{Na} = N$ at large altitudes where $k_4\,\mathrm{O} \gg k_1\,\mathrm{O_2}\cdot\mathrm{M}$. The free sodium density finally drops below N as the altitude decreases, and reaches a maximum ($\mathrm{Na} = N/2$) very close to the altitude at which

$$\frac{2k_1\,\mathrm{O_2}\cdot\mathrm{M}}{k_4\,\mathrm{O}} = 1 \qquad (23)$$

Since the annual variation of Z_T, the altitude of the peak of the twilight layer, is known, this permits the evaluation of the annual variation of $\mathrm{O_3/O}$ at Z_T. The model atmosphere chosen to give $\mathrm{N_2}$ and $\mathrm{O_2}$ as functions of altitude (Figures 23) agrees with the most recent mass spectrometric and ultraviolet determinations [*Shaefer and Nichols*, 1964; *Nier et al.*, 1964]. In Table 3, Z_T along with $(k_4\,\mathrm{O})/(k_1\,\mathrm{O_2}) = 2\mathrm{M}$ are listed. From these ratios provisional values for the atomic oxygen density, $\mathrm{O}_T(Z_T)$, required at the altitude of the twilight sodium layer may be computed using the chosen ratio k_1/k_4 (4×10^{-18} $\mathrm{cm^3}$). Of course, the ratio that seems to give the most reasonable oxygen densities has been selected. The values of $\mathrm{O}_T(Z_T)$ are also given in Table 3.

To explain the diurnal variation in the quantity of free sodium on the basis of this chemical model it is necessary now for a first try to postulate a diurnal variation in atomic oxygen between 75 and 90 km. The magnitude of this variation may be estimated month by month from the observed values of the day to twilight sodium ratios R. To achieve an increase in Na by a factor R on the basis of (22) it is necessary that $(k_4\,\mathrm{O})/(k_1\,\mathrm{O_2})$ change so that (23) will be satisfied at a point where M has increased to $R\mathrm{M}$ (or N has increased to RN). The observed R values are given in Table 3 and the altitude Z_D at which M has increased by a factor R compared with its value at Z_T. Then the daytime ratio

$$k_4\,\mathrm{O}/k_1\,\mathrm{O_2} = 2\mathrm{RM}(Z_T) = 2\mathrm{M}(Z_D)$$

is computed, and finally $\mathrm{O}(Z_D)$. The diurnal variation in Na would entail a shift downward in the layer during daytime by 8 km from 87 to 79 km in summer, and by only 3 km from 91 to 88 km in the winter, on the basis of such a model.

Qualitatively what is needed to bring about the required changes in free sodium is for the atomic oxygen peak in daytime to move downward in altitude from about 95 km in December to perhaps 90 km in June with an attendant

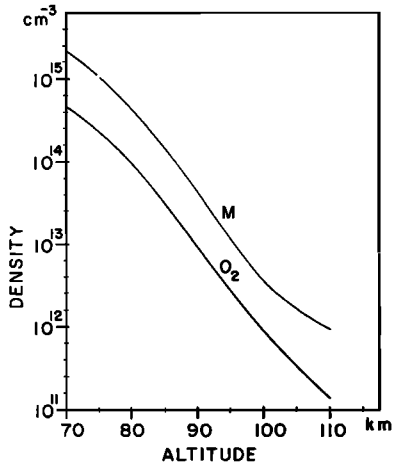


Fig. 23*a*. Distribution of total atmospheric constituents and O_3 with altitude.

increase in density at the peak from about 5×10^{11} atoms/cm^3 to perhaps 1.5×10^{12} atoms/cm^3. Below the peak the oxygen must be assumed to decrease rather slowly with decreasing altitude in summer during the daytime and rapidly in winter, so that in June the density is 6×10^{11} per cm^3 at 79 km whereas in December it is 10^{10} per cm^3 at 88 km. This requirement is illustrated in Figure 24. The values of k_1/k_4 were chosen so that the summertime oxygen densities would join smoothly at 100 km to the recent mass spectrometric determinations. To cause the larger diurnal variations in summer, what is needed is a much more rapid variation of oxygen within an hour or so of sunset and sunrise in the low-altitude part of the oxygen distribution than occurs below the peak in winter. The time constant must, in fact, decrease with altitude so as to bring about the increasing amplitude of $Z_D - Z_T$ with decreasing Z_D. Qualitatively, this, of course, is expected, since the oxygen disappears at sunset, presumably because of ozone formation by recombination with O_2

$$O + O_2 + M \rightarrow O_3 + M \qquad k_{24} \qquad (24)$$

and reappears at sunrise because of photodissociation of the ozone. This requires also that ozone not be seriously depleted in the 80- to 88-km region during the night by the H, O_3 reaction. It is also necessary that the twilight layer occur with its peak in a region where the oxygen density does not change much after 1 hour; otherwise, a morning-evening effect in twilight opposite to that observed would occur. Of course, compensatory effects of recombining Na^+ and decreasing production of Na by (6) are possible.

Diurnal variation of O and O_3. The problem is to decide whether such a diurnal and seasonal atomic oxygen variation is possible and reasonable. The photochemical problem of oxygen in this region has been attacked most recently by *Wallace* [1962] and by *Ballif and Venkateswaran* [1962, 1963]. However, since their work there

TABLE 3. Atomic Oxygen Density Required at Altitude of Twilight Layer and at Deduced Altitude of Daytime Layer to Produce Diurnal Variation in Sodium from Chemistry Alone

Z_T is the altitude of the twilight layer; $O_T(Z_T)$, the density of O needed at that altitude in twilight; R, the day to twilight abundance ratio; Z_D, the deduced altitude of the daytime layer; and $O_D(Z_D)$, the atomic oxygen density needed there. k_1/k_4 is taken to be 4×10^{-18} cm^3.

Month	Z_T, km	$k_4 O/k_1 O_2 = 2M$	$O_T(Z_T)$	R	Z_D, km	$k_4 O/k_1 O_2 = 2RMT$	$O_D(Z_D)$
Jan.	91.2	7×10^{13}	1.75×10^9	2.3	88	16×10^{13}	10×10^9
Feb.	91.2	7	1.75×10^9	3.2	86.5	22	22
Mar.	92.0	6.2	1.4	2.8	87.5	17.5	14
Apr.	91.5	6.7	1.7	3.7	86	25	28
	90.5	9.4	3.4	6	83	55	120
May	88.1	15.4	9.2	5.4	80.2	83	340
June	87.1	19	16	7	79	130	620
July	89	12.4	6.2	6.5	80.2	80	340
Aug.	88.6	14	8.4	4.3	82	60	160
Sept.	89.7	10.8	4.7	3.8	83.7	40	80
Oct.	90.4	9.4	3.1	3.3	85	30	45
Nov.	90.7	8.6	2.8	2.2	87	20	20
Dec.	91.0	8	2.5	1.9	88	15	10

has been a new and careful determination of the rate of (24) by *Kaufmann and Kelso* [1964]. The three-body coefficient measured at 300°K is 7.5×10^{-34} cm^6/sec. The temperature dependence of the reaction is in considerable doubt. *Benson and Axworthy* [1957] give −0.6 kcal as the activation energy. This rises to −1 kcal if the correct dissociation energy is used. Thus, the rate might be as high as 2.3×10^{-33} cm^6/sec at 180°K. A somewhat lower value would be obtained if a T^m dependence is assumed. The rate is probable between 1.5 and 2×10^{-33} at 180°K (Kaufmann, private communication, 1964). It will be taken here conservatively as 1.5×10^{-33} cm^6/sec. This is about 4 times higher than the value employed by *Ballif and Venkateswaran* [1962] and 17 times larger than the one used by Wallace. Thus the region in which rapid variation of O densities occurs at sunrise and sunset is shifted considerably higher than it was found to be in those treatments. The shift amounts to some 8 km for the calculations of Wallace, as a comparison of the curves of Figure 23 and those of his Figure 2 will show. The results plotted in Figure 23 were obtained by repeating his calculations with the new rate coefficient for equation 24; they show the daytime equilibrium distributions of O in summer and winter and those that would prevail 1 hour after sunset. The necessary daytime density of 1.2×10^{11} oxygen atoms/cm^3 in early May at 83 km is attainable, as is the daytime abundance of 10^{10} atoms/cm^2 at 88 km in winter. The resulting distribution of sodium in the daytime from equation 22 is sketched in Figure 25 (curve *a*). However, the change in O density is very small at these altitudes as the sun sets. In fact, they lie near the boundary of the region of rapid variability. The result is that a portion of the base of the sodium layer is removed but the peak remains at about 83 km (Figure 25, curve *c*).

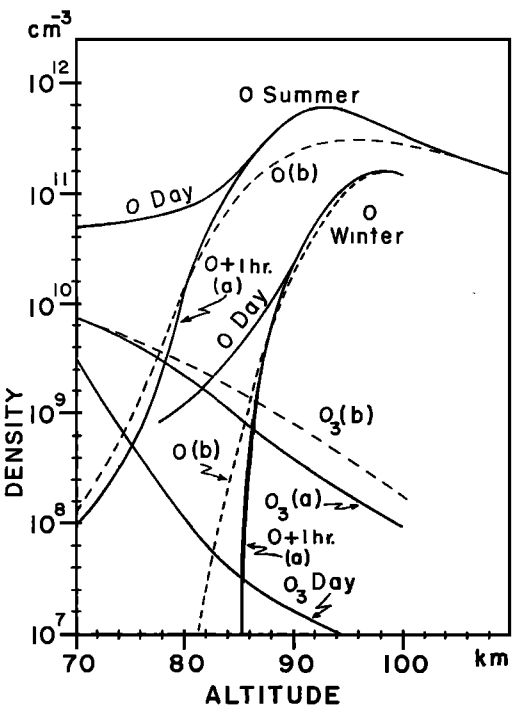


Fig. 23*b*. Distribution of O and O_3 with altitude. Solid curves for O_3 and O are calculated from photochemistry alone. Dashed curves show the effect of turbulent diffusion.

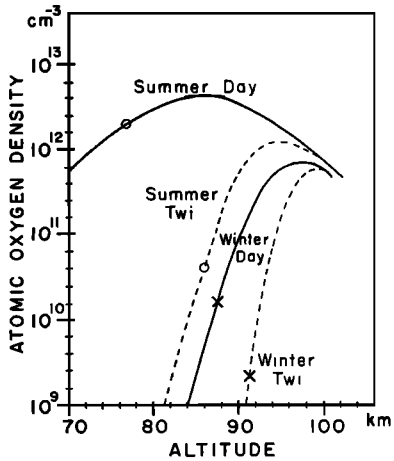


Fig. 24. Atomic oxygen densities required to produce seasonal and diurnal variation in free sodium on the basis of photochemistry alone.

There is, however, serious doubt whether such steep density gradients as those called for in the O and Na photochemical distributions can be maintained against turbulent diffusion. It has been established from observation of meteor and sodium vapor trails that strong turbulence always seems to exist between 60 and 100 km. Analysis of sodium vapor trails [*Blamont*, 1961] indicates that eddy diffusion below 100 km proceeds after a time of the order of 1000 seconds in such a way that the mean square distance traveled by a parcel of gas in time t is

$$\overline{r^2} = 4vLt \qquad (25)$$

with v of the order of 2 m/sec and L of the

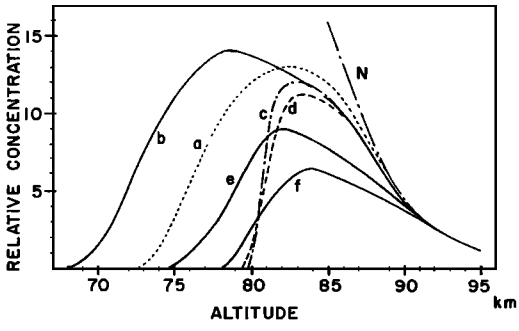


Fig. 25. Distribution of all sodium compounds in altitude (N) and distribution of atomic sodium. (a) Summer daytime, photochemistry alone; (b) summer daytime with turbulent diffusion accounted for; (c) summer twilight, photochemistry alone; (d) summer twilight, oxygen diffusion included; (e) summer twilight, oxygen and sodium diffusion included; (f) summer twilight, diffusion plus the ozone reaction included.

order of 1 km. This gives an effective coefficient for eddy diffusion of 2×10^7 cm^2/sec. Recently Kellogg (private communication, 1963) has given a somewhat different treatment to estimate the rate of large-scale vertical mixing in this region. His analysis will be summarized here for the sake of completeness. He applies the Taylor theory of diffusion by continuous movement [*Taylor*, 1920, 1935; *Brunt*, 1941] to compute the mean square distance traveled by a parcel of gas owing to its eddy motion.

$$\overline{r^2} = 2\overline{v'^2} \int^t \int^{t_1} R\xi \, d\xi \, dt_1 \qquad (26)$$

where R_ξ is the Lagrangian autocorrelation coefficient of the eddy velocity v'. Assuming that R_ξ remains unity for a while and then drops abruptly to zero when the eddy velocities are no longer correlated with their initial velocities, Kellogg obtains

$$\overline{r^2} = 2\overline{v'^2} \int^t t_1 \, dt = \overline{v'^2} t^2 \qquad (27)$$

at short times and

$$\overline{r^2} = 2\overline{v^2} It \qquad (28)$$

at long times where

$$\int_0^{t_1} R\xi \, d\xi \approx \int_0^{\infty} R\xi \, d\xi = I \qquad (29)$$

From observations in sodium trails [*Cote*, 1963; *Blamont and de Jager*, 1961; *Blamont*, 1963] it can be verified that these trails obey the short-time law and that $(\overline{v^2})^{1/2}$ is between 2 and 3 m/sec. The growth follows the short time law up to about 2000 seconds, when the sodium trails have dimensions of 1 or 2 km. After this, rapid mixing may continue by virtue of entrainment of the distribution in the Martyn-Hines internal gravity waves [*Martyn*, 1950; *Hines*, 1960, 1963]. As a conservative estimate after 1000 seconds Kellogg assumes the long time law

$$\overline{r^2} = 2(200)^2 1000^t = 2 \times 4 \times 10^7 t \text{ cm}^2 \qquad (30)$$

This gives a vertical eddy diffusion coefficient of 4×10^7 cm^2/sec at 100 km in harmony with the earlier estimates [*Blamont*, 1963]. Because the minimum allowable wavelength of a Martyn-Hines wave is reduced from 1 km to 0.1 km at 80 km the diffusion coefficient is reduced to about 2×10^7 cm^2/sec at that altitude.

Using these results it can be shown readily that an oxygen distribution such as that obtained (Figure 23) 1 hour after sunset from photochemical processes cannot be maintained. With such a distribution the diffusion loss at 91 km would be about 1.5×10^9 oxygen atoms/cm^3 sec compared with the chemical three-body recombination rate of only 3×10^4/cm^3 sec. At 86 km the oxygen density would be increasing because of flow down from the peak at a rate of 3×10^7/cm^3 sec compared with a photochemical rate of decay of 1.3×10^6/cm^3 sec.

Thus it would appear that, as rapid recombination of oxygen atoms commences below 88 km, eddy diffusion will quickly transport atoms down from higher altitudes into this chemical sink and that the distribution will be diffusion controlled in the region above 80 km. By the same token ozone molecules will be carried rapidly up to higher altitudes, where some of them will eventually be lost in collision with atoms of hydrogen and oxygen. This may remove the discrepancy regarding the altitude of the OH nightglow layer. Photochemical considerations [*Wallace*, 1962; *Ballif and Venkateswaran*, 1963], using too small a value of the recombination coefficient for reaction 24 and neglecting eddy diffusion, placed this layer between 70 and 75 km instead of between 83 and 90 km where observations [*Packer*, 1961] have placed it. *Tohmatsu and Nagata* [1963] have developed a model for the oxygen green line excitation

which is based on eddy diffusion transport of atomic oxygen. The 'diffusion coefficient required is about the same as the one used in this paper.

A very crude solution of the rate equations for O and O_3 including diffusion has been obtained which predicts the O and O_3 distributions after 1 hour (Figure 23). The diffusion was treated as though it were molecular. This is certainly not strictly justified but should give a rough approximation to what can be expected. Even so, the reduction in atomic oxygen above 85 km is still not great enough to move the peak in the sodium distribution to an altitude high enough or a density low enough to produce the desired diurnal variation (Figure 25, curve *d*).

Eddy diffusion effect on sodium distribution. However, this sodium distribution is also too sharply varying to be supported against eddy diffusion downward. The loss of sodium atoms by diffusion at 85 km occurs at a rate of about 1.1×10^{-3}/sodium atom/sec. The rate of chemical loss by process (1) is $5 \times 10^{27}\ k_1$/sodium atom/sec. So here the question of the value of k_1 rather than the ratio k_1/k_4 becomes crucial. If k_1 were as large as 5×10^{-30} cm^6/sec the rate of oxidation would be 25×10^{-3}/sodium atom/sec. Since NaO_2 and NaO will be transported into the 85-km region as rapidly as turbulence takes Na away the reconversion of these molecules to sodium will be faster than the sodium diffusion loss rate unless k_1 is 2×10^{-31} cm^6 or less. If the value of k_1 is as small as 2×10^{-32} cm^6/sec the diffusion loss will be overwhelming. The sodium distribution will decay very rapidly from the daytime equilibrium. Sodium atoms will be carried down into the region around 80 km, where they are rapidly oxidized. They will be replaced by NaO_2 and NaO molecules from below. The peak of the sodium distribution will be established where the loss of sodium by eddy diffusion and oxidation is balanced by the reduction of the NaO_2 flowing in. Although in a steady state the transport of sodium atoms downward is balanced by the reverse flow of the oxides the consequence must be a decrease in the number of free sodium atoms compared with the photochemical equilibrium at any given level near the photochemical maximum. At lower altitudes the reverse will be true, but the sodium cannot build up to high densities there because the transport carries the sodium atoms into a region in which the oxidation rate is much more rapid than that near the level of the maximum. This rate is the same as that at which the NaO_2 is reduced to Na.

To get a rough estimate of the scale of these effects a very crude analysis has been undertaken. A model has been considered in which the total density of sodium and its oxides is assumed constant with altitude. Diffusion has been treated as though it were molecular, so that the fractional densities of the various reactants become, in the steady state,

$$f_1 \equiv \mathrm{NaO} = \frac{D}{k_6\,\mathrm{O}}\frac{\partial^2 f_1}{\partial z^2} + \frac{k_4}{k_6} f_2 \tag{31}$$

$$f_2 \equiv \mathrm{NaO_2} = \frac{D}{k_4\,\mathrm{O}}\frac{\partial^2 f_2}{\partial z^2} + \frac{k_1\,\mathrm{O_2 \cdot M}}{k_4\,\mathrm{O}} f \tag{32}$$

$$f \equiv \mathrm{Na} = \frac{N + \dfrac{D}{k_4\,\mathrm{O}}\left(\dfrac{\partial^2 f}{\partial z^2} - \dfrac{\partial^2 f_2}{\partial z^2}\right)}{1 + \dfrac{2k_1\,\mathrm{O_2 \cdot M}}{k_4\,\mathrm{O}}} \tag{33}$$

if $k_4 = k_6$, with

$$\frac{\partial^2 f}{\partial z^2} + \frac{\partial^2 f_1}{\partial z^2} + \frac{\partial^2 f_2}{\partial z^2} = 0 \tag{34}$$

$$f + f_1 + f_2 = N = 1 \tag{35}$$

Use of the definitions

$$a = \frac{k_1\,\mathrm{O_2 \cdot M}}{k_4\,\mathrm{O}} \tag{36}$$

$$b = 1 + 2a \tag{37}$$

$$\omega^2 = D/(k_4\,\mathrm{O}) \tag{38}$$

gives the coupled set of differential equations

$$f = \frac{1}{b} + \frac{\omega^2}{b}\frac{\partial^2 f}{\partial z^2} - \frac{\omega^2}{b}\frac{\partial^2 f_2}{\partial z^2} \tag{39}$$

$$f_1 = \omega^2 \frac{\partial^2 f_1}{\partial z^2} + f_2 \tag{40}$$

$$f_2 = \omega^2 \frac{\partial^2 f_2}{\partial z^2} + af \tag{41}$$

The term $1/b$ in (39) is the photochemical distribution. The second term on the right of (39) represents the effect of sodium atom flow, and the third term represents the effect of flow of NaO_2. The magnitude of the flow correction depends on ω^2, the ratio of the diffusion coefficient to the reduction rate of NaO_2 and NaO and b, essentially the ratio of the reduction and oxida-

TABLE 4. Values of Parameters in Equations 39–41 Governing Distribution of Sodium and Its Oxides under Combined Influence of Chemistry and Diffusion
$k_1 = 2 \times 10^{-32}$ cm^6/sec; $k_4 = 5 \times 10^{-15}$ cm^3/sec.

Altitude, km	b^{-1}	$k_1\,O_2 \cdot M$, sec^{-1}	$k_4\,O$, sec^{-1}	$\omega^2 = D/k_4\,O$, km^{-2}	ω^2/b, km
			Daytime		
75	0.03	50×10^{-4}	2.75×10^{-4}	18	0.5
80	0.27	8.4	3.75	8	2.2
85	0.76	1.14	8	5	3.8
90	0.99	0.1	25	1.1	1.1
			Night		
75	5×10^{-4}	50×10^{-4}	0.05	600	0.3
80	3×10^{-2}	8.4	0.5	60	2.0
85	0.67	1.14	5.0	8	5.0
90	0.98	0.1	11	2.5	2.5

tion rates. The magnitudes of these coefficients are indicated in Table 4 for the oxygen distribution prevailing during the day and 1 hour after sunset during May. k_1 is taken as 2×10^{-32} cm^6/sec and k_4 as 5×10^{-15} cm^3/sec.

The striking feature in this table is the size of ω^2, which governs the NaO_2 to NaO ratio, and ω^2/b, which determines the effect of flow in altering the photochemical distribution. The fact that they are of the order of 1 to 10/km^2 means that an important redistribution will certainly occur since this is also the scale on which the important variation in $1/b$ takes place.

The solution of the differential equations, obtained numerically, is represented in Figures 26 and 27, where $1/b$ is also shown for comparison. The effect of diffusion on the daytime distribution of sodium is not great, because the slowly varying atomic oxygen distribution already causes $1/b$ to vary slowly and the large values of k_4O cause ω^2 and ω^2/b to be relatively small. In the twilight case the effects are much larger. There is, however, a significant increase in free sodium below the photochemical threshold altitude. The consequence is that the diurnal variation predicted is only of the order of 2 to 1, assuming that in twilight the steady state is practically attained. The sodium distribution that would result if these fractional values f, f_1, and f_2 are also assumed to hold when N varies with altitude is shown in Figure 25, curves b and e. The peak of the twilight layer would occur at 82 km, which is far below the observed altitude of 90 km.

The NaO and NaO_2 distributions are affected very much by the large values of ω^2 at low altitude. The diffusion is so fast in comparison with conversion of NaO to Na that ω^2 is very large, and the slightest gradient in NaO causes a large relative excess of NaO_2 at low altitudes according to (40). This situation depends on the equality of k_4 and k_6. If k_4 were large compared with k_6, the rapid conversion of NaO_2 to NaO compared with the relatively slow reduction of NaO would diminish the size of this effect.

If rather large concentrations of O_3 in the 80- to 85-km region can build up within 1 hour because of turbulent mixing and the new values for the O, O_2 three-body rate coefficient there is a possibility that the oxidation of sodium by ozone may become important in this region. This would lead to further decrease in the free sodium abundance at sunset sufficiently large perhaps to produce the desired diurnal variation. For example, if k_3 were as large as 1.5×10^{-12}, and the O_3 distribution were that shown in Figure 23, the rate of formation of NaO from Na and O_3 would compete favorably with the reduction of NaO throughout the region of the sodium maximum. The consequence would be that the term $(k_3\,O_3)/(k_6\,O)$ would need to be considered in the denominator of (20). The new set of steady-state conditions analogous to (39), (40), and (41) would become

$$f = \frac{1}{b} + \frac{\omega^2}{b}\left(\frac{\partial^2 f}{\partial z^2} - \frac{\partial^2 f_2}{\partial z^2}\right) \qquad (42)$$

$$f_1 = f_2 + cf + \omega^2\,\partial^2 f_1/\partial z^2 \qquad (43)$$

and

$$f_2 = \omega^2 (\partial^2 f_2/\partial z^2) + af \qquad (44)$$

where

$$b = 1 + \frac{2k_1 O_2 \cdot M}{k_4 O} + \frac{k_3 O_3}{k_4 O} \qquad (45)$$

and

$$a = (k_3 O_3)/(k_4 O) \qquad (46)$$

In this case the relevant parameters in the sodium twilight problem would be those given in Table 5.

The distribution of f, f_1, and f_2 that results from a solution of (42), (43), and (44) is shown in Figure 28. The photochemical distribution of f is pushed to higher altitude. Diffusion has little effect on the distribution below the peak because of the small values of ω^2/b as a result of the enhanced oxidation rate provided there by the ozone reaction. The increased direct NaO production from the Na, O_3 reaction is reflected also in the reduction in the excess of f_2 over f_1 at low altitudes.

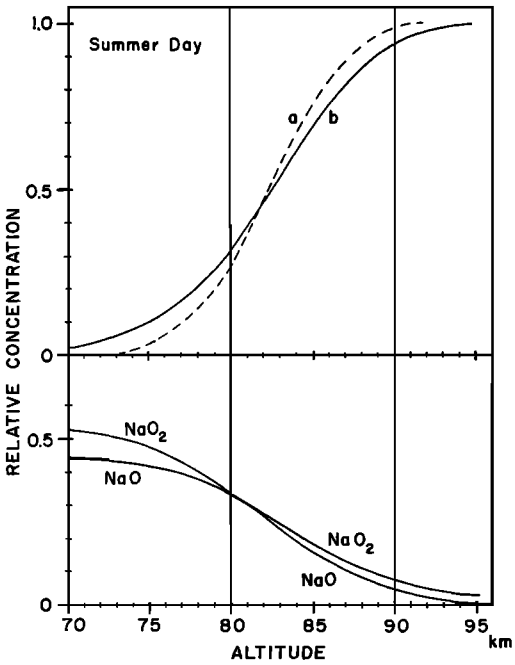


Fig. 26. Relative distribution of sodium with altitude in the absence of a gravitational field with total concentration of all forms of sodium independent of altitude. Curve *a*, chemical equilibrium; *b*, diffusion included.

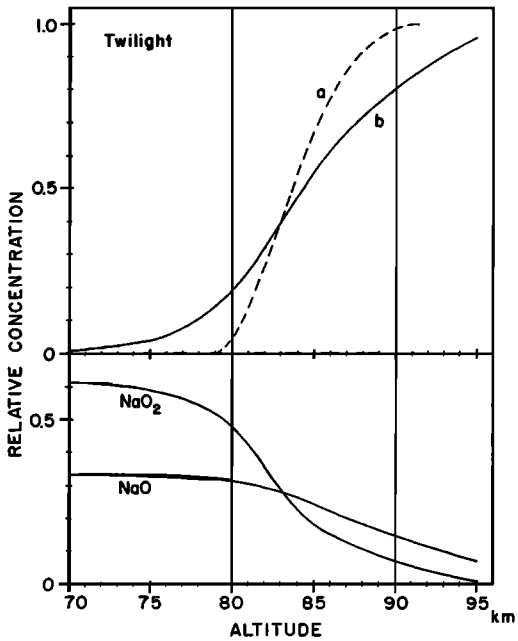


Fig. 27. Relative distribution of sodium with altitude in the absence of a gravitational field with total concentration of all forms of sodium independent of altitude. Curve *a*, chemical equilibrium; *b*, diffusion included.

The sodium twilight layer resulting is illustrated in Figure 25. The peak of the layer has moved close to 85 km, and the diurnal variation becomes 3.5/1. Further increase in k_3 would result in larger ratios and push the altitude of the twilight layer even higher.

On the basis of this mechanism the large diurnal variation and low altitude of the sodium layer in summer would be a result of the creation of much more atomic oxygen at low altitude in summer. This would have as its consequence the production of large amounts of free sodium at low altitude in the daytime followed by a large-scale oxidation, particularly of the lower portions of the layer at sunset. Both the decrease in the abundance of atomic oxygen and the attendant large increase of ozone would operate to oxidize the sodium. The scale of both effects would be increased because of the high density of the region in which they occur in summer. In winter, on the other hand, the amount of atomic oxygen at low altitudes would be diminished, the entire locale of the sodium oxidation and reduction would be moved to

TABLE 5. Values of Parameters in Equations 42–44

k_3 is taken to be 1.5×10^{-13} cm³/sec. Twilight with ozone reaction included.

Altitude, km	k_3O_3	C k_3O_3/k_4O	b^{-1}	ω^2/b
75	4.5×10^{-4}	90	5×10^{-4}	0.3
80	3	6	2.3×10^{-2}	1.4
85	2.5	0.5	0.5	4
90	1.35	0.12	0.875	2.2

higher altitudes, and the range of the diurnal variation would be smaller.

But then it would be difficult to understand why there should not be a seasonal variation in twilight abundance also with a maximum in June when the twilight layer is at its lowest altitude. Under any circumstances—even apart from considerations bearing on the diurnal variation—decrease by 5 km in the height at which half of the sodium in all forms is in the reduced state should roughly double the total amount of free sodium. If instead there is no appreciable seasonal variation in free sodium the conclusion would appear to be that there is a seasonal variation such as that presented in the conventional picture based on a 1 to 1 day to twilight ratio. Then the seasonal variation in N apparently needs to be about twice as large as that in Na. Otherwise the generally accepted chemistry of the sodium problem needs to be radically revised. This ignores, however, the possible changes caused by ionization, which may remove the need for a variation in N, as will presently be shown.

Photoionization. The ratio of morning to evening intensities observed during twilight has the magnitude and seasonal variation predicted by *Hunten* [1954]. The source of the variation according to his model was photoionization of Na during the day and recombination or mutual neutralization of Na^+ at night. The original treatment assumed that the removal process

$$Na^+ + Y^- \rightarrow Na + X \qquad (47)$$

was effective in the day as well as the night. Actually [*Omholt*, 1954] the concentration of X^- is undoubtedly very small in the daytime. On the other hand a reaction such as

$$Na^+ + O_2 + M \rightarrow NaO_2^+ + M \quad (k_{48}) \qquad (48)$$

followed by dissociative recombination

$$NaO_2^+ + e \rightarrow Na + O_2 \qquad (49)$$

may be a very fast process for sodium-ion loss, as *Sullivan and Hunten* [1964] have suggested. Hunten's treatment may, therefore, be valid with $k_{48}\, n(O_2)\, n(M)$ replacing his $\alpha' n(-)$ as the effective recombination coefficient K.

If the rate of photoionization for a sodium atom in sunlight is $i = 2 \times 10^{-5}$ per atom per second as Hunten assumed, the morning-evening ratio of 1.4 would call for an association coefficient of about 3×10^{-5} per ion per second, and no large seasonal variation in the degree of ionization would result. However, for i of the order of 1.5×10^{-5} per atom per second the observed maximum value of the morning to evening ratio would imply $K \leq 10^{-5}$ per ion per second, and a sizable seasonal variation in unionized sodium would easily be attained. The fraction of unionized sodium could readily be twice as high in December as it is in June. This would provide a ready explanation for the seasonal variation in N that is necessary to account for the failure of

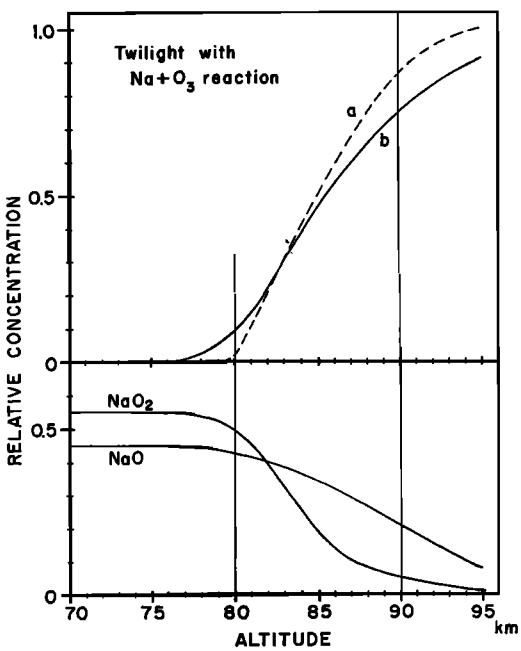


Fig. 28. Relative distribution of sodium with altitude in the absence of a gravitational field with total concentration of all forms of sodium independent of altitude. Curve *a*, chemical equilibrium; *b*, diffusion included.

the twilight abundance to increase in summer despite the low altitude of the layer.

There is a serious difficulty, however. If, during summer daytime, the amount of free sodium is of the order of 30×10^9 atoms/cm^2, then the abundance of sodium ions must be of this same order if ionization is really the mechanism producing the diurnal and seasonal effects. Thus the number of sodium electrons in the D region would equal the total number of free electrons. Since there is no known mechanism by which these electrons would be bound in the daytime, and the recombination coefficient of D-layer electrons is of the order of 3×10^{-6} cm^3/sec, it appears difficult to support a model in which the degree of ionization of sodium is larger than about 10%.

The value of k_1 used in this paper causes k_1 $O_2 \cdot M$ to vary between 1×10^{-5}/sec at 90 km and 1.14×10^{-4}/sec at 85 km. To produce diatomic ions at a rate as fast as the effective recombination rate of electrons an association rate of at least 3×10^{-4}/sec is required. However, such a requirement need be met only during summer, when there would be large amounts of atomic sodium below 85 km in the daytime. Thus it would appear to be sufficient to require

$$k_{48} \cong k_1 \cong 2 \times 10^{-32} \quad \text{cm}^6/\text{sec}$$

This would leave the morning-evening effect to be accounted for by some other mechanism.

Of course, if there is no large increase in sodium abundance during daylight some of these difficulties vanish. The number of sodium ions in the D layer would only need to be of the order of 5×10^9/cm^2. If the photoionization rate is of the order of 1.5×10^{-5}/atom/sec and the removal rate of the order of 10^{-6}/ion/sec in daytime (larger perhaps at night because of mutual neutralization), a ratio of morning to evening abundance of 1.4 at the equinoxes would lead to a large seasonal variation.

If the morning-evening effect is not due to photoionization the cause must apparently be sought in photochemistry. One possibility if the ozone oxidation reaction is important at night is that the ratio of ozone to atomic oxygen might decrease toward the end of the night. A depletion of ozone will occur because of the hydrogen reaction

$$H + O_3 \rightarrow O_2 + OH \qquad (50)$$

However, it is ordinarily assumed that the reaction

$$OH + O \rightarrow H + O_2 \qquad (51)$$

is fast enough to replenish the supply of hydrogen in order that reaction 49 may continue to produce the nightglow hyroxyl radiation. Then for each ozone molecule disappearing an oxygen atom would also be removed. The morning-evening twilight effect, therefore, remains without satisfactory explanation in the context of a large diurnal variation in free sodium.

One perplexing property of the dayglow is the decrease in intensity that sets in at a solar elevation of about 17° in the morning. A minimum occurs at the highest solar angle, and the effect appears to be symmetrical about this angle. It amounts to about a 5% change per degree of solar elevation at Tromsø and about 2% per degree at Haute Provence. The effect could be explained perhaps if the photoionization rate were to increase with solar elevation by an order of magnitude at the altitude of the dayglow layer between 0° and 20° elevation angle. Since both the three-body association rate and the ionization rates would then be of the order of 4×10^{-4}/sec at about 84 km the degree of ionization would be 50%. The time constant would be only of the order of 1 hour, however, and so recombination could restore the sodium as the solar angle decreased. But the high ionization rate would virtually wipe out the top of the layer, and eddy diffusion would need to be invoked to restore the sodium in this part of the layer. Anyway, the problem of disposing of the sodium electrons besets this explanation sorely.

Conflicting Evidence

Two sets of observational evidence have been cited against the occurrence of a diurnal variation. One is the measurement of absorption of sunlight in the daytime by atmospheric sodium performed by *McNutt and Mack* [1963]. This did not show an increase in sodium in the summer, and the abundances obtained were consistent with those given by the 1 to 1 theoretical interpretation in the twilight glow. One crucial question that may be raised about these observations has to do with the method of obtaining the level of zero intensity. A sodium absorption cell was placed in the optical path for this purpose. There is at least the possibility that the

cell changed the scattered light level in the apparatus so that the zero obtained with the cell was lower than it was without it. McNutt and Mack do not give the results obtained for D_2 and D_1 separately. It would be interesting to know whether they were consistent.

The other source of difficulty is the series of D_2/D_1 ratios obtained in twilight by *Zwick and Shepherd* [1963]. These authors compare their results with the calculations of Sherby based on a solar D_2/D_1 ratio of 0.835; they find that the measured ratios scatter above and below the theoretical $R = 1$ curve. It is interesting that the results of Zwick and Shepherd and those of McNutt and Mack are not consistent. If the absorption measurements are valid, they must give accurate values for the residual intensities at the bottom of the D_2 and D_1 solar lines. The ratio of intensities obtained there was 0.9 instead of 0.835. The residual intensities were also somewhat lower individually. If Sherby's calculations are corrected for these effects the family of curves for $I(D_2)/I(D_1)$ versus $I(D_2) + I(D_1)$ is raised considerably. The experimental data of Zwick and Shepherd then lie between the $R = 1$ and the $R = 3$ curves. Thirteen winter measurements and 1 summer measurement are between $R = 1$ and $R = 2$, 5 winter and 8 summer measurements between $R = 2$ and $R = 3$. Two summer observations lie well above the $R = 1$ curve. Thus these two experiments cannot be cited consistently either for or against the existence of a sizable diurnal effect. One interesting point is that the observations of Zwick and Shepherd ran only from January through September 4. The twilight layer is lowest at Saskatoon in the autumn. If there is an anticorrelation between the height of the twilight layer and the daytime abundance the large ratios would be expected to occur during the period just after the observations stopped.

On the other hand, the absorption measurements of *Scrimger and Hunten* [1955] as reevaluated by *Blamont and Donahue* [1961] and recently repeated by *Neo and Shepherd* [1964] also show a large daytime excess in free sodium at Saskatoon. The seasonal variation does not seem to be the same as that reported here for the dayglow. Only winter and spring observations have been reported, and then the diurnal variation was 4.5 to 1 when it is only 2 to 1 at Haute Provence. As the seasonal variation found at Tromsø with the Zeeman photometer is also altogether different from that at Haute Provence, a strong latitude effect appears to be present.

Other Metal Emissions

The results of *Sullivan and Hunten* [1964], who locate the lithium twilight layer near 80 km, about 11 km below the sodium layer, are difficult to encompass in a photochemical explanation. On the basis of Kaufmann's new values for the reaction coefficient k_{24} the density of atomic oxygen near 80 km at night in winter is about 10^7 per cm^3. The ratio $O/(O_2 \cdot M)$ is then 2.5×10^{-22}, and it is necessary that $(k_1/k_4)_{Li}$ be 1.2×10^{-22} in contrast with 4×10^{-18} for the analogous ratio in sodium reactions. If k_1 is 2×10^{-32} cm^6/sec, k_4 must be 1.5×10^{-10} cm^3/sec. If k_1 is 5×10^{-30} cm^6/sec, k_4 must be 4×10^{-8} cm^3/sec. Even the lower value of k_4 is uncomfortably large. On the basis of the older atomic oxygen models the density of O would be 10^9 per cm^3 at 80 km in winter so that the necessary values of k_4 for lithium would be relaxed to 1.5×10^{-12} cm^3/sec and 4×10^{-10} cm^3/sec. Clearly it is necessary to assume that k_1 is quite small for the lithium three-body rate to accommodate the lithium results. This in turn weakens the arguments used by Sullivan and Hunten to obtain a rapid recombination of ionized lithium. If it is assumed that the coefficient of

$$Li^+ + O_2 + M \rightarrow LiO_2^+ + M \quad (k_{52}) \qquad (52)$$

is 2×10^{-32} cm^6/sec, then at 80 km

$$k_{52}\, O_2 \cdot M = 9 \times 10^{-4}/\text{sec} \qquad (53)$$

The equilibrium fraction of neutral sodium at 90 km is

$$f_{Na} = k_{49}/(i_{Na} + k_{49}) \qquad (54)$$

where i is the ionization rate.

Now according to Sullivan and Hunten

$$i_{Li} = 14 i_{Na} \qquad (55)$$

Thus if it is assumed that

$$k_{Li}(80) = 85 k_{Na}(90) \qquad (56)$$

corresponding to equal association coefficients,

$$\frac{f_{Li}}{f_{Na}} = \frac{i + k_{48}}{14i/84 + k_{48}} \qquad (57)$$

If k for sodium is of the order of 10^{-5} at 90 km,

this makes $f_{Li} = 2f_{Na}$. But if the lower altitude of the lithium is caused mainly by the relative slowness of the three-body oxidation process it might be that

$$k_{Li}(80) \cong k_{Na}(90) \tag{58}$$

in which case

$$f_{Li} = \frac{i + k_{48}}{14i + k_{48}} \cong 0.13 \tag{59}$$

It would appear that the magnitude of the ionization corrections for lithium and sodium are in some doubt but that the lithium abundances probably should be multipled by a factor between 0.5 and 8 for comparison with sodium if the ion recombination proceeds by the mechanism postulated by Sullivan and Hunten. Similarly,

$$\frac{f_K}{f_{Na}} = \frac{i + k_{48}}{0.4i + k_{48}} \cong 1.4 \tag{60}$$

if $k_{48} \cong i$.

On the other hand, if there is a 2 to 1 sodium day to twilight abundance ratio in winter, a given twilight sodium intensity corresponds to a larger sodium abundance. According to the analysis in this paper the winter twilight sodium abundances are about 8×10^9 atoms/cm^2 instead of about 5×10^9 atoms/cm^2, which would follow from the average brightness without a diurnal variation. It would appear, therefore, that the measurements of Sullivan and Hunten might imply the following density ratios: sodium, 10,000; lithium, 0.7 to 10.5; potassium, 80.

The K/Li ratio is very close to the meteorite abundance ratio of 75 for the lower Li value. The ratios to Na are very curious. Since the Li/Na ratio falls between that for sea water and meteorites, it is possible to assume mixtures to obtain the observed ratio. This obviously cannot be done with the Na/K ratios, since the K concentration is considerably larger in meteorites and in sea water than Sullivan and Hunten observed. Since there is no evidence that meteorites have compositions at all like those of meteoric debris originating from meteors and micrometeors it may well be that the observed abundances represent the composition of this material rather than that of either sea water or meteorites. It may also be that the residence times of Li, K, and Na and their compounds are quite different in the upper atmosphere. Certainly it does not seem justifiable to seek a correlation between matter in the upper atmosphere and meteorites. Meteorites are, after all, by their very definition large objects, presumably asteroidal, which reach the earth's surface. The objects stopping at high altitude are either material of cometary origin or micrometeoric dust whose origin may be lunar but in any event is still in doubt.

The very low altitude of the lithium layer leads to difficulty in maintaining the layer throughout the night. At this altitude the atomic oxygen must be depleted seriously throughout the night [*Ballif and Venkateswaran,* 1963], especially if the new values of the ozone formation rate are considered. The only obvious way to avoid a pronounced diurnal variation appears to be to invoke an important rate of creation of neutral lithium by ionic recombination. Thus a relatively large degree of ionization is required for the lithium in the upper atmosphere. That the two effects would exactly balance throughout the year is too much to expect. Careful monitoring of the variation in lithium abundance between evening and morning should provide interesting information on the physical processes that are important in determining its behavior in the upper atmosphere.

Meteoric Source

Much effort has been expended during this study to tie the sodium dayglow annual variation to meteoric phenomena. It is true that the total radar meteor counting rate has a maximum in local summer just as the dayglow has [*Millman and McIntosh,* 1961]. But through the autumn the meteor rates decrease much more slowly than the sodium intensity, and the minimum occurs in February rather than November. If the daytime rates alone are considered the correlation is much better, but no self-consistent scheme is available to tie together an influx from meteors and the diurnal and seasonal variations in sodium abundance and altitude.

Other Modes of Dayglow Excitation

An attempt has been made to show that it is possible to select a set of not unreasonable reaction coefficients which could lead to a large diurnal variation in free sodium abundance. An essential feature in the explanation is the im-

portance attributed to turbulent mixing, particularly in affecting the ozone distribution. The seasonal trend of this variation would be in accord with the observed dayglow and twilight glow observations. We do not pretend to have demonstrated definitively that this is the actual state of affairs. In fact, it has not yet been proved experimentally that the dayglow does not have an important contribution from sources other than resonant scattering. Therefore, possible excitation mechanisms must be examined to determine whether some can be found that are consistent with the observations. If these are not to lead to a build-up of sodium that would cause an appreciable increase in daytime as compared with twilight sodium, the removal rate must be rapid. In general, the condition is that

$$E = FL$$

where the excitation rate E is a lower limit to the rate of formation of sodium, L is the desired upper limit to the sodium abundance produced by the process, and F is the removal rate. With $E = 3 \times 10^{10}/\text{cm}^2/\text{sec}$, and L, say, $10^9/\text{cm}^2$, the requirement on F is

$$F \geq 30/\text{sec}$$

As quenching of the resonance radiation begins to occur at about 50 km, this must be the lowest altitude at which the excitation process can operate. Two oxidation processes are available, (1) and (5). Requiring

$$k_1\ O_2 \cdot M = F \geqq 30/\text{sec}$$

means that

$$k_1 \geq 3 \times 10^{-31} \quad \text{cm}^6/\text{sec} \quad \text{at 50 km}$$

or

$$k_1 \geq 3 \times 10^{-29} \quad \text{cm}^6/\text{sec} \quad \text{at 70 km}$$

Hence, the excitation would surely need to extend to 50 km. These are extreme lower limits for k_1. If as few as 10% of all processes lead to excited sodium and the rest produce ground-state atoms the coefficients would have to be an order of magnitude larger. They are, therefore, unattractively large. Similarly, for the ozone oxidation process

$$k_3\ O_3 \geq 30/\text{sec}$$

at the base of the layer means

$$k_3 \geq 3 \times 10^{-11} \quad \text{cm}^3/\text{sec} \quad \text{at 50 km}$$

$$k_3 \geq 7.5 \times 10^{-7} \quad \text{cm}^3/\text{sec} \quad \text{at 70 km}$$

Here too the excitation must be as low in the atmosphere as quenching will permit, and even so the requirements on the oxidation rates are alarmingly severe. Henceforth, excitation extending to the 50-km region will be taken as required, and k_1 and k_3 will be chosen to be 3×10^{-31} cm^6/sec and 3×10^{-11} cm^3/sec. These requirements are independent of the excitation mechanism.

If the process of excitation is photodissociation of NaO_2 or NaO the requirements on the concentrations of these molecules are such that most of the sodium must be combined even at 90 km. Thus

$$E = JN_0H \tag{61}$$

where J is the photodissociation rate, N_0 the density of the oxide at 50 km, and H the scale height there. The resulting requirements on N(90 km) may readily be computed for various values of J (Table 6). To form a twilight layer at 90 km with a density of the order of 10^3 in the summer means that the denominator, unless $J \sim 10^{-1}$/sec,

$$2k_1\ O_2 \cdot M/k_4\ O$$

in (22) must be large there. For example, if $N = 10^5$ cm^{-3}, k_4 must be 4×10^{-18} cm^3/sec. The difficulty then is that k_4 O decreases with altitude so much more slowly than $k_1\ O_2 \cdot M$ that the density of Na increases above 90 km to 3000 cm^3 at 95 km and 7400 cm^{-3} at 100 km. This process is, therefore, unacceptable.

The situation is not so unfavorable if the ozone reaction, (5), is the principal one for oxidation. Then

$$\text{Na} = \frac{N}{1 + (k_3\ O_3)/(k_4\ O)} \tag{62}$$

with $k_3 = 3 \times 10^{-11}$ cm^3/sec. For the denominator of (62) to be as large as 100 at 90 km, k_4 must be 6×10^{-18} cm^3 sec. Then the crucial requirement is that the ratio of O_3 to O not fall off too quickly with altitude. Thus, if at 110 km the ozone density is 10^6 per cm^3 and the oxygen density 1.5×10^{12}, the denominator will be 33 while N will have decreased by a factor of 10.

In this case the density of sodium will have decreased by a factor of 0.3, which is only about one-third as much as the rest of the atmosphere. Above the turbopause the situation will worsen. Thus there is the difficulty that the sodium scale height will be much larger than that of the atmosphere as a whole in conflict with all evidence. This, in fact, is a general difficulty with models that call for a low level of sodium dissociation at high altitude. To produce a layer like the one observed, the reducing agent above the level of maximum sodium density must decrease with altitude at least as rapidly as the oxidizing agent. Thus excitation by photodissociation appears to be an unlikely mechanism for the production of the dayglow. The oxidizing reaction rates must be unrealistically high. Most of the sodium must be combined even at 90 km, and this leads to difficulties in forming the twilight layer. Finally, the process does not explain the seasonal variation. It is necessary to invoke an influx of sodium compounds in the summer. This along with the reduced ratio of ozone to atomic oxygen would cause the twilight abundance to vary in a sense opposite to the observed one.

If a chemical process such as the Chapman reaction

$$\mathrm{NaO}^* + \mathrm{O} \rightarrow \mathrm{Na}^* + \mathrm{O}_2 \qquad (63)$$

is considered, the requirement is that

$$E = k_4^* L_1 \mathrm{O} \qquad (64)$$

where $L_1 = N(50)\ H$ is the number of NaO molecules per cm^2 above 50 km, and H is the atmospheric scale height at 50 km. Under the most favorable conditions, with all the NaO vibrationally excited, the condition on $k_4^*\ L_1$ is that

$$k_4^* L_1 = 3 \times 10^{10}/\langle \mathrm{O} \rangle \cong 0.6 \qquad (65)$$

$$k_4^*\ N(50)\ H = 0.6 \qquad (66)$$

Since $N(90) = N(50)/500$, this condition on k_4^* and N is

$$k_4^* = 2 \times 10^{-9}/N \qquad (67)$$

Now, to obtain

$$\mathrm{Na} = \frac{N}{(k_5\ \mathrm{O}_3)/(k_4^*\ \mathrm{O})} = 10^3 \qquad (68)$$

TABLE 6

J, sec^{-1}	N_0H cm^{-2}	N_0(50 km), cm^{-3}	N(90 km), cm^{-3}
10^{-2}	3×10^{12}	5×10^6	10^4
10^{-3}	3×10^{13}	5×10^7	10^5
10^{-4}	3×10^{14}	5×10^8	10^6

it is necessary that

$$2 \times 10^{-9}\ \mathrm{O}/(k_5\ \mathrm{O}_3) = 10^3 \qquad (69)$$

at 90 km. This is possible only for

$$k_5 = 10^{-7} \quad \mathrm{cm}^3/\mathrm{sec} \qquad (70)$$

This condition is physically impossible. The same sort of result is obtained for the three-body oxidation process. This mechanism can surely be ruled out.

If excitation processes are to involve direct excitation of sodium atoms when there are only of the order of 10^9 atoms/cm^2 present in summer daytime, the excitation rate needs to be about 30/atom/sec. If the reaction coefficient were as large as 10^{-11} cm^3/sec the average density of the colliding particle would have to be 3×10^{12}/cm^3. This is 30% of the O_2 density and 6% of the N_2 density at 90 km. For electrons the requirements are incredible. On the whole the problems of postulating a photochemical or collisional excitation mechanism are much greater than those posed by the hypothesis of a diurnal abundance variation.

Conclusions

There is a large diurnal variation in the abundance of free sodium atoms in the mesosphere, particularly in summer. As the mechanism of producing the increase in summer daytime the large diurnal variation in O and O_3 enhanced by eddy diffusion effects on the sodium and its oxides would appear to be a possibility. There may be an additional contribution from photodissociation.

The lamentable lack of measured values for any of the alkali reactions needed places the entire discussion in this paper somewhat in the realm of speculation. It would still be premature to claim that the phenomenon observed with the Zeeman photometer has been conclusively demonstrated to be the sodium dayglow, or that it is entirely caused by resonant scattering if it

should be D-line emission. There is conflicting evidence from absorption and fine structure ratio measurements. Rocket experiments to determine the vertical distribution of the glow in the daytime would be most helpful. If the altitude were about 50 km the indication would be that the excitation mechanism is photochemical. If it were 5 to 10 km lower than the twilight layer particularly in summer the mechanism proposed in this paper would find strong support.

An attempt has been made here to set limits to the range of reaction rates and atmospheric motions which would permit an explanation of the phenomenon observed on the supposition that it is the sodium dayglow. There appears to be nothing unreasonable about the chemistry required to account for a large diurnal and seasonal effect in the sodium layer, nor is any feature of the model at variance with the present picture of the upper atmosphere. A radical revision in the hitherto accepted three-body oxidation rate of sodium is a necessary condition but also is indicated from an analysis of the experimental determination of this rate. The role played by very rapid eddy diffusion is great. Diffusion is particularly important, along with improved reaction rates, in increasing the altitude at which there are important diurnal variations in atomic oxygen and ozone. On this basis a revision upward of the expected ozone concentration in the 85-km region at night has been indicated and is probably crucial in bringing about a sodium diurnal variation of the sort suggested by the observations. It will also eliminate one of the major difficulties with the O_3, H mechanism for OH* production in placing the site of maximum rate in the neighborhood of 85 km.

Obviously more attention needs to be given to the problem of vertical motion in the mesosphere. The coefficients for vertical diffusion called for in this paper are very large. The authors are aware that the demands they make on rapid transport are great, and the case should not be taken as closed. Nevertheless, if diffusion is slow it is difficult to obtain from chemical processes alone the kind of diurnal variation in the ozone atomic oxygen ratio that would be needed to produce the diurnal and seasonal sodium fluctuations reported here.

Acknowledgments. A very useful discussion with D. M. Hunten on the chemistry of the sodium problem is gratefully acknowledged. The work of Jean Paul Schneider, Jean Bereyziat, Pierre Coufleau, and Marie Lise Chanin in obtaining the observations was indispensable.

This work was supported in part by the National Science Foundation, Atmospheric Sciences Section, under grant (G-21999).

References

Ballif, J., and S. V. Venkateswaran, A study of the hydroxyl (OH) and sodium (Na) emissions in the night sky, Institute of Geophysics and Planetary Physics, University of California at Los Angeles, 1962.

Ballif, J., and S. V. Venkateswaran, On the temporal variations of the OH nightglow, *J. Atmospheric Sci., 20,* 1, 1963.

Bates, D. R., The physics of the upper atmosphere, in *The Earth as a Planet,* edited by G. P. Kuiper, p. 576, University of Chicago Press, 1954.

Bawn, C. E. H., and A. G. Evans, The rates of reaction of sodium atoms with oxygen, nitric oxide, and other oxides, *Trans. Faraday Soc., 33,* 1580, 1937.

Benson, S. W., and E. Axworthy, Jr., Mechanism of the gas phase, thermal decomposition of ozone, *J. Chem. Phys., 26,* 1718, 1957.

Blamont, J. E., Observations de l'émission atmosphérique des raies D du sodium au moyen d'un appareil à balayage magnétique, in *The Airglow and the Aurorae,* edited by Armstrong and Dalgarno, p. 99, Pergamon Press, London, 1956.

Blamont, J. E., Turbulence in the atmospheric motions between 90 and 130 km of altitude, *Planetary Space Sci., 10,* 89, 1963.

Blamont, J. E., and C. de Jager, Upper atmospheric turbulence near the 100 km level, *Ann. Geophys., 17,* 134, 1961.

Blamont, J. E., and T. M. Donahue, The dayglow of the sodium D lines, *J. Geophys. Res., 66,* 1407–1423, 1961.

Blamont, J. E., T. M. Donahue, and W. Weber, The sodium twilight airglow, 1955–1957, 2, *Ann. Geophys., 14,* 282, 1958.

Brandt, J. C., and J. W. Chamberlain, Resonance scattering by atmospheric sodium, 5, Theory of the day airglow, *J. Atmospheric Terrest. Phys., 13,* 90, 1958.

Brunt, D., *Physical and Dynamical Meteorology,* chapter 12, Cambridge University Press, 1941.

Bullock, W. R., and D. M. Hunten, Vertical distribution of sodium in the upper atmosphere, *Can. J. Phys., 39,* 976, 1961.

Chamberlain, J. W., D. M. Hunten, and J. E. Mack, Resonance scattering by atmospheric sodium, 4, Abundance of sodium in twilight, *J. Atmospheric Terrest. Phys., 12,* 153, 1958.

Chapman, S., Notes on atmospheric sodium, *Astrophys. J., 90,* 309, 1939.

Clyne, M. A. A., and B. Thrush, Rates of elementary processes in the chain reaction between

hydrogen and oxygen, *Proc. Roy. Soc. London, A, 275,* 544, 1963.

Cote, O. R., Wind, diffusion, and turbulence: Analysis of sodium vapor trails in the 80 to 140 km region of the atmosphere, *Paper 63-300,* American Institute of Aeronautics and Astronautics, Fort Collins, Colorado, July 1963.

Cronin, H. E., and C. L. Noelcke, *Final Rept., U.S.A.F. contract AF19(604)-640,* Geoscience, Inc., Washington Grove, Md., 1955.

Demtröder, W., Bestimmung von Oszillaborenstärken durch Lebensdauermessungen für die Elemente Ga, Al, Mg, Tl, und Na, *Z. Physik, 166,* 42, 1962.

Donahue, T. M., A calculation of the sodium dayglow intensity, *J. Geophys. Research, 61,* 663–666, 1956.

Donahue, T. M., and J. E. Blamont, Sodium in the upper atmosphere, *Ann. Geophys., 17,* 116, 1961.

Donahue, T. M., and R. Resnick, Resonance absorption of sunlight in twilight layers, *Phys. Rev., 98,* 1622, 1955.

Donahue, T. M., and V. R. Stull, Excitation of the sodium twilight glow, *Ann. Geophys., 15,* 481, 1959.

Grainger, J. F., and J. Ring, Anomalous Fraunhofer line profiles, *Nature, 193,* 762, 1962.

Hines, C. O., Internal gravity waves at ionospheric heights, *Can. J. Phys., 38,* 1441, 1960.

Hines, C. O., The upper atmosphere in motion, *Quart. J. Roy. Meteorol. Soc., 89,* 1, 1963.

Hunten, D. M., A study of sodium in twilight, 1, Theory, *J. Atmospheric Terrest. Phys., 5,* 44, 1954.

Hunten, D. M., Transmission functions for twilight studies, *J. Atmospheric Terrest. Phys., 24,* 333, 1962.

Hunten, D. M., A. Vallance Jones, C. D. Ellyett, and E. C. McLauchlan, Sodium twilight at Christchurch, New Zealand, *J. Atmospheric Terrest. Phys., 26,* 67, 1964.

Kaufmann, F., Aeronomic reactions involving hydrogen; a review of recent laboratory studies, *Ann. Geophys., 20,* 106, 1964.

Kaufmann, F., and J. R. Kelso, Rate constant of the reaction $O + 2O_2 \rightarrow O_3 + O_2$, *Proc. Faraday Soc.,* 1964.

Martyn, D. F., Cellular atmospheric waves in the ionosphere and troposphere, *Proc. Roy. Soc. London, A, 201,* 216, 1950.

McNutt, D. P., and J. E. Mack, Telluric absorption, residual intensities and shifts in the Fraunhofer D lines, *J. Geophys. Res., 68,* 3419–3429, 1963.

Millman, P. M., and B. A. McIntosh, A preliminary report on radar meteor counts, *Proc. Symp. Astron. Phys. Meteors,* Smithsonian Astrophysical Observatory, August 28 to September 1, 1961.

Neo, Y. P., and G. Shepherd, Measurement of the daytime abundance of upper atmospheric sodium, *Can. J. Phys., 42,* 1964.

Nier, A. O., J. H. Hoffman, C. Y. Johnson, and J. C. Holmes, Neutral composition of the atmosphere in the 100- to 200-kilometer range, *J. Geophys. Res., 69,* 979–989, 1964.

Omholt, A., Considerations regarding the sodium lines in the nightglow and twilight, *J. Geophys. Res., 62,* 207, 1957.

Packer, D. M., Altitudes of the night airglow radiations, *Ann. Geophys., 17,* 67, 1961.

Polanyí, J. C., Chemical processes, in *Atomic and Molecular Processes,* edited by D. R. Bates, Academic Press, New York, 1962.

Potter, A. E., and B. S. Del Duca, Origin of the sodium airglow, *J. Geophys. Res., 65,* 3915–3923, 1960.

Scrimger, J. A., and D. M. Hunten, The intensity at the bottom of the Fraunhofer D lines, *Can. J. Phys., 33,* 780, 1955.

Shaefer, E. J., and M. H. Nichols, Recent results obtained from a rocket-borne mass spectrometer, *Space Research IV,* North-Holland Publishing Company, Amsterdam, 1964.

Sherby, J. W., Relationship of the intensity of the sodium twilight flash to the daytime abundance, Ph.D. thesis, unpublished, University of Pittsburgh, 1961.

Sullivan, H. M., and D. M. Hunten, Lithium, sodium, and potassium in the twilight airglow, *Can. J. Phys., 40,* 1964.

Taylor, G. I., Diffusion by continuous movements, *Proc. London Math. Soc., 2,* 421, 1920.

Taylor, G. I., Statistical theory of turbulence, *Proc. Roy. Soc. London, A, 151,* 421, 1935.

Tohmatsu, T., and T. Nagata, Dynamical studies of the oxygen green line in the airglow, *Planetary Space Sci., 10,* 103, 1963.

Vallance Jones, A., Metallic emissions in the twilight and their bearing on atmospheric dynamics, *Planetary Space Sci., 10,* 117, 1963.

Wallace, L., The OH nightglow emission, *J. Atmospheric Sci., 19,* 1, 1962.

Zwick, H. H., and G. Shepherd, Ratio and absolute brightness measurements of the sodium D lines in the twilight glow, *Can. J. Phys., 41,* 343, 1963.

(Manuscript received May 5, 1964; revised June 16, 1964.)