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14. Abstract/Notes  <i>Using recently proposed chemistry which includes the NaOH molecule, static calculations simulating the nocturnal sodium layer have been shown to give results in good agreement with an average of sodium measurements. In order to further evaluate this Na layer model, a dynamic time dependent atmospheric photochemistry-vertical diffusion model has been developed to calculate the diurnal variation of sodium and compare it with recent measurements. The diurnal calculations show that the Na model fails to reproduce the measured diurnal behavior of the Na layer, which, for example, shows little variation in abundance between day and night. The situation is further aggravated if we include the reaction <math>\text{NaO}_2 + \text{O} \rightarrow \text{NaO} + \text{O}_2</math>. After a thorough review of the reaction rates, it is shown that the major modification which needs to be introduced with respect to the previous model, is the elimination of the reaction <math>\text{NaOH} + \text{H} \rightarrow \text{Na} + \text{H}_2\text{O}</math>. The production of the NaOH molecule is thus effectively transformed into a height dependent sink for Na. The sensitivity of the new model is tested for variations of the reaction rates and the eddy diffusion coefficient and the results are shown to be in much better agreement with experiment.</i>			
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## THE ATMOSPHERIC NEUTRAL SODIUM LAYER, 2, DIURNAL VARIATIONS

by

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Abstract. Using recently proposed chemistry which includes the NaOH molecule, static calculations simulating the nocturnal sodium layer have been shown to give results in good agreement with an average of sodium measurements. In order to further evaluate this Na layer model, a dynamic time dependent atmospheric photochemistry-vertical diffusion model has been developed to calculate the diurnal variation of sodium and compare it with recent measurements. The diurnal calculations show that the Na model fails to reproduce the measured diurnal behavior of the Na layer, which, for example, shows little variation in abundance between day and night. The situation is further aggravated if we include the reaction  $\text{NaO}_2 + \text{O} \rightarrow \text{NaO} + \text{O}_2$ . After a thorough review of the reaction rates it is shown that the major modification which needs to be introduced with respect to the previous model is the elimination of the reaction  $\text{NaOH} + \text{H} \rightarrow \text{Na} + \text{H}_2\text{O}$ . The production of the NaOH molecule is thus effectively transformed into a height dependent sink for Na. The sensitivity of the new model is tested for variations of the reaction rates and the eddy diffusion coefficient and the results are shown to be in much better agreement with experiment.

Revised August 1982

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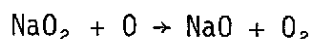
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## Introduction

The aim of this paper is to compare calculated variations of sodium density to the diurnal variations measured in the sodium layer and sodium nightglow. In a previous paper (Kirchhoff et al. 1981b, paper I) a detailed discussion of atmospheric sodium layer modeling was presented showing the advantages of the constant flux model over previous models. Using the photochemistry of Ferguson (1978) and Liu and Reid (1979), who first suggested that NaOH may play an important role in the chemistry of the sodium layer, and after choosing a mesospheric reference model of atmospheric parameters, we compared the calculated sodium density to a measured average sodium profile. It was concluded that the inclusion of reactions leading to the formation of NaOH results in a realistic vertical equilibrium distribution of sodium, achieved in previous models only by the inclusion of arbitrary and unrealistic boundary conditions. All calculations assumed equilibrium steady state conditions.

The idea of NaOH being a major sodium constituent has been criticized by Murad and Swider (1979), who, considering possible reactions of NaOH with chlorinated species, suggest that the final product would be NaCl. The same authors also claim exothermicity for the reaction



but do not quote the appropriate reaction rates. These additions to the basic Liu and Reid model will introduce modifications to the model of paper I, as will be shown later.

The nocturnal variations of the atmospheric sodium layer are well known from laser radar measurements. Results for the Northern Hemisphere, around  $50^{\circ}\text{N}$ , have been reported by Sandford and Gibson (1970), Gibson and Sandford (1971), and Megie and Blamont (1977). Early results in the Southern Hemisphere were presented by Kirchhoff and Clemesha (1973), and a detailed study of the nighttime sodium morphology based on data for several years at latitude  $23^{\circ}\text{S}$ , was reported in Simonich et al. (1979). One of the strongest features observed by Simonich et al. is a large decrease of Na density during the night at the bottom of the layer. The amount of this decrease at 80 km is about a factor of 5.

Early daytime measurements of Na using the same technique have been reported by Gibson and Sandford (1972). Results for just a few measured sodium profiles revealed no pronounced change in total abundance between day and night. The results of Clemesha et al. (1982), for the Southern Hemisphere, analysing the diurnal variations of the Na layer over a series of complete consecutive cycles of 24 hs confirm the earlier findings and reveal a number of new characteristics including a strong semidiurnal oscillation in the sodium abundance, but a diurnal variation only in the region of 80 km. The measurements do not show the rapid changes at sunrise and sunset that might be expected to result from changes in ozone concentration. The semidiurnal oscillation of the abundance seems to be tidal in origin, and the 80 km variation might be mainly photochemical, as suggested by Clemesha et al. (1982). Granier and Megie (1982) have also made daytime observations of the sodium layer but reported no consistent diurnal or semidiurnal variations. However, a more detailed analysis of the French data apparently shows a diurnal variation at 80 km (Megie, 1982, private communication).

The variation of sodium airglow emission during the night is not very large, in general, at our latitude. On the average it is symmetrical about midnight where the intensity is at its minimum. Towards dawn and dusk there is an increase in intensity of the order of some 30% (Kirchhoff et al., 1979; 1981a). Results for a number of stations in the Northern Hemisphere are discussed by Fukuyama (1977).

#### Atmospheric model summary

In parallel to the sodium photochemistry we have developed a comprehensive atmospheric density model which extends between heights of 30 and 140 km. The chemical reactions of this model as well as reaction rates and references are shown in Table 1, and have been adopted from Hampson and Garvin (1975, 1978) or following Kasting and Donahue (1980). The upper and lower boundaries are located well beyond the height extremes of the Na layer (70-110 km) and therefore the choice of boundary values has very little influence on the Na layer itself.

A numerical method of solving the equations of continuity and diffusion has been developed by Shimazaki (1967) and Shimazaki and Laird (1970, 1972). More recently Moreels et al. (1977) have developed a similar atmospheric model aiming at the study of the time variations of the OH emissions. Megie and Blamont (1977) have used this model to study Na variations but shortcomings of their model for Na have been pointed out in paper I.

Our present model, besides using more recently determined reaction rates, uses the now standard technique of constituent groupings, which offers some computational advantages over separate constituent computations (Liu and Donahue, 1974; Fishman, 1977). We distinguish between the long lived species  $H_2O$ ,  $H_2$ , and the major family groupings of odd oxygen  $O_x = O + O_3 + O(^1D) + NO_2$ , and odd hydrogen  $HO_x = H + OH + HO_2 + 2H_2O_2$ , which are solved using the complete equation of continuity, and the short lived species calculated assuming photochemical equilibrium. The individual densities are finally scaled using the group particle density.

The vertical grid spacing is 1 km. Computing times are much larger during the day, when photodissociation coefficients must be calculated, and during twilight, which requires smaller time steps because of the fast variations that occur during this period. The temperature profile as well as the diffusion coefficients are assumed to be constant with time. For more or less arbitrary input conditions the model must undergo about 5 cycles of 24 hours in order that after such a cycle the densities return to their previous values with a change of less than about 5%.

The sodium constituents are incorporated into this time dependent atmospheric density model in order to study their diurnal variation. Depending on the Na reaction rates shown in Table 2, grouping among the Na constituents is also possible because of very fast interconversions. One such Na family, for example, could be  $\text{Na}_1 = \text{Na} + \text{NaO}$ . Because of the much shorter time constants involved for the Na constituents, especially in the 70 to 80 km region, the sodium constituents time variations are calculated by a subdivision of the integration time steps. Solar fluxes and absorption cross-sections are taken from Shimazaki and Laird (1972), Nicolet (1975), and Moreels et al. (1977). For a discussion on boundary conditions see for example Moreels et al. (1977). A discussion on numerical techniques and the problem of numerical stiffness is given in Kasting (1979). The model calculations apply for  $^{23}\text{O}$ S during equinox. For the eddy diffusion coefficient we follow Blum and Schuchardt (1978) using for K the height dependence

$$K = 6.13 \times 10^3 \exp((h-30)/10.86) \text{ cm}^2 \text{ s}^{-1}$$

where h is height in km, but above 102 km we assume K is constant.

To summarize we show in Figure 1 the basic integration cycle of the continuity equation for each time step. Input parameters are all initial densities, temperature and diffusion profiles, as well as reaction rates and dissociation rates. The long lived species are solved first using a finite difference technique as already mentioned, followed by the

determination of the short lived species through an implicit photochemistry step. These are then scaled by the group densities in an iterative process until relaxation is achieved. After the calculation of the main atmospheric densities, the sodium constituents are determined, assumed to belong to the long lived species, closing the calculations of the time step.

Figure 2 shows the calculated densities of O, O<sub>3</sub>, M, H, OH, HO<sub>2</sub>, at 12 and 24 hs local time, in the height range of interest. The arrows indicate the upper or lower abscissa scales. The characteristics of the day night variation of the densities are similar to those obtained by other authors. The strongest variations occur for O<sub>3</sub> at all heights. For O and H the variations are very large only below 80 km.

Because of its possible direct influence on sodium it is worth analysing the diurnal variation of ozone in more detail. Figure 3 shows the variations of O<sub>3</sub> density as a function of time at several heights. It can be seen that the variations due to photolysis are considerable in the height region of interest. Above 84 km the change occurs abruptly during the twilight periods, and there is practically no variation during the day or during the night. Below this height, however, close to the peak hydrogen density, the loss of ozone is sufficiently large during the night for a significant nocturnal variation to occur.

### Sodium Chemistry

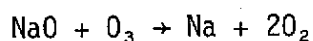
The reactions and rates for sodium as used in the static model of paper I are repeated for convenience in Table 2. Inclusion of this chemistry into the diurnal calculations gives the result shown in Figure 4. The basic production of sodium is assumed to be the deposition from meteoroids (Gadsden, 1968; Clemesha et al., 1978) centered at 94 km, having a Gaussian shape, and an integrated strength of  $7 \times 10^3 \text{ cm}^{-2} \text{ s}^{-1}$ . The diurnal variation of Na density is shown at 80 km, as well as the Na profile at 24 hs and 12 hs. A strong day-night variation is obtained, the abundance of Na being  $3.4 \times 10^9 \text{ cm}^{-2}$  at 24 hs

and  $5.5 \times 10^9 \text{ cm}^{-2}$  at 12 hs. A large and very fast variation of Na (shown at 80 km) occurs during the twilight periods, induced through the ozone variation. Besides these large variations it is apparent also that the peak of the Na layer is much lower during the day, around 86-88 km. The model reproduces the Na layer satisfactorily only at night, as can be seen by the layer calculated for 24 hs and as expected from the static calculations of paper I in which the layer was simulated for nocturnal conditions.

The strong diurnal variations obtained through the calculations are mainly due to the dependence of Na on atmospheric ozone through reaction 5



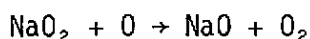
which is a fast process, representing a large production term for  $\text{NaO}_2$ . In terms of densities, for example, there are about 1400  $\text{NaO}_2$  molecules at 80 km at midnight, with only 265 Na atoms per  $\text{cm}^3$ . As ozone is rapidly increased or decreased there is an equally fast switching between Na and  $\text{NaO}_2$ . It is clear, then, that there is a major discrepancy between the model predictions and the actual behavior of atmospheric Na. It is interesting to note, however, that reaction 5 is essential in the static calculation to place the Na layer peak at the correct height and thus that any change in the rate constant assumed for reaction 5 would upset the static model. The value of the production rate of  $\text{NaO}_2$  is actually unknown since reaction 5 can also branch to



with a total reaction rate of  $1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  (Kolb and Elgin, 1976). Liu and Reid (1979) mention that the reaction rate for the production of  $\text{NaO}_2$  should be less than  $5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  in order that there be no variation in the height of the peak between day and night, but we find that no value of the reaction rate or branching ratio is capable of giving an acceptable sodium distribution over a



24-hour cycle. It is important to note, finally, that the situation is even worse if one follows the recent suggestion of Murad and Swider (1979) to include the reaction



in the chemistry of Table 2. This reaction, which is expected to be rather fast, makes the  $\text{NaO}_2$  density decrease in favor of an increase in Na at the bottom of the layer thus distorting the layer even further. Summarizing, the existing model is unsatisfactory because the equilibrium between Na and NaOH makes the sodium density below the peak highly sensitive to the ozone density. To resolve this problem we suggest that NaOH is not reduced to Na, and thus the formation of NaOH represents a sink so far as free sodium is concerned. In this way the sensitivity of the sodium density to the ozone concentration is greatly reduced. Before going on to justify this suggestion and discuss its implications the sodium reactions and their rates will be examined in a little more detail.

#### Review of the Na chemistry

Sodium reactions and up-dated reaction rates are shown in Table 3. Reactions 1, 4, and 5, except for the branching ratio, have been calculated by Kolb and Elgin (1976) assuming that these reactions proceed via the so called electron jump mechanism. Bates and Ojha (1980) have updated rates 1 and 4. Some support for these is given through the Na glow emission cycle which produces a calculated intensity of the D line emission consistent with the measured values. Of all the sodium reactions shown in Table 3 only the reaction rate for reaction 2 has been partially measured. Kolb and Elgin (1976) cite the experiment of Carabetta and Kaskan (1968) in which the rate was determined at temperatures between 1420 and 1600 K. Apparently, no temperature dependence was found between these values, the reaction rate being quoted at  $8.2 \times 10^{-34} \text{ cm}^6 \text{ s}^{-1}$ .

A general first guess for an unknown Na reaction rate has been obtained in the past by considering the rates for the analogous hydrogen reaction and applying theoretical "corrections" to compensate for the different cross-sections and masses. It should be noted, however, that the hydrogen reactions listed in Table 1 are not without their uncertainties as well. For reaction 8,  $\text{HO}_2 + \text{O}$ , for example, it appears that no laboratory measurement has been made yet. Values between 1 and  $7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  have been recommended by Nicolet (1975), and we use an average value.

For reaction 11 of Table 1,



there is also a large uncertainty involving its rate. A high value of  $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  (Hochanadel et al., 1972) has been used as well as a lower value of  $3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Hudson, 1977), preferred by the NASA 1977 evaluation, and used in Duerer et al. (1977). The equivalent sodium reaction could be important for the high value of the reaction rate, since it would produce amounts of NaOH significant specially at night, which would represent a net loss for sodium. It could represent a model alternative if reaction 7 of Table 3 turns out to be endothermic.

Finally, a number of different values have been obtained for the rate of reaction 4 of Table 1,



varying at 200 K from as low as  $2.8 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$  to a high value close to  $1.5 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ . According to Nicolet (1975), the value quoted also by Hampson and Garvin (1975) is the average of two laboratory determinations. To obtain the rate of reaction 2 at low temperature, it is assumed that this rate behaves as reaction 4 of Table 1, and thus the value of the rate for reaction 2 is as shown in Table 3. All remaining reaction rates of Table 3 have been determined through this

comparative method. For reaction 3 the equivalent rate given by Lloyd (1974) for  $\text{H} + \text{HO}_2$  (reaction 16 of Table 1) is  $6.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at 200 K. Using a correction factor of 2.0, from Megie (1976), the rate for Na should be  $1.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  as given in Table 3. Reaction 6 has only a secondary role in the chemistry shown. In terms of the equivalence idea reactions 6 and 8 are the same. Reactions 3 and 7 are also equal, and so are their reaction rates. Presently, however, there is a large uncertainty in the calculated exothermicity of this reaction (Liu and Reid, 1979). Reaction 9 is included as suggested by Murad and Swider (1979). This reaction was not included in the model of paper I. The value of its reaction rate shown in Table 3 has been adopted on the basis of the rate given by Burrows et al. (1977), the correction factor again from Megie (1976) is 1.4, giving for this rate the value of  $2.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .

Because of the assumed temperature dependence, the absolute value of reaction rate 2 at low temperature is, as all others in Table 3, subject to error. A value of  $2 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}$  has been cited by Hunten (1967) based on a result presented at a conference by Kaskan. The high temperature value, however, was published only three years later (Carabetta and Kaskan, 1968) which appears to indicate that the authors have repeated what appears to be a very difficult laboratory experiment. The low temperature value, nevertheless, remains uncertain. It must be noted that using the equivalent Na-H idea, reaction rate 2 should be much higher, of the order of  $5 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$ , instead of the  $2.9 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}$  at 200 K.

As mentioned earlier, the reduction of NaOH by hydrogen is assumed not to occur in our up-dated model. There appears to be little justification for Liu and Reid's original inclusion of this reaction, and there is, of course, no equivalent hydrogen reaction. More important, perhaps, is Murad and Swider's (1979) suggestion that NaOH would react with chlorine to give NaCl, thus effectively removing sodium from the cycle, so far as free sodium is concerned, and having the same effect as assuming that NaOH is not reduced by hydrogen. This change in the

reaction scheme has, of course, a major effect on the model, changing the situation on the bottomside of the layer from one of chemical quasi-equilibrium to one where the divergence of the vertical flux is balanced by the rate of NaOH production.

### Results and discussion

The diurnal variation of sodium density at 80 km and the sodium profile at 24 hs are shown in Figure 5 using the new model summarized in Table 3. The profile for 12 hs is not shown because it would be plotted almost on top of the other, and there is virtually no variation above 86 km. The source function as well as the diffusion coefficients are the same in Figures 4 and 5. In this case we use a branching ratio of .25 for reaction  $K_{sa}$ , that is,  $K_{sa}$  is  $3.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . It can be seen that the diurnal variation of Na density shown at 80 km is very much reduced from the previous model shown in Figure 4. A diurnal variation in density occurs only below about 80 km, and the variation of the total abundance is very small. The abundance for case a, for example, is the same at noon and midnight. Cases b and c are shown to test the sensitivity of the model to changes in reaction rate  $K_7$ . In c this rate is zero and in b it is one tenth its value in a. The nocturnal variation of Na at 80 km is of the order of a factor of 2 between maximum and minimum density. The layer peak is at 88 km, lower than the 94 km indicated by the observations, and there is practically no change of the layer densities above 84 km between day and night. Also shown in Figure 5, at midnight, are the densities of NaO and NaO<sub>2</sub>. NaO peaks at 80 km whereas NaO<sub>2</sub> peaks at 78 km. With respect to the sodium nightglow, since the intensity is given by the height integral of the product NaO<sub>3</sub>, the nocturnal variation of sodium nightglow is quite similar for the two models which is not surprising since around midnight the Na layer has not changed very much, as already mentioned. The nocturnal decrease in intensity is larger in the first half of the night, decreasing from about 55 to 40 Rayleighs with a further decrease of 5 Rayleighs between midnight and dawn. As pointed out in Kirchhoff et al. (1979), the nocturnal variation of the nightglow intensity cannot be

correctly reproduced in models which do not include tidal oscillations, which are believed to be responsible for the increase in the intensity after local midnight.

To understand the factors which control the layer it is helpful to consider the chemical equilibrium ratios. On the basis of the chemistry shown in Table 3 and in equilibrium, the ratios  $X_2 = [\text{NaO}]/[\text{Na}]$  and  $X_3 = [\text{NaO}_2]/[\text{Na}]$  can be written as

$$X_2 = (X_3 [O] K_9 + \underline{[O_3] K_1})/A \quad (1)$$

$$A = \underline{[O] K_4} + [\text{HO}_2] K_6 + [O_3] K_5$$

$$X_3 = ([O_2] [M] K_2 + X_2 \underline{[O_3] K_{5a}})/B \quad (2)$$

$$B = [\text{OH}] K_8 + \underline{[O] K_9} + [\text{H}] K_7$$

and the loss of total sodium L is given by

$$L/[\text{Na}] = \underline{[\text{HO}_2] K_3} + X_2 [\text{HO}_2] K_6 + X_3 [\text{H}] K_7 + X_3 [\text{OH}] K_8 \quad (3)$$

where the underlined terms are dominant over most of the height range. For  $X_3$  the term  $[O] K_9$  is close to 200 times larger than  $[\text{H}] K_7$  and even more compared to  $[\text{OH}] K_8$ .

An interesting feature in the diurnal variations can be seen in Figure 5, in the morning twilight period, when there is a fast Na increase. Referring to equations 1 and 2, during the day the fractions  $X_2$  and  $X_3$ , at 80 km, are very small, less than about .02, and therefore any change in these fractions reflects very little on Na. The fractions  $X_2$  and  $X_3$ , however, increase during the night. At midnight these values are .17 and .01, respectively, and during the morning twilight  $X_2 = .35$  and  $X_3 = .05$ , so that a change in  $X_2$  has a larger effect on Na. Practically all NaO is transformed into Na atoms in the morning twilight, shown in Figure 5 by the fast increase of Na at 80 km.

The loss terms given in equation 3 are shown in Tables 4 and 5, calculated for midnight and noon respectively, using the reaction rates of Table 3. From these tables it can be seen that reactions 7 and 8 are important only in the lowest part of the layer (below 80 km) where the term  $X_3$  is very large. At and above 80 km reaction 3 represents most of the loss, day and night. The chemical time constant  $\tau$  has a very fast variation with height, from a few seconds at 76 km to hundreds of thousands of hours at 96 km. The chemical and diffusion time constants become comparable at about 84 km. Above this height the layer is shaped mainly by diffusion, and the actual height distribution of the loss rate has little effect. Only below 84 km does this function have a large effect on the sodium density profile. This result of the analysis is in agreement with the experimental evidence.

The peak of our simulated layer is about 5 km too low when compared with the experimental results for our latitude. A change in the height of the peak can be achieved either by increasing the loss rate, thus effectively raising the sink height, or by changing the eddy diffusion profile.

An examination of equations 2 and 3 shows that there are several ways of increasing the loss terms, through changes of reaction rates, and thus increasing the peak height. The quantitative changes that result from the various options on the rates have been determined through the solution of the continuity and flux equation in a static Na model which uses the atmospheric parameters calculated for midnight with the dynamic model. Thus for example, increasing reaction rates  $K_3$  and  $K_7$  by a factor of 10 places the layer peak at 90 km. Since the loss term dominates through  $K_3$ , a very similar result is obtained by considering the possibility that  $K_7 = 0$ , and keeping the factor of 10 increase in  $K_3$ . An increase in reaction rate  $K_2$  is less efficient in increasing the layer height because reaction 5 is dominant. An increase of a factor of 20 can increase the height of the peak by less than 1 km. A decrease in reaction rate  $K_9$  can also increase the height of peak density. A decrease of a factor of 100 in  $K_9$  places the height of the peak at 92 km.

Since diffusion dominates at the peak of the layer, as shown previously, the approximate relationship

$$\phi = Kn/H$$

must hold at the peak, where  $\phi$  is the flux of sodium,  $K$  is the eddy diffusion coefficient,  $n$  is the sodium density and  $H$  is the atmospheric scale height. Thus, it is clear that to maintain a peak density of approximately  $3$  to  $5 \times 10^3$  Na atoms  $\text{cm}^{-3}$ ,  $\phi$  must be modified every time a change in  $K$  is made. In Figure 6 we show the Na layer calculated through the static model (open circles) using for the eddy diffusion coefficient

$$K = 6.13 \times 10^3 \exp((h-30)/16.3) \text{ cm}^2 \text{ s}^{-1}.$$

In comparison to the previous cases, this makes  $K$  smaller by about a factor of 2 at 70 km, and by almost a factor of 10 at 100 km. As can be seen in Figure 6, the peak of the layer is now at 92 km. For comparison the dashed curve shows case a from the previous Figure. The modification in  $K$  is, of course, arbitrary and intended only to determine the sensitivity of the peak height to changes in  $K$ . In view of our lack of precise knowledge of reaction rates and diffusion coefficients there is little point in attempting to find a set of parameters which gives an exact fit to our experimental profile. The foregoing analysis does show, however, that a good fit can be obtained within the range of possible values of the parameters involved. It is interesting to note that the fairly large variations which would be expected to occur in the eddy diffusion profile provide a convenient explanation for the considerable variability observed in the experimental profiles.

An alternative for the bottomside sink of Na has been proposed recently in the form of dust particles, also of meteoroid origin, on which the sodium compounds would condense (Hunten et al., 1980). The loss function given in terms of a cross-section per unit volume in

Hunten et al. (1980), is a function of several parameters of the dust particles. Although details of Hunten's (1981) model have been criticized by Clemesha et al. (1981), condensation of sodium or its compounds on aerosol particles could eventually represent an additional or alternative Na loss. We hope to include this, as well as tidal oscillations, as the subject of a future paper.

#### Summary

We have shown that the Na layer chemistry proposed by Liu and Reid (1979) results in a large daytime increase in sodium density on the bottomside of the layer, not observed in the daytime measurements. In a modification of this model, production of NaOH is treated as a sink for free sodium, which is equivalent to including reactions of NaOH with chlorine, as suggested by Murad and Swider (1979), producing the stable compound NaCl. We have also updated the reaction rates believed to be important for the Na chemistry and determined the sensitivity of the model to changes in reaction rates and the eddy diffusion coefficient. We have tested this new model in a simulation of the 24 hr variations of sodium obtaining results in much better agreement with experiment.

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### Figure captions

Fig. 1. Basic integration cycle of the continuity equation for each time step.

Fig. 2. Density profiles of the basic atmospheric constituents in the height region between 70 and 110 km calculated for noon (continuous lines) and midnight (dashed lines).

Fig. 3. Ozone density variations with time at selected heights. There is a small height region in which there is considerable variation during day and nighttime.

Fig. 4. Diurnal variations of Na obtained with the previous Na model. The twilight variation as well as the layer obtained for noon do not agree with experimental results.

Fig. 5. Diurnal variations of Na obtained with the new Na model, in much better agreement with experiment. Cases b and c show the sensitivity of the model to changes of  $K_7$ , decreased by a factor of 10 in b and zeroed in c.

Fig. 6. Static calculation of the sodium layer to show the effect of changing the eddy diffusion coefficient and the displacement of the peak of the layer. The dashed lines show the Na layer calculated in case a of the previous Figure, for comparison.

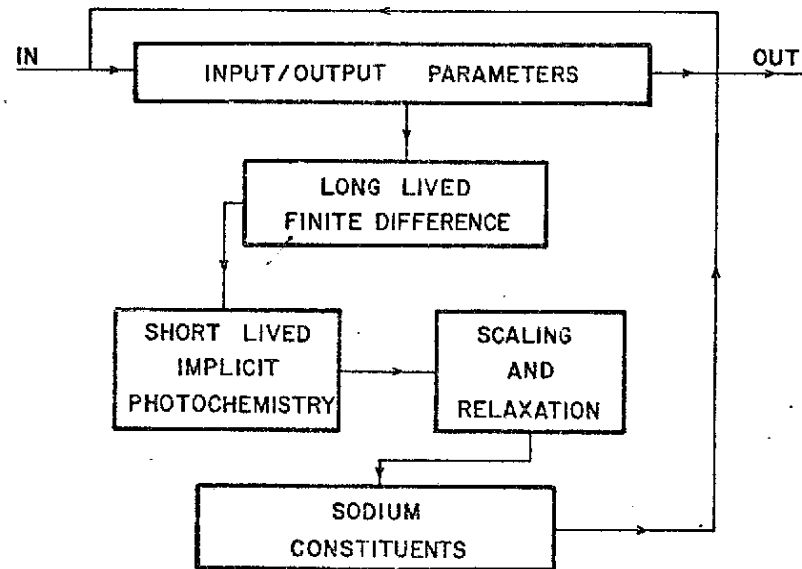


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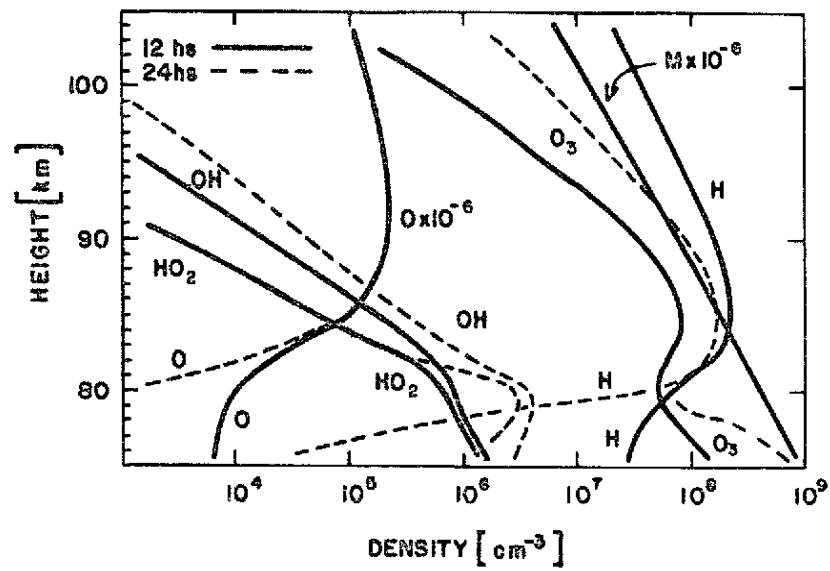


Fig. 2. Density profiles of the basic atmospheric constituents in the height region between 70 and 110 km calculated for noon (continuous lines) and midnight (dashed lines).

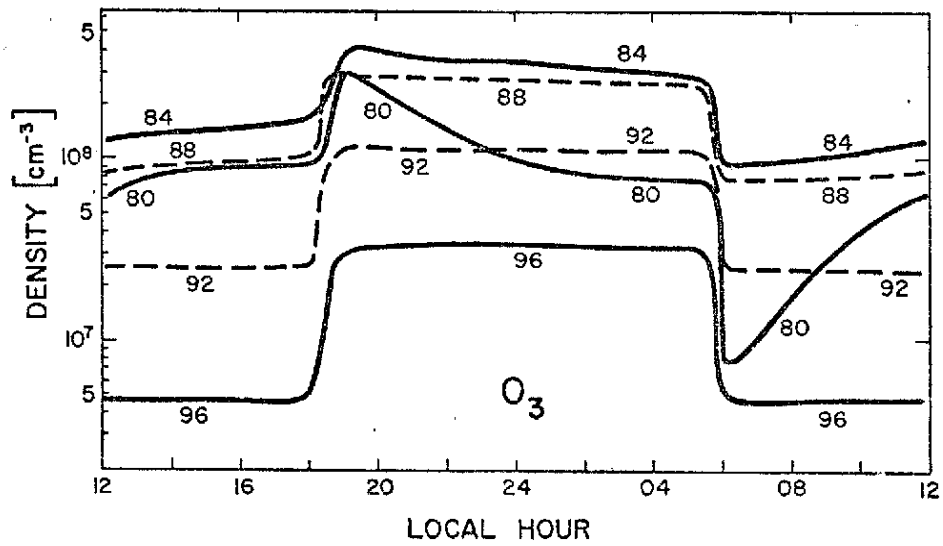


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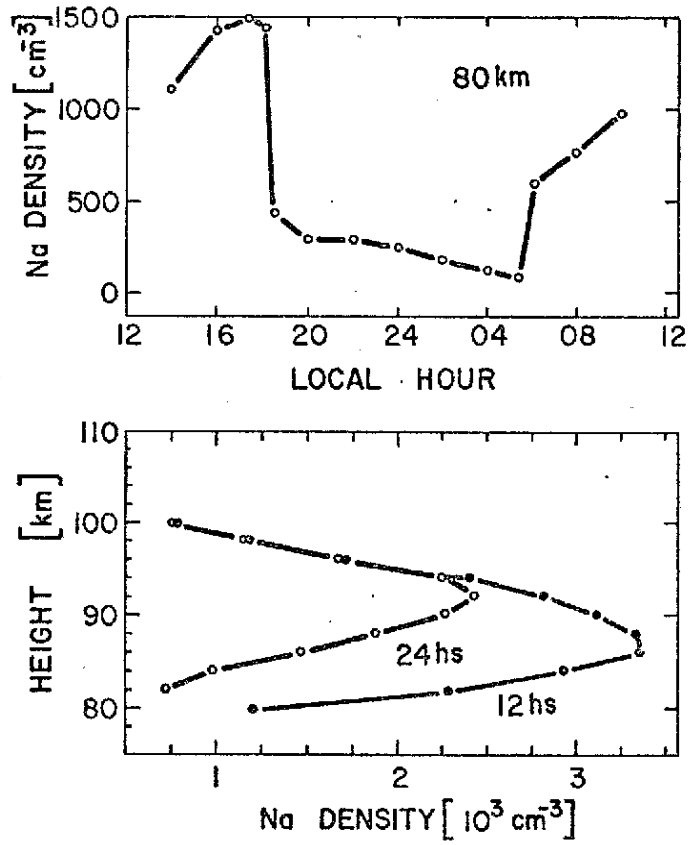


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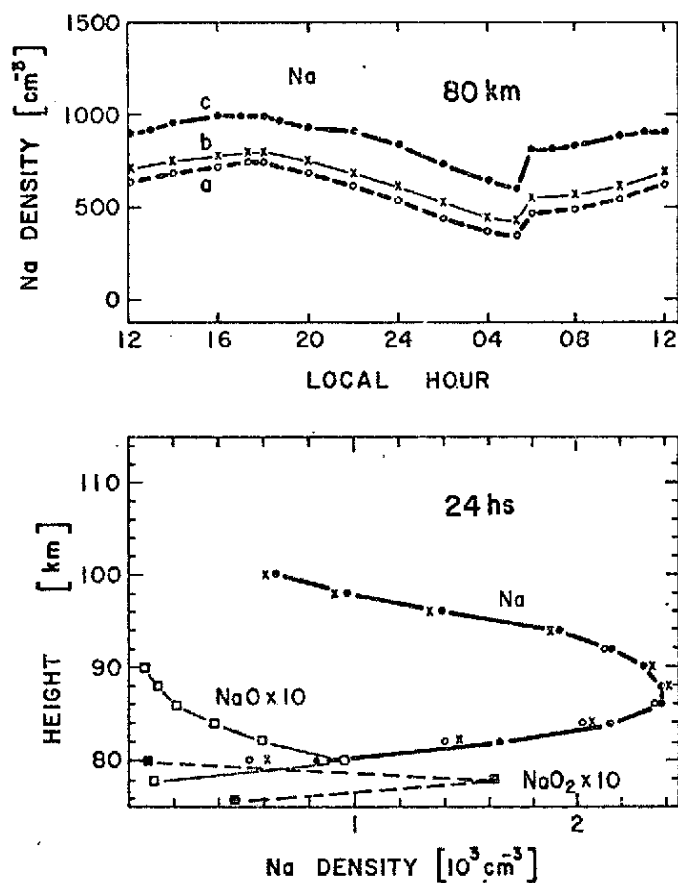


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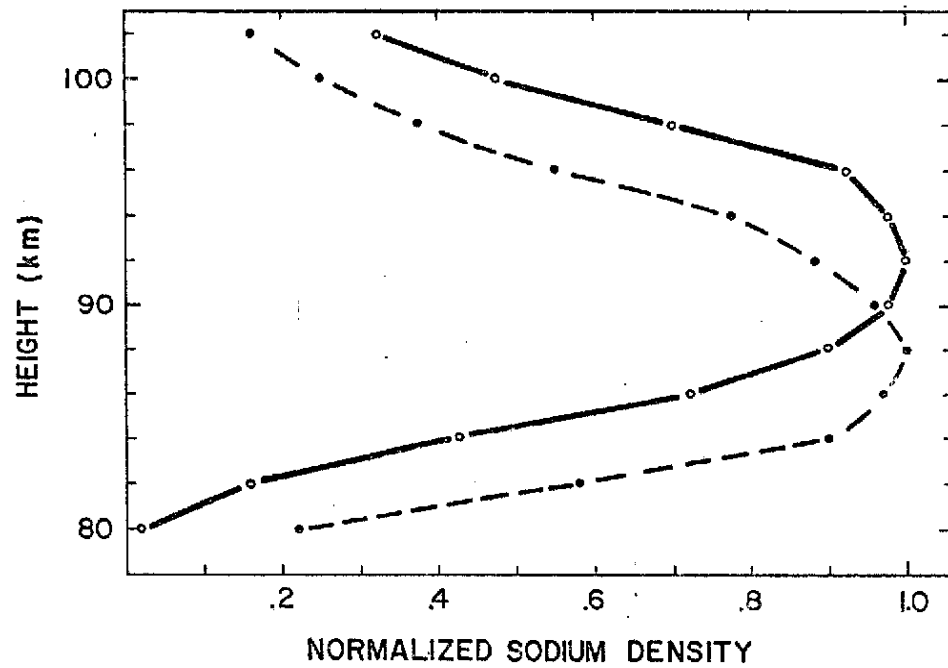


Fig. 6. Static calculation of the sodium layer to show the effect of changing the eddy diffusion coefficient and the displacement of the peak of the layer. The dashed lines show the Na layer calculated in case a of the previous Figure, for comparison.

Table 1. Reactions and rates for the atmospheric model

	Reaction	Rate	Reference
1	$O+O+M$	$2.76 \times 10^{-34} \exp(710/T)$	Campbell and Thrush (1967)
2	$O+O_2+M$	$6.6 \times 10^{-35} \exp(510/T)$	Hampson and Garvin (1978)
3	$O+O_3$	$1.9 \times 10^{-11} \exp(-2300/T)$	Hampson (1973)
4	$H+O_2+M$	$2.1 \times 10^{-32} \exp(290/T)$	Hampson and Garvin (1975)
5	$H+O_3$	$1.0 \times 10^{-10} \exp(-516/T)$	Clyne and Monkhouse (1977)
6	$OH+O$	$4.2 \times 10^{-11}$	Wilson (1972)
7	$OH+O_3$	$1.5 \times 10^{-12} \exp(-1000/T)$	Hudson (1977)
8	$HO_2+O$	$3.5 \times 10^{-11}$	Burrows et al. (1977)
9	$HO_2+O_3$	$3.3 \times 10^{-14} \exp(-1000/T)$	Simonaitis and Heicklen (1973)
10	$O(^1D)+H_2O$	$2.1 \times 10^{-10}$	Streit et al. (1976)
11	$OH+HO_2$	$3 \times 10^{-11}$	Hudson (1977)
12	$H+H+M$	$8.3 \times 10^{-33}$	McEwan and Phillips (1975)
13	$H_2+O$	$5.0 \times 10^{-13} T^{1/2} \exp(-4400/T)$	Nicolet (1971)
14	$H+HO_2$	$4.2 \times 10^{-11} \exp(-350/T)$	Baulch et al. (1972)
15	$H+HO_2$	$4.2 \times 10^{-10} \exp(-950/T)$	Lloyd (1974)
16	$H+HO_2$	$8.3 \times 10^{-11} \exp(-500/T)$	Lloyd (1974)
17	$O(^1D)+H_2$	$1.0 \times 10^{-10}$	Davidson et al. (1977)
18	$HO_2+HO_2$	$3.0 \times 10^{-11} \exp(-500/T)$	Hampson (1973)
19	$OH+H_2O_2$	$1.0 \times 10^{-11} \exp(-750/T)$	Hudson (1977)
20	$OH+OH$	$1.4 \times 10^{-12}$	Clyne and Down (1974)
21	$O+H_2O_2$	$2.75 \times 10^{-12} \exp(-2125/T)$	Davis et al. (1974)
22	$H+H_2O_2$	$2.3 \times 10^{-12} \exp(-1400/T)$	Hampson and Garvin (1978)
23	$O(^1D)+O_3$	$1.2 \times 10^{-10}$	Streit et al. (1976)
24	$O(^1D)+N_2$	$3.0 \times 10^{-11}$	Streit et al. (1976)
25	$H+OH+M$	$6.1 \times 10^{-26} / T^2$	McEwan and Phillips (1975)

Table 2. Reactions and rates for sodium as used in the static model of paper I.

Reactions				Rates
1	$\text{Na} + \text{O}_3$	$\rightarrow$	$\text{NaO} + \text{O}_2$	$3.3 \times 10^{-10}$
2	$\text{Na} + \text{O}_2 + \text{M}$	$\rightarrow$	$\text{NaO}_2 + \text{M}$	$8.4 \times 10^{-34} \exp(290/T)$
3	$\text{Na} + \text{HO}_2$	$\rightarrow$	$\text{NaOH} + \text{O}$	$7.0 \times 10^{-12}$
4	$\text{NaO} + \text{O}$	$\rightarrow$	$\text{Na} + \text{O}_2$	$1.6 \times 10^{-10}$
5	$\text{NaO} + \text{O}_3$	$\rightarrow$	$\text{NaO}_2 + \text{O}_2$	$5.0 \times 10^{-11}$
6	$\text{NaO} + \text{HO}_2$	$\rightarrow$	$\text{NaOH} + \text{O}_2$	$1.0 \times 10^{-11}$
7	$\text{NaO}_2 + \text{H}$	$\rightarrow$	$\text{NaOH} + \text{O}$	$7.0 \times 10^{-12}$
8	$\text{NaO}_2 + \text{OH}$	$\rightarrow$	$\text{NaOH} + \text{O}_2$	$1.0 \times 10^{-11}$
9	$\text{NaOH} + \text{H}$	$\rightarrow$	$\text{Na} + \text{H}_2\text{O}$	$2.0 \times 10^{-11} \exp(-800/T)$

Table 3. Updated reactions and rates for sodium used in this model.

	Reactions			Rates
1	Na + O <sub>3</sub>	→	NaO + O <sub>2</sub>	3.4 x 10 <sup>-10</sup> (a)
2	Na + O <sub>2</sub> + M	→	NaO <sub>2</sub> + M	6.76 x 10 <sup>-34</sup> exp(290/T) (b,d,j)
3	Na + HO <sub>2</sub>	→	NaOH + O	1.4 x 10 <sup>-11</sup> (f,g,j)
4a	NaO + O	→	Na + O <sub>2</sub>	6.6 x 10 <sup>-11</sup> (a)
4b	NaO + O	→	Na* + O <sub>2</sub>	3.3 x 10 <sup>-11</sup> (a)
5a	NaO + O <sub>3</sub>	→	NaO <sub>2</sub> + O <sub>2</sub>	3.5 x 10 <sup>-11</sup> (i,j)
5b	NaO + O <sub>3</sub>	→	Na + 2O <sub>2</sub>	1.05 x 10 <sup>-10</sup> (i,j)
6	NaO + HO <sub>2</sub>	→	NaOH + O <sub>2</sub>	1.0 x 10 <sup>-11</sup> (c)
7	NaO <sub>2</sub> + H	→	NaOH + O	1.4 x 10 <sup>-11</sup> (f,g,j)
8	NaO <sub>2</sub> + OH	→	NaOH + O <sub>2</sub>	1.0 x 10 <sup>-11</sup> (c)
9	NaO <sub>2</sub> + O	→	NaO + O <sub>2</sub>	2.5 x 10 <sup>-11</sup> (h,g,j)
10	NaOH + Cl	→	NaCl + OH	(e)

(a) Bates and Ojha (1980); (b) Carabetta and Kaskan (1968);  
(c) Liu and Reid (1979); (d) Hampson and Garvin (1975);  
(e) Murad and Swider (1979); (f) Lloyd (1974); (g) Megie (1976);  
(h) Burrows et al. (1977); (i) Kolb and Elgin (1976); (j) This work.



Table 4. Loss terms for sodium from equation 3 and time constant  $\tau$  calculated at midnight. Reaction rates are from Table 3.

HEIGHT (km)	HO <sub>2</sub>	L O S K <sub>3</sub>	S S X <sub>2</sub> HO <sub>2</sub>	T E K <sub>6</sub>	R M S X <sub>3</sub> H K <sub>7</sub>	(s <sup>-1</sup> ) X <sub>3</sub> OH K <sub>8</sub>	$\tau$ (hs)
76	1.82	10 <sup>-5</sup>	3.66	10 <sup>-4</sup>	1.68	10 <sup>-3</sup>	2.78 10 <sup>-1</sup> 9.93 10 <sup>-4</sup>
80	3.43	10 <sup>-5</sup>	4.37	10 <sup>-6</sup>	9.25	10 <sup>-6</sup>	5.31 10 <sup>-7</sup> 5.70
86	2.18	10 <sup>-7</sup>	1.39	10 <sup>-9</sup>	6.68	10 <sup>-8</sup>	8.24 10 <sup>-11</sup> 0.75 10 <sup>2</sup>
90	2.13	10 <sup>-8</sup>	4.74	10 <sup>-11</sup>	5.78	10 <sup>-9</sup>	2.40 10 <sup>-12</sup> 1.03 10 <sup>4</sup>
96	9.09	10 <sup>-10</sup>	3.82	10 <sup>-13</sup>	1.15	10 <sup>-10</sup>	8.89 10 <sup>-15</sup> 2.71 10 <sup>5</sup>

Table 5. Loss terms for sodium from equation 3 and time constant  $\tau$  calculated at noon. Reaction rates are from Table 3.

HEIGHT (km)	HO <sub>2</sub>	L O S K <sub>3</sub>	S S X <sub>2</sub> HO <sub>2</sub>	T E K <sub>6</sub>	R M S X <sub>3</sub> H K <sub>7</sub>	(s <sup>-1</sup> ) X <sub>3</sub> OH K <sub>8</sub>	$\tau$ (hs)
76	1.95	10 <sup>-5</sup>	1.05	10 <sup>-6</sup>	1.75	10 <sup>-6</sup>	6.89 10 <sup>-8</sup> 1.25 10 <sup>1</sup>
80	8.82	10 <sup>-6</sup>	1.46	10 <sup>-7</sup>	5.72	10 <sup>-7</sup>	5.51 10 <sup>-9</sup> 2.91 10 <sup>1</sup>
86	2.18	10 <sup>-7</sup>	4.69	10 <sup>-10</sup>	1.63	10 <sup>-8</sup>	7.57 10 <sup>-12</sup> 1.19 10 <sup>3</sup>
90	2.18	10 <sup>-8</sup>	1.27	10 <sup>-11</sup>	1.31	10 <sup>-9</sup>	1.53 10 <sup>-13</sup> 1.20 10 <sup>4</sup>
96	9.34	10 <sup>-10</sup>	5.31	10 <sup>-14</sup>	4.32	10 <sup>-11</sup>	5.02 10 <sup>-16</sup> 2.84 10 <sup>5</sup>