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16. Summary/Notes Atmospheric sodium distributions derived according to the recent Liu and Reid model for the sodium photochemistry, which includes reac tions leading to the formation of NaOH, are compared with lidar measurements and good agreement is found. Attempts to reproduce the observed vertical distribution of atmospheric sodium by photochemical models are hampered by a lack of precise knowledge of the appropriate reaction rates. It is easy to show, however, that on the basis of the usual Chapman photochemistry only a most unreasonable choice of rate coefficients would lead to the observed vertical distribution, even when a source is included in the model. Models of this sort, apparently compatible with the observations, have invariably contained the implicit assumption of an unexplained sink, unreasonable distributions of the reacting species, or have not been in equilibrium. A number of these models also suffer from the defect of leading to values of the sodium airglow emission much smaller than that observed. It is concluded that, unlike previous models, the Liu and Reid model for the sodium photochemistry is capable of explaining both the observed vertical distribution of sodium, and the intensity of the sodium nightglow.

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THE ATMOSPHERIC NEUTRAL SODIUM LAYER, I, RECENT MODELING COMPARED TO MEASUREMENTS

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ABSTRACT

Atmospheric sodium distributions derived according to the recent Liu and Reid model for the sodium photochemistry, which includes reactions leading to the formation of NaOH, are compared with lidar measurements, and good agreement is found. Attempts to reproduce the observed vertical distribution of atmospheric sodium by photochemical models are hampered by a lack of precise knowledge of the appropriate reaction rates. It is easy to show, however, that on the basis of the usual Chapman photochemistry only a most unreasonable choice of rate coefficients would lead to the observed vertical distribution, even when a source is included in the model. Models of this sort, apparently compatible with the observations, have invariably contained the implicit assumption of an unexplained sink, unreasonable distributions of the reacting species, or have not been in equilibrium. A number of these models also suffer from the defect of leading to values of the sodium airglow emission much smaller than that observed. It is concluded that, unlike previous models, the Liu and Reid model for the sodium photochemistry is capable of explaining both the observed vertical distribution of sodium, and the intensity of the sodium nightglow.

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INTRODUCTION

Monitoring of the sodium nightglow intensity as well as the detection of sodium densities as a function of height through laser radar measurements have greatly increased our knowledge of the morphology of the atmospheric sodium layer. The theoretical treatment of the sodium layer, and of its alkaline metal relatives, has in comparison been slow to develop, probably because of our ignorance of appropriate reaction rates. This makes any theoretical treatment somewhat speculative. However, in spite of this difficulty, the possibility of gaining a better insight into the physics of the layer formation, together with our improved knowledge of the layer morphology, warrants the attempt.

Recently Simonich et al. (1979), published a comprehensive report on the sodium layer morphology, based on laser radar sounding at 23°S, and Kirchhoff et al. (1979) discussed in some detail the Na D line intensities and variations. Several features which are consistently observed have been tentatively interpreted in terms of sodium layer theory, but a thorough comparison between theory and experiment, especially when D line intensity variations are also taken into account, has not yet been made.

The most recent and apparently most successful neutral sodium layer theory seems to be that of Liu and Reid (1978). These authors proposed a new set of reactions, including in the Na photo-

chemistry the up to then ignored NaOH molecule. They have calculated the height distributions of the Na constituents, showing that NaOH is dominant below the Na peak. The Na layer itself, in the height region of the laser radar measurements between 70 and 110 km, however, was shown with very little detail and was not compared to measured data. The main purpose of this paper is to see to what extent this static model can explain the observed sodium layer. In a following paper we test the sensitivity of the model to changes in the input parameters, and calculate the nocturnal variation that results from a dynamic, time dependent mesospheric model.

The calculations assume that sodium is injected into the atmosphere through meteor ablation, that it is transformed into NaO, NaO $_2$, and NaOH through chemical reactions, and that equilibrium is maintained by a downward flux of Na constituents, equal to the meteoric influx, finally lost in a lower atmosphere sink. This model of atmospheric sodium, which clearly differs considerably from purely photochemical models, appears to have been introduced by Mitra (1973). To remind us that the model includes an extraterrestrial influx of sodium, besides photochemistry, we refer to it as the Flux-model.

BACKGROUND ON ATMOSPHERIC SODIUM

Early research on atmospheric sodium dates back to the mid 1930's, when extensive photometric observations of the sodium line at 5893Å were made during the night and twilight (Bernard, 1938a; Cabannes et al., 1938). Soon after the discovery of the line in the airglow, neutral sodium atoms were identified as being responsible for its emission (Bernard, 1938b). Dejardin (1938) appears to have been the first to speculate as to whether the origin of the sodium is cosmic or terrestrial, Cabannes et al. (1938) favoring the extraterrestrial hypothesis. Subsequent airglow measurements led to the identification of resonant scattering by sunlight as the physical process responsible for the excitation of the Na atoms during twilight. In the late 50's, Chamberlain (1956) begun a series of papers entitled "Resonance scattering by atmospheric sodium", which set out the theory which enables sodium

densities and abundances to be calculated from twilight observations at 5893%. At about the same time, sodium dayglow measurements were begun.

Extensive dayglow measurements were carried out using a magnetic scanning resonance cell photometer (e.g. Blamont and Donahue, 1964), showing essentially what was interpreted as a daytime enhancement of sodium abundance over that measured during twilight, a result that is inconsistent with more recent laser radar measurements in the daytime (Gibson and Sandford, 1972). Chanin and Goutail (1975) have commented on these dayglow measurements, suggesting that they might have involved large errors because they did not take the earth's albedo into account.

During the past 10-years, a great deal of detailed information on the nocturnal behavior of the atmospheric sodium layer has been obtained by the laser radar technique (Sandford and Gibson, 1970; Blamont et al., 1972; Kirchhoff and Clemesha, 1973; and more recently Megie et al., 1978; and Simonich et al., 1979), which is able to measure the vertical distribution of sodium throughout the night. On the other hand, little progress has been achieved in terms of laboratory testing and measuring the reaction rates of the proposed Na chemistry.

Chapman (1939) laid down the first photochemical theory for the atmospheric Na, in which the now well known Chapman mechanism describes the closed circuit reaction scheme from ground state to excited and back to ground state sodium. Several other reactions have been proposed (see review by Kvifte, 1973) but the main problem remains the absence of laboratory measurements of reaction rates. Early model calculations (Hunten, 1967) have estimated reaction rates from known reactions involving hydrogen, allowing for a small correction due to the difference in mass between Na and H.

More recently, mass spectrometer measurements of positive ions in the stratosphere by Arnold et al. (1977) and Arnold et al. (1978) indicated the presence of a complex new type of ion cluster. Ferguson (1978) has shown that most of the detected ion masses can be interpreted

as being NaOH clusters of the form ${\rm NaOH_2}^+({\rm NaOH})_{\rm m}$ $({\rm H_2O})_{\rm n}$, and made first order calculations to show that the NaOH concentration at a height of 40 km should be of the order of 10^5 cm $^{-3}$. Thus a new sodium compound, NaOH, has been added to the generally accepted species NaO, NaO₂, and Na $^+$, which are expected to exist around the well known neutral sodium layer peak at about 94 km. As we have mentioned already, Liu and Reid (1978), based on Ferguson's suggestion, calculated the height distribution of the sodium compounds, showing that the sodium hydroxide molecule may be dominant below the peak of the neutral sodium layer.

SODIUM LAYER MODELING

Basic sodium photochemistry rests on the original Chapman mechanism which assumes photochemical equilibrium between oxidation by ozone, producing sodium monoxide,

$$Na + O_3 \rightarrow NaO + O_2$$
, k_1

followed by reduction of the oxide to produce excited sodium in the ^{2}P state.

$$Na0 + 0 \rightarrow Na (^{2}P) + 0_{2}, k_{4}$$

which emits the Na D lines

Na
$$(^{2}P) \rightarrow Na (^{2}S) + hv$$

In the absence of a Na source, vertical diffusion would lead to a situation of mixing equilibrium where the mixing ratio of total sodium, i.e., the concentration of sodium plus its compounds relative to the major atmospheric constituents, would be independent of height. Under these circumstances the sodium densities are given by

$$[Na] = K_0 \exp(-(h-h_0)/H_a)/D$$

where

$$D = (1+[0_3] k_1/[0] k_4)$$

with K_0 equal to [Na] + [Na0] at height h_0 , and where the brackets are indicative of densities. At the top of the layer the free sodium has a scale height H_a equal to that of the main atmosphere. The calculated distribution of Na is shown in curve \underline{a} of Figure 1, where the average measured profile Na_i is also shown for comparison. The [0] and $[0_3]$ profiles used are shown in Figure 2, together with other parameters discussed later. For the normalization we used $Na_0 = 3.5 \times 10^3$ cm⁻³ at $h_0 = 94$ km, and the atmospheric scale height $H_a = 6$ km. The reaction rates are given in Table 1.

It is interesting to note that the sodium D line emission intensity, calculated through the simplified chemistry shown so far, is compatible with the measured values. The distribution of Na with height, however, is quite inadequate, as can be seen from Figure 1. A better fit between the model and experimental profiles can be achieved by including the effect of ionization above the layer peak, but no reasonable choice of the parameters involved will provide even an approximate fit to the observed layer below a height of about 94 km. The basic problem of this simplified model is that the sodium is almost entirely in its free state over the entire range of the observed layer.

The calculated Na profile is considerably modified if we abandon the constant mixing ratio hypothesis and include a source near to the peak of the layer, and a sink lower down in the atmosphere. This approach has been investigated by Gadsden (1970), Mitra (1973) and Fiocco et al. (1974). Both Gadsden and Mitra's models involve implicit, but unexplained, sinks only a few km below the peak of the layer, and thus appear to be of little value in increasing our understanding of the sodium distribution. Fiocco et al.'s model involves a sink at the more reasonable height of 67 km, but the profiles which they show do not appear to be in diffusive equilibrium.

We have next calculated the effect of including a source at 98 km and a sink at 71 km, along with the Chapman photochemistry. The results are given as curve b in Figure 1, for a flux of 7×10^3 atoms cm⁻² s⁻¹, and diffusion coefficient as shown in Figure 2. It is clear from Figure 1 that although the inclusion of the flux is an improvement over the assumption of mixing equilibrium, the calculations are still quite different from the experimental profile.

In view of the above discussion we are forced to the conclusion that either the ratio of the rate coefficients k_1/k_4 is out by several orders of magnitude, or some other mechanism is required to decrease the free sodium concentration below 90 km. Ferguson's (1978) suggestion that NaO and NaO₂ are converted to NaOH appears to be the only mechanism which has so far been presented.

At this point it should be mentioned that Megie and Blamont's (1977) model results apparently contradict the above conclusion. These workers present a dynamic model in which they use the experimental Na profile as a starting point. The model includes the Chapman chemistry and diffusion, but no source. Since they find less than 3% change in free sodium abundance after a period of 48 hours of model simulation they conclude that their model satisfactorily represents the sodium layer. However, at all heights below 90 km, this model involves a large positive vertical gradient of total sodium, Na + NaO and thus cannot be in mixing equilibrium (or quasi mixing equilibrium if a source is also considered), suggesting that the photochemistry is incomplete. The inclusion of the NaOH molecule in the Na photochemistry, as described in the following section, can satisfactorily solve this problem.

PHOTOCHEMISTRY

It will be assumed that the sodium photochemistry during the nighttime is determined by the set of reactions given in Table 1. Reactions (1) and (4) correspond to the previously mentioned Chapman mechanism, for which the reaction rates have been updated by Kolb and

Elgin (1976). Reaction (2) seems to be the only one for which there has been a laboratory measurement of the rate, but unfortunately, the value quoted by Carabetta and Kaskan (1968) is valid in the temperature range from 1420 to 1600 K. The remaining reactions have been proposed by Ferguson (1978) to account for the existence of NaOH, as already mentioned, with the exception of reaction (5), included by Liu and Reid (1978), from which we use the estimated reaction rates.

In terms of the neutral sodium density Na, the equilibrium concentrations of the constituents NaO, NaO $_2$ and NaOH, can be written as

$$[Na0] / [Na] = [03] k1/([0]k4 + [03]k5 + [H02]k6)$$

$$[NaO_2] / [Na] = ([O_2] [M] k_2 + [O_3] k_5 [NaO] / [Na]) / P$$

$$[NaOH] / [Na] = (P [NaO2]/[Na] + [HO2]k3 + [HO2]k6 [NaO]/[Na])/[H]k9$$

with

$$P = [H]k_7 + [OH]k_8$$

The ratio $[Na^+]/[Na]$ is based on measured values, namely $[Na^+]$ from Zbinden et al. (1975), and Narcisi and Bailey (1965), and [Na] from data of Simonich et al. (1979).

CHOICE OF MODEL ATMOSPHERE

Not enough information based on actual measurements is yet available for the main input parameters. The choice of input density profiles must therefore be arbitrary to some degree. We have tried to minimize this by using locally measured parameters.

After choosing an appropriate shape for the atomic oxygen density profile, the maximum density of 0 is calculated from measurements of the 0I 5577 $^{\circ}$ line intensities, obtained at our latitude (23.2 $^{\circ}$ S) by

Takahashi et al. (1977). Details of this procedure can be found in Reed and Chandra (1975). The atomic oxygen profile so obtained can be seen in Figure 2. It is very close to the one reported by Moreels et al. (1977), and only slightly less, at the peak, than the measurements of Dickinson et al. (1974).

For ozone we adopted the density profile for 25.8° N, 43.1° W from data of Hays and Roble (1973). The hydrogen density is then calculated assuming equilibrium between production and loss of ozone. The dominant reactions for this equilibrium between 70 and 110 km, at night, are

$$0 + 0_2 + M \rightarrow 0_3 + M$$
 (R 10)

and

$$H + O_3 \rightarrow OH + O_2$$
 (R 11)

Reaction rates are $k_{10}=8.2 \times 10^{-35} \exp(455/T)$ according to Benson and Axworthy (1965), and $k_{11}=1.5 \times 10^{-12} \, T^{1/2}$ according to Nicolet (1971). The calculated H densities, as can be seen from Figure 2, are well within the ranges of magnitudes reported in the literature. Peak density is close to that of the winter profile of Shimazaki and Laird (1972), which is a factor of four less than that of Moreels et al. (1977).

The temperature profile has been extrapolated from information in the US Standard Atmosphere Supplements, 1966, and from local measurements of the OH (8,3) rotational temperature (Takahashi et al., 1974). The 0_2 and N_2 profiles are calculated according to this temperature variation. The less reactive species OH and $H0_2$ are taken from Shimazaki and Laird (1972), and the eddy diffusion coefficient is based on data of Blum and Schuchardt (1978). The whole set of chosen input parameters is shown in Figure 2. The measured average sodium profile, Na_1 , is also shown.

The relative importance of production and loss terms, according to the reactions of Table 1 and the input data of Figure 2, can be seen in Figure 3.

For NaO at heights above about 76 km one can see that production is dominated by reaction (1) and loss by reaction (4). Thus, in the absence of dynamic effects, and in equilibrium

$$[Na0] = [Na] [0_3]k_1/[0]k_4$$

which is generally used to calculate the sodium nightglow intensity, as mentioned before.

For NaO_2 the production below about 90 km is larger through reaction (5), but above this height the contribution obtained through reaction (2) is about the same as that of (5). Loss is almost entirely dominated by reaction (7), such that in equilibrium and below 90 km

$$[NaO_2] = [NaO] [O_3]k_5/[H]k_7$$

For NaOH, above about 76 km, reactions (7) and (9) dominate such that

$$[NaOH] = [NaO2]k7/k9$$

It should be noted, from the production or loss curves for Na and NaO of Figure 3, that, in comparison to the rates for NaO $_2$ and NaOH, the main rates for Na and NaO are larger by a factor of nearly 3 orders of magnitude. The time constant for the loss of Na at 90 km is close to 30 sec., while the diffusion time constant is of the order of a few hours. A strong link is therefore estabilished between NaO and Na.

The chemical transformation between source and sink can be conveniently followed through the diagram of Figure 4. Ablation by meteors

(Gadsden, 1968) represents the Na source effective above the peak of the layer. A sink is assumed in the stratosphere. This could conveniently be represented by the transformation of sodium constituents into cluster ions, as suggested by Ferguson (1978), although Murad and Swider (1979) believe that NaOH will be destroyed in the stratosphere by reactions with chlorinated species. The permanent transport between source and sink is maintained by eddy diffusion. During the trip from source to sink the comparatively rapid oxidation and reduction of sodium produce the Na D lines; NaO_2 is formed from Na and NaO, and finally NaO_2 produces NaOH. Summarizing, the atmospheric sodium layer is assumed to be formed through the deposition of extraterrestrial material into the upper atmosphere, where photochemistry and eddy diffusion then control the shaping of the Na layer, while a constant flux of sodium containing material is dumped into the stratospheric sink.

The height variation of sodium density is obtained from the equation of total density \mathbf{n}_{T}

$$n_T = [Na] + [NaO] + [NaO_2] + [NaOH] + [Na^+]$$

the photochemical relations implied in Table 1, and the fact that the downward flux of total sodium must be a constant, independent of height (Thomas, 1974),

$$\phi_T = \sum \phi_i = S_0$$

Some sodium parameters of interest are shown in Table 2. Those parameters that can be varied in the model, and values adopted as initial or boundary conditions are as follows.

The value of input flux, S_0 , adopted is 7.5 x 10^3 cm $^{-2}$ s $^{-1}$. This is about the average value as quoted in the literature, as can be seen from Table 2. The source is assumed to deposit the entire flux above a certain height, adopted as 98 km. For simplicity the densities of all sodium compounds are assumed to be zero at the sink height of 30 km. The assumption of finite densities at this height would have a negligible effect on the densities computed above 75 km where the free sodium exists.

From what has been said so far it is clear that a neutral sodium layer theory can be accurate only from a little above the peak of the layer downwards. In our case this threshold of the flux model is at about 98 km. For a model to succeed in the upper half of the layer, where the scale height is of the order of only 2 km, the sodium ion chemistry must be included, the most recent treatment of which seems to be that of Richter and Sechrist (1979). However, the inclusion of the ion chemistry alone will probably not be enough, because of transport effects of electrodynamic origin. In this model we have included the effects of ionization in a semi-empirical manner by simply assuming that a fixed fraction of the free sodium is ionized at a given height. This fraction was determined from the Na⁺ measurements of Zbinden et al. (1975), taken together with the Na measurements of Simonich et al. (1979).

RESULTS AND DISCUSSION

The calculated Na profile is shown in Figure 5, where it is compared to Nai, the laser radar measured average profile. The profiles for NaO, NaO2, NaOH and Na $^+$ are also shown, as well as the production of excited sodium, Na $^+$. The intensity of the D2 line is calculated as 86 R, a value that is representative for equinox conditions, and the Na abundance is 4.1 x 10^9 atoms cm $^{-2}$. The value of S0 has been chosen within the ranges of acceptable values (Table 2), to make the calculated peak sodium density equal to that of our average experimental profile. The success of the flux-model may be judged by the goodness of fit to the experimental profile at heights below the peak.

The calculated profile fits the experimental measurements quite well. It is interesting to note that the model reproduces, to some extent, the secondary peak at about 85 km frequently observed in the measurements (Simonich et al., 1979). This secondary peak is a regular feature of the sodium layer at our latitude, and is most prominent in the early evening hours. Even when profiles taken at this time are averaged over many days the secondary peak is frequently visible.

The usual representation of the H density profile is one that has a peak density around 80-84 km, with decreasing densities above and below the peak. A small region of minimum density, above the maximum at 81 km, is therefore, perhaps, peculiar. Nevertheless, the calculated minimum in Na density is, of course, due to a minimum in the H density which, so it appears, occurs in the height region where 0_3 has a small maximum. It is interesting to note that the H profile deduced by Evans and Llewellyn (1973) shows two small density minima at heights of about 83 and 89 km.

The calculated layer is rather insensitive to changes of source height. Variations of a few kilometers in this parameter cause little change in the calculated layer, and these occur mainly above the peak. Changes in sink height have a negligible effect.

The sensitivity of the flux model with respect to changes in input parameters and possible situations that simulate seasonal variations are discussed in a following paper, where the nocturnal variations are also calculated by a dynamic time dependent mesospheric model, and compared to the measured variations.

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FIGURE CAPTIONS

- Fig. 1 Calculated sodium density profile assuming that sodium constituents are Na and NaO, only. Case a is for conditions of mixing equilibrium and case b includes a downward flux between a source above 98 km and a sink at 71 km. Na; is the measured average profile.
- Fig. 2 Atmospheric parameters adopted as input for the model calculations. The eddy diffusion coefficient $K_{\mbox{dif}}$ and the temperature T are given in units of cm² s⁻¹ and K, respectively.
- Fig. 3 Production and loss rates as a function of height for the four sodium constituents.
- Fig. 4 Block diagram showing the transformations of sodium constituents between source and sink.
- Fig. 5 Flux-model sodium density profile calculated with the input parameters of Figure 2. The production of excited sodium in units of ${\rm cm}^{-3}~{\rm s}^{-1}$ is designated by Na*, and Na; is the average measured profile shown for comparison.

TABLE CAPTIONS

- Table 1 Chemical reactions involving sodium compounds during the nighttime.
- Table 2 Sodium parameters.

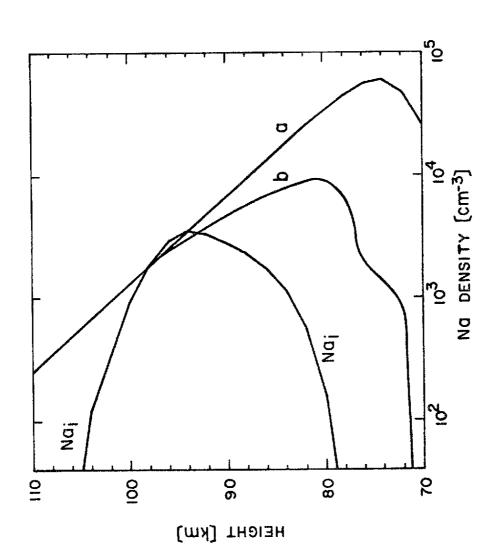


Fig. 1 - Calculated sodium density profile assuming that sodium constituents are Na and NaO, only. Case a is for conditions of mixing equilibrium and case b includes a downward flux between a source above 98 km and a sink at 71 km. Nai is the measured average profile.

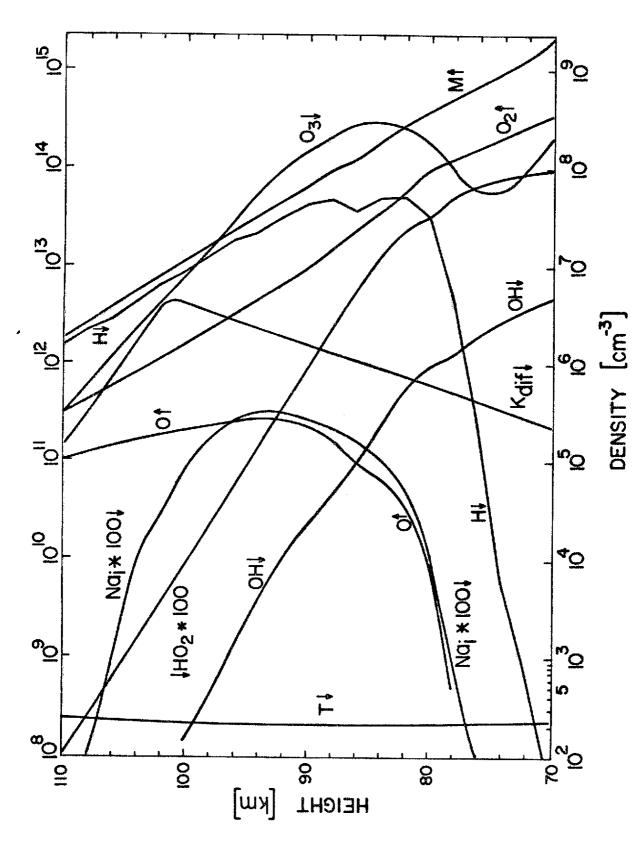


Fig. 2 - Atmospheric parameters adopted as input for the model calculations. The eddy diffusion coefficient K_{dif} and the temperature T are given in units of cm² s⁻¹ and K, respectively.

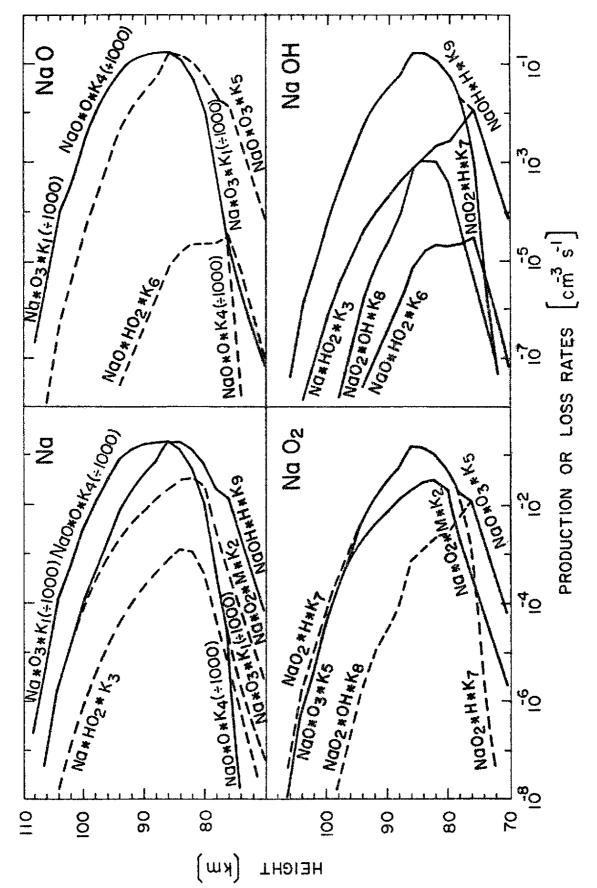


Fig. 3 - Production and loss rates as a function of height for the four sodium constituents.

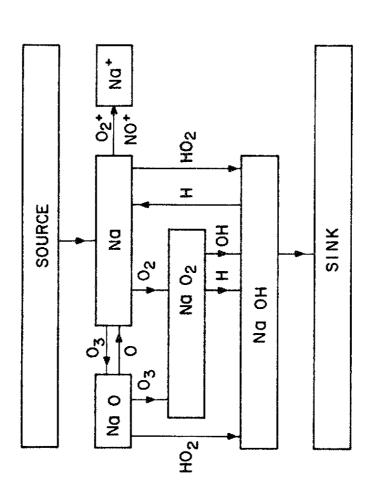


Fig. 4 - Block diagram showing the transformations of sodium constituents between source and sink.

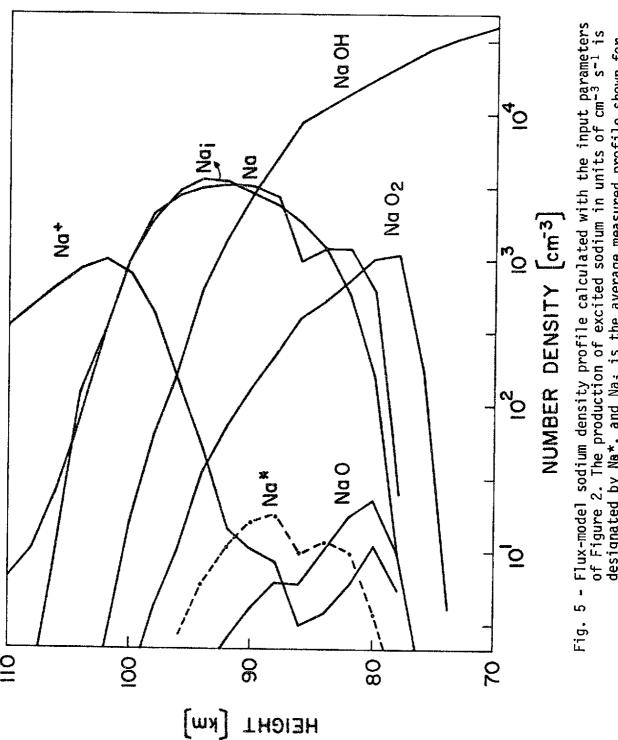


Fig. 5 - Flux-model sodium density profile calculated with the input parameters of Figure 2. The production of excited sodium in units of cm⁻³ s⁻¹ is designated by Na*, and Na; is the average measured profile shown for comparison.

TABLE 1

CHEMICAL REACTIONS INVOLVING SODIUM COMPOUNDS DURING NIGHTTIME

	REACTION	RATE
1	$Na + O_3 \rightarrow NaO + O_2$	3.3 x 10 ⁻¹⁰
2	$Na + O_2 + M \rightarrow NaO_2 + M$	$8.4 \times 10^{-34} \exp(290/T)$
3	Na + $HO_2 \rightarrow NaOH + O$	7×10^{-12}
4	$NaO + O \rightarrow Na* + O_2$	1.6 x 10 ⁻¹⁰
5	$Na0 + O_3 \rightarrow NaO_2 + O_2$	5 x 10 ⁻¹¹
6	$Na0 + HO_2 \rightarrow NaOH + O_2$	10-11
7	NaO ₂ + H → NaOH + O	7 x 10 ⁻¹²
8	$NaO_2 + OH \rightarrow NaOH + O_2$	10-11
9	NaOH + H \rightarrow Na + H ₂ O	$2 \times 10^{-11} \exp(-800/T)$

'ABLE 2 - SODIUM PARAMETERS

PARAMETER	SOURCE	VALUE
Na influx from meteors	Cabannes et al. (1938) Junge et al. (1962)	l5 tons/year = 1.5 x 10^7 g/year = 2.4 x 10^3 atoms/cm ² /s 80 tons/year = 8 x 10^7 g/year = 1.3 x 10^4 atoms/cm ² /s
Hydrogen escape flux (for comparison)	Hunten and Strobel (1974)	$10^{8} \text{ atoms/cm}^{2}/\text{s}$
Na abundance in atmosphere	Measurements	$5 \times 10^9 \text{ atoms/cm}^2 = 1.9 \times 10^{-13} \text{ g/cm}^2$ Total mass of Na in atmosphere = 10^3 kg
Residence time constant $ au_1$	Measurements and theory	$\tau_1 = \frac{5 \times 10^9}{10^4} = 5 \times 10^5 \text{s} = 139 \text{ hs} = 5.8 \text{ days}$
Diffusion time constant r ₂ at 96 km	Measurements and theory	$\tau_2 = \frac{H^2}{K} = \frac{4 \times 10^{10}}{4 \times 10^6} = 10^4 \text{s} = 2.8 \text{ hs}$