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14. Abstract/Notes <i>Recent results for sodium reaction rates have led to a reassessment of the importance of atmospheric sodium constituents and their distribution with height. The largest changes occur at the bottom of the neutral atmospheric sodium layer. A much larger reaction rate coefficient for the three body production of NaO₂ makes this constituent potentially much more dense below about 80 km, whereas the inclusion of photolysis produces a large diurnal variation in the NaOH loss frequency. Because many of the Na reaction rates are still uncertain static calculations for four different options on reaction rates have recently been offered in the literature. We show that only one of these choices is able to produce diurnal variations that are in agreement with recent measurements.</i>			
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ATMOSPHERIC SODIUM CHEMISTRY AND DIURNAL VARIATIONS: AN UP - DATE

by

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Abstract. Recent results for sodium reaction rates have led to a reassessment of the importance of atmospheric sodium constituents and their distribution with height. The largest changes occur at the bottom of the neutral atmospheric sodium layer. A much larger reaction rate coefficient for the three body production of NaO_2 makes this constituent potentially much more dense below about 80 km, whereas the inclusion of photolysis produces a large diurnal variation in the NaOH loss frequency. Because many of the Na reaction rates are still uncertain static calculations for four different options on reaction rates have recently been offered in the literature. We show that only one of these choices is able to produce diurnal variations that are in agreement with recent measurements.

The atmospheric neutral sodium layer has received increased attention in recent years. Because of the strong chemical activity below the peak of the layer it has been possible, for example, to study mesospheric ozone (Kirchhoff et al., 1981a), and dynamic aspects such as mesospheric winds (Clemesha et al., 1981), and the eddy diffusion coefficient (Kirchhoff and Clemesha, 1983c) have also been explored. Clustering of ions has been considered (Richter and Sechrist, 1979) and most observing stations have reported wave like structures in the sodium layer (Sandford and Gibson, 1970; Blamont et al., 1972; Kirchhoff and Clemesha, 1973; Rowlett et al., 1978). After a period of essentially purely photochemical treatments involving the Na D line emission cycle, Liu and Reid (1979) calculated sodium constituents and their distribution with height including the NaOH molecule, following a suggestion of Ferguson (1978), and adding to this the effect of a sodium source believed to be of extraterrestrial origin. Extremely sharp layered sodium inputs have in fact been observed (Clemesha et al., 1978; Clemesha et al., 1980) and the dissipation characteristics of a sodium cloud have been simulated (Kirchhoff and Clemesha, 1983b). Static modelling calculations were also made by Kirchhoff et al. (1981c) reviewing the layer theory in some detail and comparing such calculations to laser radar measurements to check their validity.

Diurnal variations are more difficult to simulate. An attempt to include time variations has been presented by Megie and Blamont (1977). A thorough more recent complete diurnal calculation has been presented by Kirchhoff and Clemesha (1983a), when daytime measurements of Na became also available for comparisons (Gibson and Sandford, 1972; Clemesha et al., 1982; Granier and Megie, 1982). The original chemistry of Ferguson (1978) and Liu and Reid (1979) was shown to be unable to reproduce the day-night behavior of the sodium layer in these diurnal calculations. Kirchhoff and Clemesha (1983a) have shown, however, that it is possible to obtain diurnal variations in Na consistent with the observations by making the NaOH production an irreversible loss process for neutral sodium. In this way a height

dependent loss function for sodium was obtained that had to be balanced by flux divergence.

A dramatically increased value for the reaction rate for the three body production of NaO_2 has been obtained recently by Husain and Plane (1982), and Rowland and Makide (1982) have considered that NaOH is subject to photolysis. These changes in the basic Na chemistry have been investigated in a static calculation (Sze et al., 1982) and sodium constituents for four options on reaction rates were calculated, of which three gave reasonable Na distributions. In the calculations to be described here we use basically the same model discussed in Kirchhoff and Clemesha (1983a). The aim of this work is to test the new chemistry in a complete diurnal calculation, as an extension of Sze et al. (1982), and as an up-date of Kirchhoff and Clemesha (1983a).

Results and Discussion

In Table 1 we show the Na chemistry used in the calculations. Reactions 3, 7, and 8, were not included in Sze et al. (1982), although their contributions are small. Reaction rate 16 was considered zero in Kirchhoff and Clemesha (1983a), and reactions 18 and 19 may be neglected, especially when the concentration of NaOH is small. The photolysis rate of NaOH represents the largest loss of this species and therefore there will be a large change in the loss frequency of NaOH between day and night. It should be noted, however, that the production of NaOH is a slow process if $K_9 = 0$. There will be, nevertheless, a tendency for the daytime NaO_2 to be transformed into NaOH at night. The daytime photolysis rate will again decrease the NaOH density, rather suddenly in the morning twilight, and NaO_2 will be produced through the fast three body reaction.

The different options considered by Sze et al (1982) involve mainly reactions 9 and 12. With a large $K_9 = 1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, a large production of NaOH results and the concentration of this species becomes large at the bottom of the layer. Options with K_{12}

either small ($K_{12} = 1.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$) or large ($K_{12} = 1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) make NaO_2 large or small, respectively. On the basis of the physics of the layer formation it should be noted that an incorrect diurnal variation must result if K_{12} is too large. Total sodium at the bottom of the layer must be distributed in such a way as to cause a downward eddy flux, and thus it will have a time constant much larger than a day. Obviously this flux must equal the extraterrestrial sodium input provided by meteoroid ablation. But photolysis will cause a fast decrease of the NaOH density in the morning twilight and therefore NaOH can no longer be the sole major Na constituent at the bottom of the layer. The alternative is that NaO_2 should be the major Na constituent, which is now possible with the larger K_2 , and opting for a small K_{12} .

Figures 1 and 2 show the distributions with height of the major Na species using the chemistry of Table 1. This choice of the rates corresponds to option A2 of Sze et al. (1982), and their static calculation is similar to our results for noon (Figure 1). At midnight (Figure 2) the density of NaOH is much larger, peaking at 76 km with a corresponding decrease in the NaO_2 density. For comparison with observations we show also a data average represented by crosses in Figure 2. The Na density has decreased at the bottom of the layer and NaO has increased in the region of the peak (86 km). Figure 3 shows the diurnal variation for Na and NaOH at 80 km. Since the production of NaOH is rather small in this case, it takes several hours for the NaOH density to increase, at the expense of the NaO_2 density, despite the lack of an effective nocturnal loss process. The abundance is $4.0 \times 10^9 \text{ cm}^{-2}$ at noon and $3.7 \times 10^9 \text{ cm}^{-2}$ at midnight, and the D_2 line intensity induced through reaction 5 is 15R at noon and 46R at midnight. These values are very close to observed averages (Simonich et al. 1979; Kirchhoff et al., 1981b). The nocturnal variation at the bottom of the Na layer, as reported by Simonich et al. (1979), shows a decrease of Na below about 84 km. From a series of profiles taken in June, July, and August 1979, this nocturnal decrease of Na is found to be about a factor of 2 at 83 km, increasing to about a factor of 10 at

81 km. In the calculations of Figure 3 the Na decrease during the night is about a factor of 7 at 80 km.

The inclusion of reaction 9 has the effect of increasing the height of maximum NaOH production by about 10 km. If this production is too large it can affect the Na density in the region of the peak where NaO_2 is already small, because then an increase in NaOH during the night must occur at the expense of Na. Also, the variation of NaOH density at the evening twilight will be faster. Numerical results will, of course, depend on the assumed amount of water vapor in the atmosphere. With a concentration of $4.5 \times 10^7 \text{ H}_2\text{O}$ molecules cm^{-3} at 90 km we calculate that about 400 NaOH molecules cm^{-3} can be produced per hour, for $K_9 = 1.0 \times 10^{-10}$. Clearly, NaOH will be formed at the expense of Na, which must not happen according to laser radar observations. Rate K_9 must be small enough to ensure that Na is not affected in the region of the peak. Our calculations show that with the high value of $K_9 = 1.0 \times 10^{-10}$ the Na abundance is reduced by 25% during the night and the density at 90 km for midnight is reduced by 800 atoms cm^{-3} . The laser radar results, on the other hand, show negligible changes in these quantities between day and night (Gibson and Sandford, 1972; Clemesha et al., 1982). Using $K_9 = 1.0 \times 10^{-11}$, the calculated results for Na are practically the same as if K_9 were zero, but NaOH at the bottom of the layer is larger. With respect to reaction 9 we conclude, therefore, that it will only alter slightly the absolute density of NaOH (NaO_2) at the bottom of the layer and that K_9 must be less than 1.0×10^{-10} . The diurnal variation for $K_9 = 1.0 \times 10^{-11}$ is shown by a dotted line in Figure 3. As noted earlier, Na is practically unaffected.

Summary

Calculating the diurnal variation of atmospheric sodium, we show that only one of the three options that gave realistic Na distributions with height in Sze et al. (1982) is able to produce diurnal variations in agreement with measurements. This is the case in

which NaO_2 is the major constituent at the bottom of the layer. Under these conditions the chlorine species appear to play only a negligible role but we actually know very little about them above 70 km. For example, it may turn out that NaCl is actually larger, at the bottom of the layer, than present estimates. The nocturnal variation of Na is actually more complicated, indicating a minimum density at about 03:00 hours local time, caused by the action of tides whose effects we are planning to include in future work. Perhaps the main conclusion to be drawn from this work is that modifications to the sodium chemistry cannot be tested adequately by a static model. The accurate information relating to the diurnal variation of the atmospheric sodium distribution, now available, permits a more critical test of the chemistry than was possible earlier. As has been shown here, models and reaction rates capable of adequately reproducing the static distribution of sodium under certain conditions, are not necessarily capable of reproducing the measured distribution over a period of 24 hours. In particular, any model which results in a large change in abundance between day and night is obviously inadequate.

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Figure Captions

Figure 1- Sodium constituents calculated for noon.

Figure 2- Sodium constituents calculated for midnight. The crosses represent an average of experimental profiles.

Figure 3- Diurnal variation of Na and NaOH at 80 km. The dotted curve represents the NaOH variation for $K_9 = 1.0 \times 10^{-11}$.

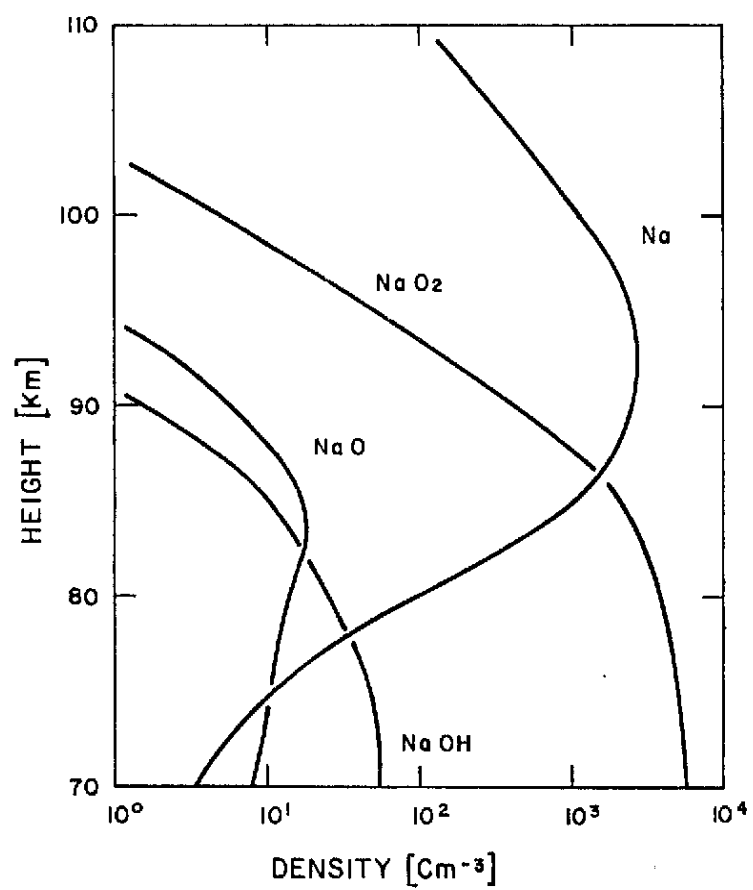


Fig. 1

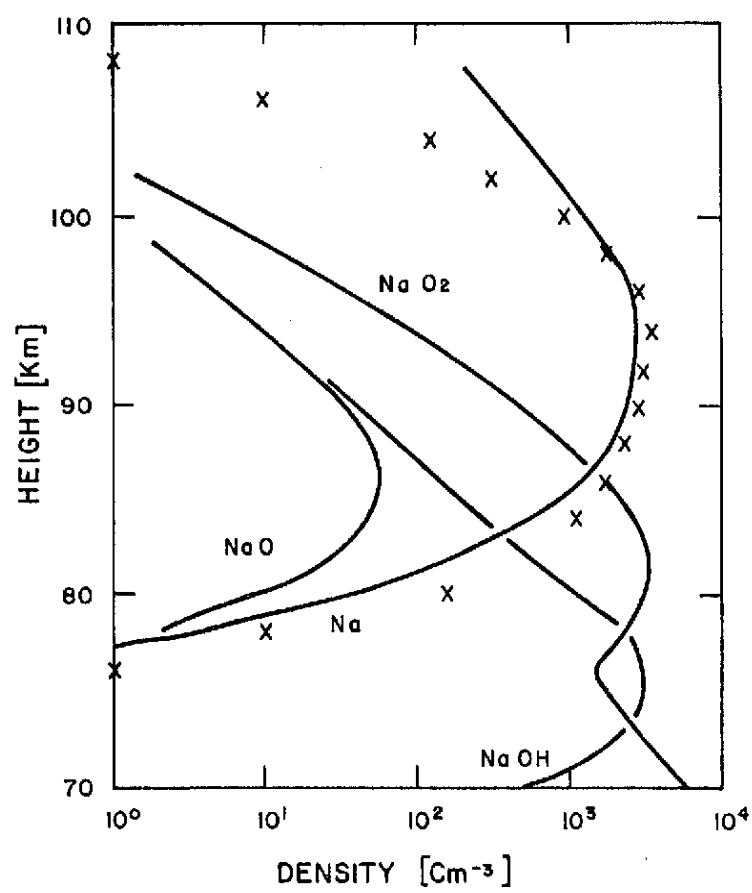


Fig. 2

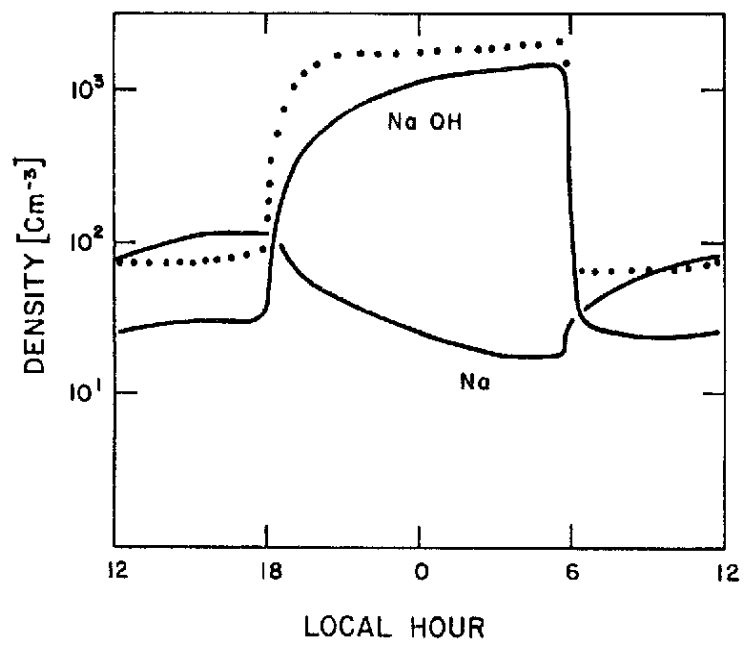


Fig. 3

Table 1- Sodium chemistry. The rates are given in cm^3s^{-1} for two body, cm^6s^{-1} for three body reactions.

REACTIONS						RATES	
1	Na	+ O ₃	→	NaO	+ O ₂	3.4×10^{-10}	a
2	Na	+ O ₂ + M	→	NaO ₂	+ M	$6.7 \times 10^{-31} \exp(290/T)$	b
3	Na	+ HO ₂	→	NaOH	+ O	1.4×10^{-11}	c
4	NaO	+ O	→	Na	+ O ₂	2.8×10^{-11}	d
5	NaO	+ O	→	Na*	+ O ₂	1.2×10^{-11}	d
6	NaO	+ O ₃	→	NaO ₂	+ O ₂	3.5×10^{-11}	c
7	NaO	+ O ₃	→	Na	+ 2O ₂	1.0×10^{-10}	c
8	NaO	+ HO ₂	→	NaOH	+ O ₂	1.0×10^{-11}	e
9	NaO	+ H ₂ O	→	NaOH	+ OH	see text	d
10	NaO	+ H	→	Na	+ OH	1.0×10^{-14}	d
11	NaO ₂	+ hν	→	Na	+ O ₂	1.0×10^{-4}	d
12	NaO ₂	+ O	→	NaO	+ O ₂	1.0×10^{-13}	d
13	NaO ₂	+ OH	→	NaOH	+ O ₂	1.0×10^{-11}	e
14	NaO ₂	+ H	→	NaOH	+ O	1.0×10^{-13}	d
15	NaOH	+ hν	→	Na	+ OH	2.0×10^{-3}	f
16	NaOH	+ H	→	Na	+ H ₂ O	1.4×10^{-12}	e
17	NaOH	+ O('D)	→	NaO	+ OH	1.0×10^{-10}	d
18	NaOH	+ HCl	→	NaCl	+ H ₂ O	1.0×10^{-11}	g
19	NaCl	+ hν	→	Na	+ Cl	1.0×10^{-2}	h

a- Bates and Ojha (1980); b- Husain and Plane (1982);
c- Kirchhoff and Clemesha (1983a); d- Sze et al. (1982);
e- Liu and Reid (1979); f- Rowland and Makide (1982);
g- Murad et al. (1981); h- Rowland and Rogers (1982).