

NUMERICAL MODEL OF THE SODIUM LAYER IN
THE MESOSPHERE:
SEASONAL AND DIURNAL VARIATION

Michihiro UCHIUMI and Motowo FUJIWARA

*Department of Physics, Faculty of Science, Kyushu University,
10-1, Hakozaki 6-chome, Higashi-ku, Fukuoka 812*

Abstract: This paper describes some computational results on the mesospheric sodium layer using the newly measured chemical reaction rate coefficients. After the most updated neutral chemistry, the calculated winter/summer ratio is consistent with the observational results. The time constant of sodium atoms is found to be shorter than 20 s (70-90 km). This short time constant invalidates a previous model of sodium gravity waves, which assumes that sodiums are chemically conservative during their vertical moving induced by gravity waves. We proposed a new mechanism here to explain the wavelike structures of the sodium layer driven by gravity waves.

1. Introduction

Since SLIPHER (1929) observed an emission near 590 nm in the night sky, the morphology of the mesospheric sodium layer have been studied with the measurements of twilight airglow, day glow (ground based and balloon- and rocket-borne), absorption of solar radiation, emissions of night glow, auroral and meteor trail, and resonant scattering by lidar. The sodium layer shows a seasonal variation; its column abundance is higher in winter and lower in summer, and the peak height is lower in winter and higher in summer. The winter/summer ratio of the observed column abundance increases with the latitude. For a detailed description on observational techniques and results, the reader is referred to the reviews by HUNTEN (1967) and BROWN (1973).

Since CHAPMAN (1939) proposed a mechanism for the nighttime emission, several authors have made efforts to understand the observed features of the sodium layer: vertical distribution, and diurnal and seasonal behavior, etc. These modeling studies had to proceed without experimental information about the reaction rates of relevant sodium chemistry. The reaction rate coefficients of sodium compounds were calculated by analogy with atomic hydrogen reaction (BROWN, 1973). KOLB and ELGIN (1976) estimated three unknown rate coefficients, (1), (2) and (8) in Table 1, by the electron jump mechanism (or the hapoon mechanism). This mechanism was successful in calculating the reaction rate coefficients of alkali-halogen molecules. BATES and OJHA (1980), however, suggested that the electron jump mechanism may not be applicable to alkali-oxygen molecule reactions. On the other hand, HUSAIN and PLANE (1982) measured the rate coefficients of termolecular reaction (3) of Table 1, which was thousandfold faster than the previous value (CARABETTA and KASKAN, 1968). This invalidates earlier modeling efforts. Several reaction rate coefficients have been

measured in the recent few years. Almost all measured rate coefficients are faster than the values previously speculated. The chemical time constant of the sodium is shorter than that expected previously because of the change in the rate coefficients. The purpose of this paper is to present numerical studies of sodium compounds at 70–100 km by using the rate constants which were newly measured and to discuss the seasonal and diurnal variation of the sodium layer and the response to the atmospheric gravity waves.

2. Reaction Rate Coefficients

The reactions and rate coefficients for sodium adopted in the present model are listed in Table 1. We used the reactions of (1) to (12) in this table. Ion reactions and rate coefficients are quoted from JEGOU *et al.* (1985) for reference. All neutral chemical reactions are the same as reactions of SWIDER (1985) which are the same as reactions from (1) to (12) of SZE *et al.* (1982). The new rate coefficients are, however, used in reactions of (1), (2), (3), (8) and (12). The rates (1), (3), (8) and (12) are based on the recent measurements. As the rate coefficients of (4) has been measured by ROWLAND and MAKIDE (1982), five of neutral reactions in Table 1 are known. The value of reaction (3) is taken from SILVER *et al.* (1985). The values of reaction (1) and (8) are taken from AGER and HOWARD (1985). The lower limit of value of reaction (12), 4×10^{-12} cm³/s is determined by SILVER *et al.* (1984). The rate coefficients of (2) are estimated as follows.

Table 1. Neutral reactions and rate coefficients adopted in this model, and ionic reaction and rate coefficients for reference. See text. Read $A(-n)$ as $A \times 10^{-n}$. Units are cm³/s, except cm⁶/s for (3) and s⁻¹ for (4), (5) and (21). For (25) and (26), the reader is referred to JEGOU *et al.* (1985).

No.	Reactions	Rates	Reference
1.	$\text{Na} + \text{O}_3 \rightarrow \text{NaO} + \text{O}_2$	6.7(-10)	(a)
2.	$\text{NaO} + \text{O} \rightarrow \text{Na}(^2\text{P}, ^2\text{S}) + \text{O}_2$	1(-10)	(b)
3.	$\text{Na} + \text{O}_2 + \text{N}_2 \rightarrow \text{NaO}_2 + \text{N}_2$	1.9(-30) (T/300) ^{-1.1}	(c)
4.	$\text{NaOH} + h\nu \rightarrow \text{Na} + \text{OH}$	2(-3)	(d)
5.	$\text{NaO}_2 + h\nu \rightarrow \text{Na} + \text{O}_2$	5(-3)	(e)
6.	$\text{NaO}_2 + \text{O} \rightarrow \text{NaO} + \text{O}_2$	1(-13)	(e)
7.	$\text{NaO} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{OH}$	1(-10)	(e)
8.	$\text{NaO} + \text{O}_3 \rightarrow \text{NaO}_2 + \text{O}_2$	1.1(-10)	(a)
9.	$\text{NaO} + \text{H} \rightarrow \text{Na} + \text{OH}$	1(-14)	(e)
10.	$\text{NaO}_2 + \text{OH} \rightarrow \text{NaOH} + \text{O}_2$	1(-11)	(f)
11.	$\text{NaO}_2 + \text{H} \rightarrow \text{NaOH} + \text{O}$	1(-13)	(e)
12.	$\text{NaOH} + \text{H} \rightarrow \text{Na} + \text{H}_2\text{O}$	4(-12)	(g)
21.	$\text{Na} + h\nu \rightarrow \text{Na}^+ + e^-$	1.7(-5)	(h)
22.	$\text{Na} + \text{NO}^+ \rightarrow \text{Na}^+ + \text{NO}$	8(-10)	(h)
23.	$\text{Na} + \text{O}_2^+ \rightarrow \text{Na}^+ + \text{O}_2$	6(-10)	(h)
24.	$\text{Na}^+(\text{H}_2\text{O}) + e^- \rightarrow \text{Na} + \text{H}_2\text{O}$	3(-6)	(h)
25.	$\text{Na}^+ + \text{H}_2\text{O} + \text{X} + \text{X} \rightarrow \text{Na}^+(\text{H}_2\text{O}) + \text{X} + \text{X}$		(h)
26.	$\text{Na}^+(\text{H}_2\text{O}) + \text{H}_2\text{O} + \text{X} + \text{X} \rightarrow \text{Na}^+(\text{H}_2\text{O})_2 + \text{X} + \text{X}$		(h)

(a) AGER and HOWARD (1985), (b) see text, (c) SILVER *et al.* (1985), (d) ROWLAND and MAKIDE (1982), (e) SZE *et al.* (1982), (f) LIU and REID (1979), (g) SILVER *et al.* (1984), (h) JEGOU *et al.* (1985).

There is no measurement of the rate coefficient of the reaction (2), which is of a great importance in the atmospheric sodium chemistry. SZE *et al.* (1982) calculated crossing distance $r_x=2.3 \text{ \AA}$ using the ionization potential of 7.8 eV (HILDENBRAND, 1972) according to the electron jump mechanism. At $T=200 \text{ K}$, using the kinetic collision theory for this r_x , SZE *et al.* (1982) calculated $k=7.6 \times 10^{-11} \text{ cm}^3/\text{s}$. But it is underestimated in our opinion. We calculated $k=9.8 \times 10^{-11} \text{ cm}^3/\text{s}$. BATES and OJHA (1980) suggested that the electron jump mechanism may not be applicable to the reactions of (2) and (1). Unless the mechanism is valid, the rate coefficient of reaction (2) is an order of $10^{-11} \text{ cm}^3/\text{s}$. So SZE *et al.* (1982) assumed $k=4.0 \times 10^{-11} \text{ cm}^3/\text{s}$ in their model. On the other hand, the rate coefficient obtained by a recent measurement for reaction (1) was a little larger than that calculated by the electron jump mechanism. Moreover, calculations in the rate coefficients of alkali-halogen molecules were developed by a refined electron jump model (GISLASON, 1979). The electron jump model offers a lower limit of the rate coefficients. Thus the electron jump mechanism can be likely used for reaction (2), so that the rate must be slightly greater than $9.8 \times 10^{-11} \text{ cm}^3/\text{s}$. Accordingly, we used the rate coefficient $1 \times 10^{-11} \text{ cm}^3/\text{s}$.

Table 2. Reaction rate coefficients for four options of SZE *et al.* (1982).

	Sodium model			
	A1	A2	B1	B2
$J_5 \text{ (s}^{-1}\text{)}$	10^{-4}	10^{-4}	10^{-4}	5.0×10^{-3}
$k_6 \text{ (cm}^3 \text{ s}^{-1}\text{)}$	10^{-10}	10^{-13}	10^{-10}	10^{-13}
$k_7 \text{ (cm}^3 \text{ s}^{-1}\text{)}$	0.	0.	10^{-10}	10^{-10}

SZE *et al.* (1982) calculated sodium constituents for four options on reaction rates (A1, A2, B1 and B2), of which three (A2, B1 and B2) gave reasonable sodium distributions. Table 2 shows the rate coefficients used in their model. KIRCHHOFF (1983) suggested that only one (A2) of these choices is able to produce diurnal variations that are in agreement with lidar measurements. In this paper, A2 and B2 of these options are chosen. Model A and B in this paper correspond respectively to A2 and B2 of SZE *et al.* Table 1 represents the rate coefficients of model B. On the other hand, the coefficients of model A are $10^{-4} / \text{s}$ for J_5 , and 0 for k_7 .

3. Model

The concentrations of sodium compounds were calculated at 2 km intervals in one-dimensional model and normalized to the total sodium species profiles of LIU and REID (1979). Calculations are based on a static solution of the relative sodium compound distribution. Since the time constants of all the neutral sodium processes in the mesosphere are much shorter than the eddy transport lifetime of about one day (HUNTEN, 1975; SWIDER, 1985), the eddy transport is neglected in our calculations. The concentrations of atmospheric constituents (O , O_2 , O_3 , H , OH , H_2O) have been taken from SHIMAZAKI (1984), which were calculated for 35° latitude in equinoxes.

Figures 1a and 1b show the profiles of sodium compounds for models A and B. The neutral chemistry alone does not give any reasonable explanation for the cut off

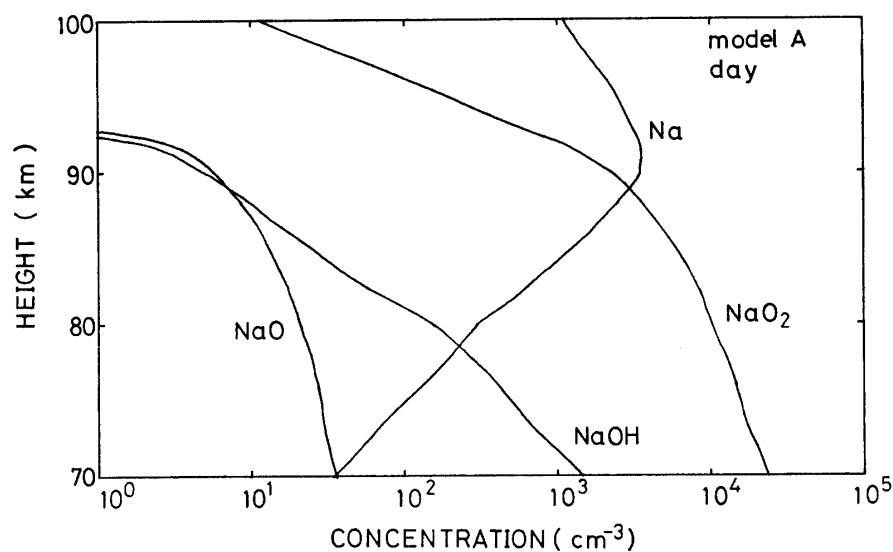


Fig. 1a. Height distributions of neutral sodium compounds computed for noon condition using the rate coefficients of model A. See text.

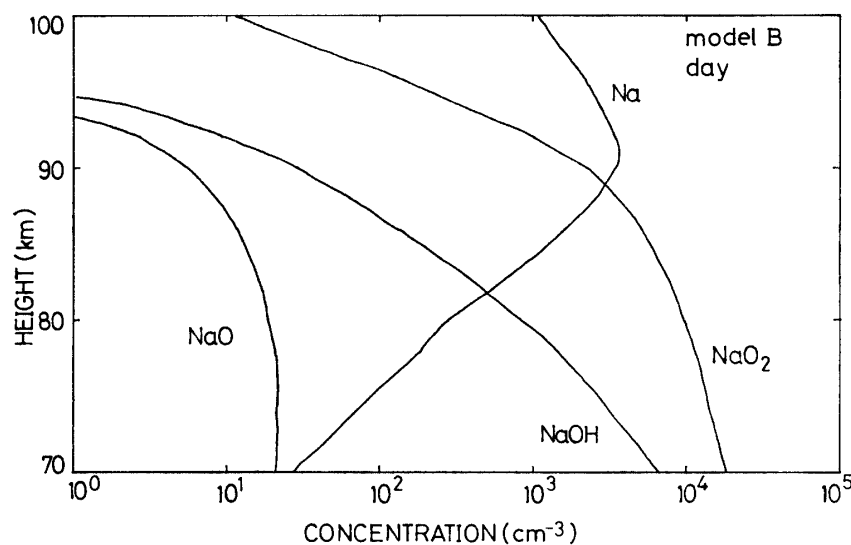


Fig. 1b. Height distributions of neutral sodium compounds computed for noon condition using the rate coefficients of model B listed in Table 1.

in the top of the sodium layer. The scale height of the sodium layer is defined as the height at which the sodium density falls to e^{-1} of its peak value. The lidar observations showed that the topside scale height of the sodium layer, *i.e.* the scale height above the peak, is far smaller than the atmospheric scale height. THOMAS *et al.* (1983) suggested that the ionization and clustering processes would reduce the topside scale height of the layer. We do not, however, take account of ion clustering reactions for elucidating the sensitivity of neutral reactions to the atmospheric temperature and density. Therefore, the topside scale height of the sodium layer in our calculations is larger than the observed one.

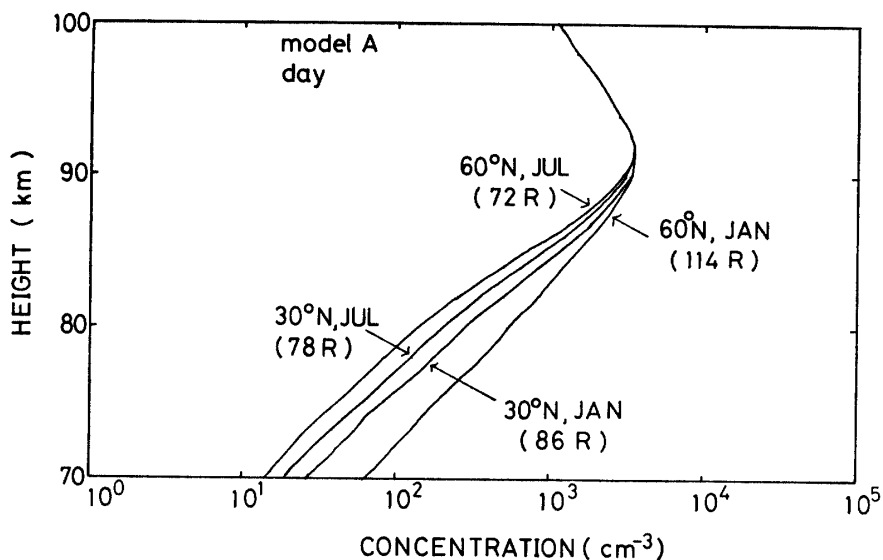


Fig. 2a. Sodium density for January and July at 60° and 30°N calculated with the rate coefficients of model A. Numerals in the brackets stand for the calculated airglow intensities (units are Rayleigh). See text.

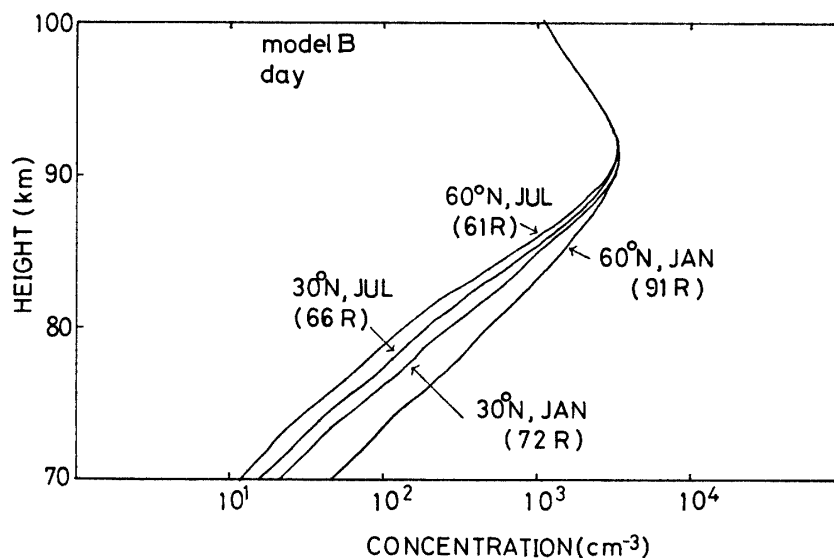


Fig. 2b. Sodium density for January and July at 60° and 30°N calculated with the rate coefficients of model B listed in Table 1. See the caption of Fig. 2a.

The mesosphere is warm in winter and cold in summer. SWIDER (1985) suggested that the reaction scheme including the atmospheric temperature and density dependence of reaction (3) would be responsible for the seasonal variation of the sodium layer. Figure 2a shows profiles of model A in January and July at 60° and 30°N. The sodium density at 80 km increases in winter by a factor of 4 at 60°N, and by a factor of 2 at 30°N. These values are consistent with the observations (UCHIUMI *et al.*, 1985a, b, 1986). On the other hand, Fig. 2b shows a profile for model B, which also offers an explanation of seasonal variation of the sodium layer. For simplicity, it is assumed

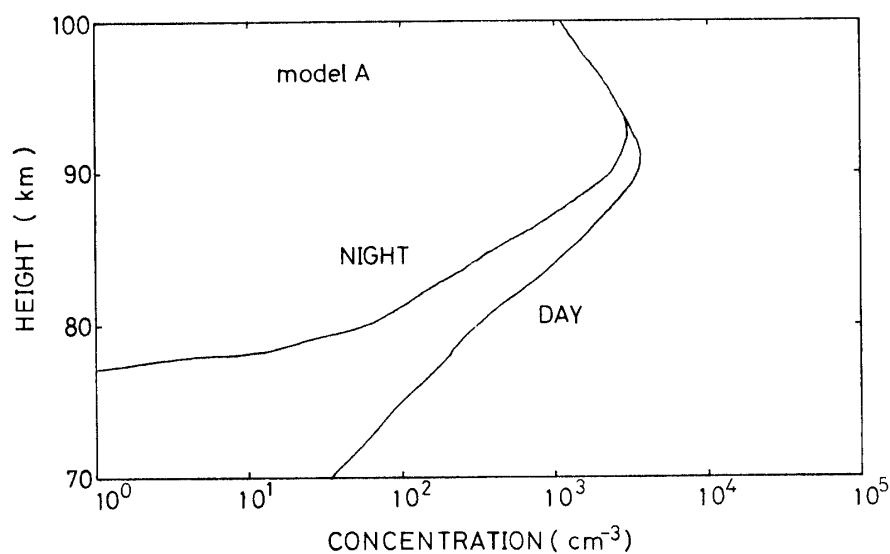


Fig. 3a. Height dependence of sodium atom density computed for noon and midnight using the rate coefficients of model A. See text.

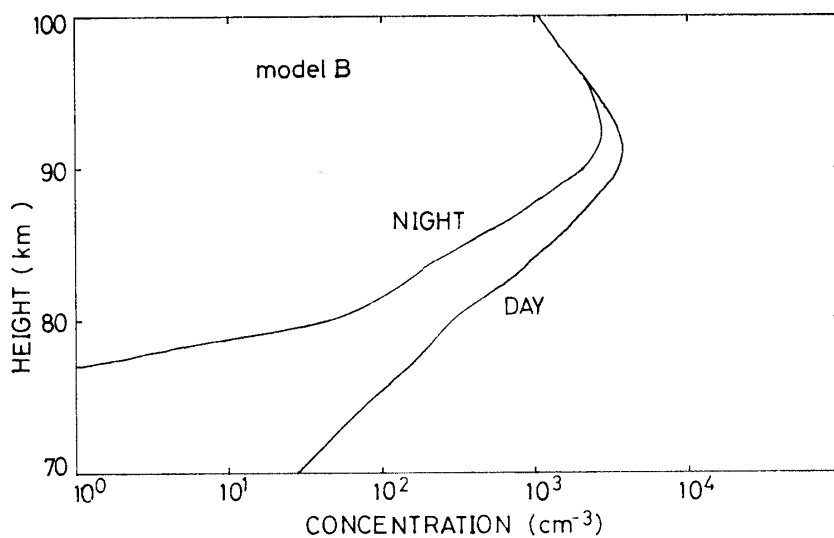


Fig. 3b. Height dependence of sodium atom density computed for noon and midnight using the rate coefficients of model B listed in Table 1.

that the atmospheric condition changes meridionally only in temperature, and O_2 and N_2 concentrations.

The diurnal variations of the sodium layer are shown in Figs. 3a and 3b for models A and B. The daytime/nighttime ratios are 3.4 at 84 km in model A and 4.3 at 84 km in model B.

The photochemical time constants of the mesospheric sodium compound are computed using both neutral and ionic reactions shown in Table 1. The time constant of sodium atoms is less than 20 s at the height range of 70–90 km (Fig. 4). Thus if sodium atoms are transported vertically due to gravity waves, the atoms will react with ambient gases readily during the transport and the sodium/other sodium com-

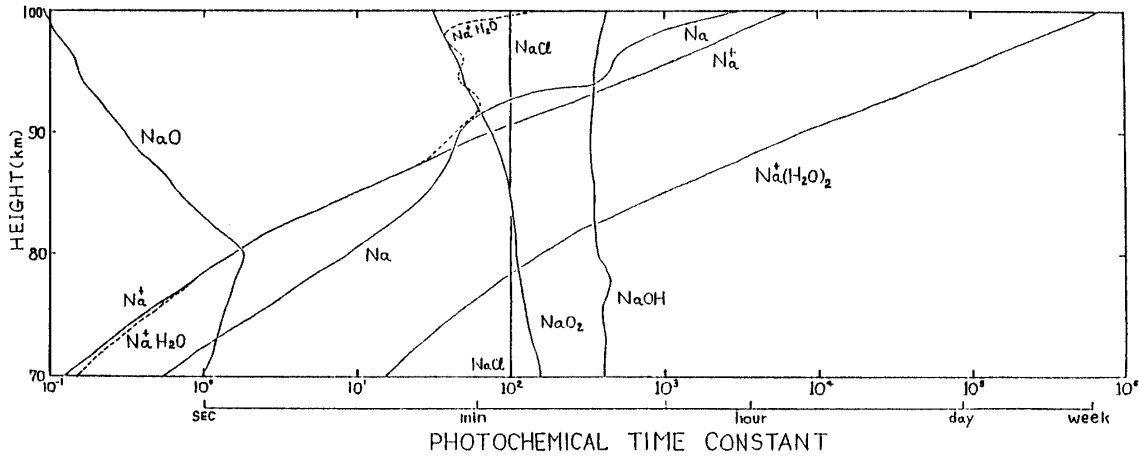


Fig. 4. Height profiles of photochemical time constants at noon for sodium compounds.

pounds ratio immediately reach a steady state which is determined by the chemical reactions with ambient gases at each height. Thus the perturbation of the sodium layer due to gravity waves will vanish under these circumstances.

The three body reaction (3) is predominant in the neutral chemistry of the sodium layer. The $[N_2]$ and $[O_2]$ ($[N_2]$ denotes the density of N_2) on the left-hand side of this reaction display truly an effect from gravity waves, because the chemical time constants of N_2 and O_2 are very large. Thus, if $[N_2]$ and $[O_2]$ become dense at a certain height, then reaction (3) will proceed fast there. Inversely, if $[N_2]$ and $[O_2]$ become sparse there, then the reaction will be slow. As far as one considers this reaction alone, one can reach the next intuitive aspect. If the density of N_2 and O_2 oscillates owing to gravity waves, then sodium atoms must also oscillate. It appears that the phase of the sodium density variation would lag by about 180° compared with ambient atmosphere. In fact, the calculation including other reactions reveals such a tendency as given below.

The density of sodium is a function of the densities of ambient gases, N_2 , O_2 , O ,

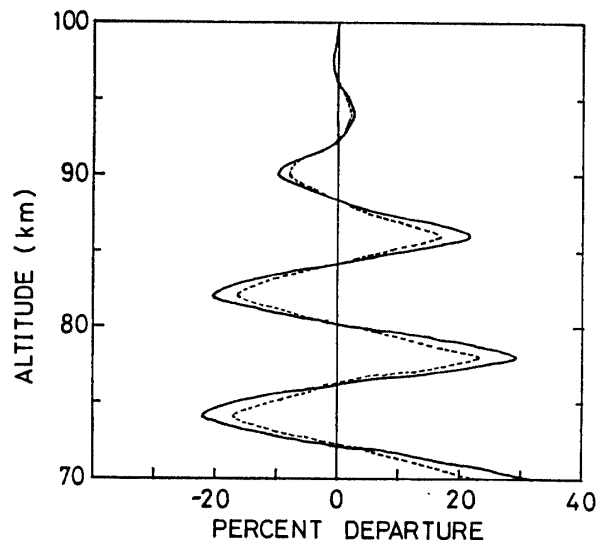


Fig. 5. Density departures (%) from the sodium density of Fig. 1 condition. Wave structures show gravity wave effects generated through direct chemical reactions (broken line) and both direct and indirect reactions (solid line). See text.

O_3 , OH, H_2O . Here, we assume the perturbations of $[N_2]$ and $[O_2]$ as follows.

$$[N_2] = [N_2]_o + 0.1 [N_2]_o \cdot \sin(\omega t + kz),$$

$$[O_2] = [O_2]_o + 0.1 [O_2]_o \cdot \sin(\omega t + kz),$$

where $[N_2]_o$ and $[O_2]_o$ are the averaged density, and we assumed that the perturbations are 10% of them. Suppose that the perturbations of $[N_2]$ and $[O_2]$ affect the densities of the other constituents by chemical reactions. At first, we consider the [Na] oscillation due to gravity waves is induced only by two gases, $[N_2]$ and $[O_2]$. In this case, all we have to consider on the effect of gravity waves is only the reaction (3), in which sodium atoms react directly with N_2 and O_2 . Figure 5 (broken line) shows the percent departure of the sodium density due to gravity waves. Next, since O and O_3 react with O_2 , the perturbation of $[O_2]$ affects chemically the [O] and $[O_3]$. Thus, the [Na] oscillation due to gravity waves is induced indirectly by $[O_2]$ via [O] and $[O_3]$. Here we take account of the indirect effect in the calculation by a pure oxygen model. Figure 5 (solid line) shows the percent departure of the sodium density caused by the effect via O and O_3 in addition to the direct effect. Since H_2O , H and OH react very slowly with O_2 , we need not to take these gases into account. Figure 5 shows that the amplitude of gravity waves are about 20% of the average density at 80 km. It implies that the gravity waves in the sodium layer are amplified by a factor of about 2 at 80 km compared with those in the ambient atmosphere. The figure also shows that the factor decreases gradually with altitude.

4. Discussion

Using the updated neutral chemistry, the calculated seasonal change of the sodium concentration at 70–90 km is in agreement with the observed one. This is attributed to the temperature dependence of termolecular reaction of (3), which is expressed by $k = k_0 T^{-n}$. For sodium, $n = 1.1$ is confirmed by experiments (SILVER *et al.*, 1985). On the other hand, $n = 0.6$ was measured for potassium (SILVER *et al.*, 1985). Thus, it is expected that the mesospheric potassium content would vary by a smaller factor in comparison with sodium, provided that the mesospheric potassium has chemical reactions and rates similar to sodium ones. In fact, lidar observations show that the potassium abundance does not almost vary throughout a year (MEGIE *et al.*, 1978). These tendencies give a support to SWIDER's (1985) hypothesis.

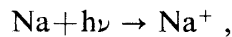
On the other hand, the diurnal variation of the sodium layer is noticeable, as shown in Fig. 3. The calculated profile is consistent with the observed one, particularly below the peak of the layer. The calculated daytime/nighttime ratio in model A is smaller than that in model B. The observed daytime/nighttime ratio is 1 ± 0.15 (CLEMESH *et al.*, 1982) and 1 ± 0.3 (GRANIER and MEGIE, 1982). This will imply that the chemical reactions and the rate coefficients do not suffice to explain the diurnal variation of the sodium layer. The reasons why there is too much sodium at daytime than at nighttime are pointed out below. The photodissociation reaction (4) and (5) work only during daytime.

Each of the minor constituents (O, O_3 , H, OH), associated with reactions adopted here, takes the different densities at daytime and nighttime. The daytime/nighttime

Table 3. Daytime/nighttime ratios of the densities of the minor constituents at 80 km. The data are taken from SHIMAZAKI (1984).

Constituents	Ratio
O	4.29
O ₃	0.380
H	1.12
OH	0.172
H ₂ O	1.00

ratios of these constituents at 80 km are shown in Table 3. The abundant ozone at nighttime decrease sodium atoms by reaction (1). The abundant oxygen atom at daytime increases sodium atoms by reaction (2). Likewise each of the constituents varies so as to increase sodium atoms at daytime rather than at nighttime. $J_5=0$ reduces the diurnal variation of the sodium. The photoionization process of sodium atom,



has the rate coefficient $J=1.7 \times 10^{-5}/\text{s}$, which is usually used (RICHTER and SECHRIST, 1979). We did not take it into account in this paper, but it will be too small to reduce the daytime sodium. The photodissociation rate coefficient may be greater than $1.7 \times 10^{-5}/\text{s}$. The dust hypothesis (FIOCCO and VISCONTI, 1973) is hopeless to improve this situation which increases sodium at daytime because of evaporation of sodium atoms from the sunlit dust. Further measurements of some unknown reaction rates should be performed.

Wavelike structures in the sodium layer have been observed with typical wavelength of 3–15 km and phase velocity 1–3 m/s (ROWLETT *et al.*, 1978). These wave-like structures were attributed to atmospheric gravity waves. The density response of atmospheric layer structure to gravity waves has been theoretically studied by CHIU and CHING (1978). SHELTON *et al.* (1980) used CHIU and CHING's approach to derive a linear model for the density response of the sodium layer to gravity waves. In their model, it is assumed that sodium atom is chemically conservative. The time constant of the sodium is, however, very small, so that the mechanism is no longer valid, especially in the lower part of the sodium layer. Thus, it must be noticed that the wave-like structures can be interpreted in terms of the coupling between gravity waves and the chemical reactions.

Figure 5 shows that the sodium density oscillates due to chemical reactions. In this way, the sodium layer will oscillate out of phase with the ambient atmosphere particularly below the peak of the sodium layer. The amplitude in sodium layer is larger by a factor of about 2 at 80 km than that in the ambient atmosphere. It must be noticed that the sodium density oscillates also dynamically owing to gravity waves. Thus the sodium layer will oscillate in phase with the ambient atmosphere, particularly in the top part of the sodium layer where the time constant of sodium atoms is somewhat longer (see Fig. 4). Considering that the sodium density oscillates dynamically and chemically owing to gravity waves, one can anticipate that the phase of the oscillation would reverse at a certain height. In fact, the lidar observations showed a

phase reversal at a height range of 89.5–92 km (SHELTON *et al.*, 1980). This observational results support our opinion.

In conclusion, the wavy structure in the sodium layer, which have been attributed to the gravity waves, must appear chemically via reaction (3) and dynamically.

5. Conclusion

The rate constants of the neutral chemical reactions adopted here are taken from the recent measurements. The model is consistent on the seasonal variation of the sodium layer. The reaction scheme, however, is not perfect, because it deduces a large diurnal variation of the sodium layer which is inconsistent with the observational results. The updated reactions cannot retrieve sufficient sodium atoms at nighttime to fit observed profiles. Further measurements of some unknown reaction rates should be performed. Since the model leads to a reasonable sodium profile at diurnally averaged condition, we will not have to change essentially the model in the future.

The photochemical time constant of the mesospheric sodium is found to be short. It is shorter than 20 s at height range of 70 to 90 km. The wavelike structures in the sodium layer has been considered as a response to atmospheric gravity waves by some authors. We suggested that the coupling between gravity waves and the chemical reactions must be taken into account. Moreover, we also suggested a new reasonable mechanism; the observed wavelike structure of sodium layer moving vertically will be explained by a density dependent termolecular reaction, *i.e.* $\text{Na} + \text{O}_2 + \text{N}_2 \rightarrow \text{NaO}_2 + \text{N}_2$.

Acknowledgments

We would like to thank Dr. M. HIRONO, Professor Emeritus of Kyushu University, for valuable comments. This work was supported by the Japan Society for the Promotion of Science.

References

- AGER, J. W., III, and HOWARD, C. J. (1985): Kinetic studies of some sodium reactions of atmospheric importance (abstract). *Eos Trans. AGU*, **66**, 317.
- BATES, D. R. and OJHA, P. C. (1980): Excitation of the Na D-doublet of the nightglow. *Nature*, **286**, 790–791.
- BROWN, T. L. (1973): The chemistry of metallic elements in the ionosphere and mesosphere. *Chem. Rev.*, **73**, 645–667.
- CARABETTA, R. and KASKAN, W. E. (1968): The oxidation of sodium, potassium and cesium in flames. *J. Phys. Chem.*, **72**, 2483–2489.
- CHAPMAN, S. (1939): Note on atmospheric sodium. *Astrophys. J.*, **90**, 309–316.
- CHIU, Y. T. and CHING, B. K. (1978): The response of atmospheric and lower ionospheric layer structures to gravity waves. *Geophys. Res. Lett.*, **5**, 539–542.
- CLEMESHA, B. R., SIMONICH, D. M., BATISTA, P. P. and KIRCHHOFF, V. W. J. H. (1982): The diurnal variation of atmospheric sodium. *J. Geophys. Res.*, **87**, 181.
- FIOCCO, G. and VISCONTI, G. (1973): On the seasonal variation of the upper atmospheric sodium. *J. Atmos. Terr. Phys.*, **35**, 165–171.
- GISLASON, E. A. (1979): Reaction models for alkali halide systems. *Alkali Halide Vapors*, ed. by P.

- DAVIDOVITS and D. L. MCFADDEN. New York, Academic Press, 415–440.
- GRANIER, C. and MEGIE, G. (1982): Daytime lidar measurements of the mesospheric sodium layer. *Planet. Space Sci.*, **30**, 169.
- HILDENBRAND, D. L. (1972): Thermochemistry of the molecular species LiO, LiO⁺ and Li₂O⁺. *J. Chem., D. M. Phys.*, **57**, 4556–4560.
- HUNTEN, D. M. (1967): Spectro studies of the twilight airglow. *Space Sci. Rev.*, **6**, 493–573.
- HUNTEN, D. M. (1975): Vertical transports in atmospheres. *Atmospheres of Earth and Planets*, ed. by B. M. McCORMAC. D. Reidel, Dordrecht, 59–72.
- HUSAIN, O. and PLANE, J. M. C. (1982): Kinetic investigation of the reaction between Na + O₂ + M by time-resolved atomic resonance absorption spectroscopy. *J. Chem. Soc., Faraday Trans. 2*, **78**, 163–178.
- JEGOU, J. P., GRANIER, C., CHANIN, M. L. and MEGIE, G. (1985): General theory of the alkali metals present in the earth's upper atmosphere, II. Seasonal and meridional variations. *Ann. Geophys.*, **3**, 299–312.
- KIRCHHOFF, V. W. J. H. (1983): Atmospheric sodium chemistry and diurnal variations; An up-date. *Geophys. Res. Lett.*, **10**, 721–724.
- KOLB, C. E. and ELGIN, J. B. (1976): Gas phase chemical kinetics of sodium in the upper atmosphere. *Nature*, **263**, 488–490.
- LIU, S. C. and REID, G. C. (1979): Sodium and other minor constituents of meteoric origin in the atmosphere. *Geophys. Res. Lett.*, **6**, 283–286.
- MEGIE, G., BOS, F., BLAMONT, J. E. and CHANIN, M. L. (1978): Simultaneous nighttime lidar measurements of atmospheric sodium and potassium. *Planet. Space Sci.*, **26**, 27–35.
- RICHTER, E. S. and SECHRIST, C. F., Jr. (1979): A cluster ion chemistry for the mesospheric sodium layer. *J. Atmos. Terr. Phys.*, **41**, 579–586.
- ROWLAND, F. S. and MAKIDE, Y. (1982): Upper stratospheric photolysis of NaOH. *Geophys. Res. Lett.*, **9**, 473–475.
- ROWLETT, J. R., GARDNER, C. S., RICHTER, E. S. and SECHRIST, C. F., Jr. (1978): Lidar observations of wavelike structure in the atmospheric sodium layer. *Geophys. Res. Lett.*, **5**, 683–686.
- SHELTON, J. D., GARDNER, C. S. and SECHRIST, C. F., Jr. (1980): Density response of the mesospheric sodium layer to gravity wave perturbations. *Geophys. Res. Lett.*, **7**, 1069–1072.
- SHIMAZAKI, T. (1984): The photochemical time constants of minor constituents and their families in the middle atmosphere. *J. Atmos. Terr. Phys.*, **46**, 173–191.
- SILVER, J. A., STANTON, A. C., ZAHNISER, M. S. and KOLB, C. E. (1984): Gas-phase reaction rate of sodium hydroxide with hydrochloric acid. *J. Phys. Chem.*, **88**, 3123–3129.
- SILVER, J. A., ZAHNISER, M. S., STANTON, A. C. and KOLB, C. E. (1985): Temperature-dependent intermolecular reaction rate constants for potassium and sodium peroxide formation. 20th International Symposium on Combustion, Pittsburgh, Combustion Inst. Pa., 605–612.
- SLIPHER, V. M. (1929): Emissions in the spectrum of the light of the night sky. *Publ. Astron. Soc. Pac.*, **41**, 262–263.
- SWIDER, W. (1985): Enhanced seasonal variations for chemical rates with inverse temperature dependencies; Application to seasonal abundance of mesospheric sodium. *Geophys. Res. Lett.*, **12**, 589–591.
- SZE, N. D., KO, M. K. W., SWIDER, W. and MURAD, E. (1982): Atmospheric sodium chemistry, 1. The altitude region 70–100 km. *Geophys. Res. Lett.*, **9**, 1187–1190.
- THOMAS, J. L., ISHERWOOD, M. C. and BOWMAN, M. R. (1983): A theoretical study of the height distribution of sodium in the mesosphere. *J. Atmos. Terr. Phys.*, **45**, 587–594.
- UCHIUMI, M., HIRONO, M. and FUJIWARA, M. (1985a): The seasonal variation of night-time sodium layer at 33°N. *Mem. Natl Inst. Polar Res., Spec. Issue*, **36**, 264–272.
- UCHIUMI, M., HIRONO, M. and FUJIWARA, M. (1985b): Lidar observations of the nighttime sodium layer at 33°N. *Handbook for MAP, 18, Symposium November 26–30, 1984, Kyoto*, ed. by S. KATO. 417–420.
- UCHIUMI, M., HIRONO, M. and FUJIWARA, M. (1986): The seasonal variation of night-time sodium layer at 33°N (II); Error analysis and results from 1981 to 1984. *Mem. Natl Inst. Polar Res., Spec. Issue*, **42**, 132–142.

(Received October 7, 1986; Revised manuscript received January 20, 1987)