

Manuscript title: Sporadic sodium layer: A possible tracer for the conjunction between the upper and lower atmospheres

Authors: Shican Qui, Ning Wang et al.

Manuscript no.: **acp-2020-1079**

The authors have dealt with many of the points raised in the initial round of reviews. However, there are still two major matters that need to be addressed further.

1. The mechanism for sporadic Na layer production

Both in the response to the reviewers, and in the revised manuscript, the authors have explored the ion-molecule mechanism for Na_s production (Cox and Plane, 1989). They make a curious statement: “if we neglect k_1 as being too small with an order of 10^{-30} ”. But if this reaction does not occur, how does Na^+ become neutralized?! I think the authors have not realised that this is a *third*-order reaction, so that the second-order rate coefficient is given by $k[\text{N}_2]$. Instead, they have assumed an arbitrary concentration of Na^+CO_2 ions with a concentration of 100 cm^{-3} – without any justification, other than the rate of production of Na atoms via dissociative recombination with electrons is of the right order to explain their observations.

I would suggest a major rewrite of this section of the paper. The following is reproduced from the supporting information to a recent paper (Jiao et al., *GRL*, 2017) from Plane’s group in Leeds.

Table S1. Ion-molecule reaction rate coefficients for Na (adapted from *Plane et al.* [2015])

No.	Reaction	Rate coefficient ^a
1	$\text{Na} + \text{O}_2^+ \rightarrow \text{Na}^+ + \text{O}_2$	2.7×10^{-9}
2	$\text{Na} + \text{NO}^+ \rightarrow \text{Na}^+ + \text{NO}$	8×10^{-10}
3	$\text{Na}^+ + \text{N}_2 (+ \text{M} = \text{N}_2 \& \text{O}_2) \rightarrow \text{Na}^+\text{N}_2$	$4.8 \times 10^{-30} (T/200 \text{ K})^{-2.2}$
4	$\text{Na}^+ + \text{CO}_2 (+ \text{M}) \rightarrow \text{Na}^+\text{CO}_2$	$3.7 \times 10^{-29} (T/200 \text{ K})^{-2.84}$
5	$\text{Na}^+\text{N}_2 + \text{CO}_2 \rightarrow \text{Na}^+\text{CO}_2 + \text{N}_2$	6×10^{-10}
6	$\text{Na}^+\text{N}_2 + \text{O} \rightarrow \text{NaO}^+ + \text{N}_2$	4×10^{-10}
7	$\text{NaO}^+ + \text{O} \rightarrow \text{Na}^+ + \text{O}_2$	1×10^{-11}
8	$\text{NaO}^+ + \text{N}_2 \rightarrow \text{Na}^+\text{N}_2 + \text{O}$	1×10^{-12}
9	$\text{NaO}^+ + \text{O}_2 \rightarrow \text{Na}^+ + \text{O}_3$	5×10^{-12}
10	$\text{NaO}^+ + \text{CO}_2 \rightarrow \text{Na}^+\text{CO}_2 + \text{O}$	6×10^{-10}
11	$\text{Na}^+\text{X} (\text{X} = \text{O}, \text{N}_2, \text{CO}_2) + \text{e}^- \rightarrow \text{Na} + \text{X}$	$1 \times 10^{-6} (200 \text{ K}/T)^{0.5}$

^a Units: bimolecular reactions, $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$; termolecular reactions, $\text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$

Application of reaction branching probabilities to reactions 3-11 yields the following first-order rate coefficient for the neutralization rate of Na^+ ions [Plane, 2004]:

$$k(\text{Na}^+ \rightarrow \text{Na}) = k_3[\text{N}_2][\text{M}] \times \text{Pr}(\text{Na}^+ \cdot \text{N}_2 \rightarrow \text{Na}) + k_4[\text{CO}_2][\text{M}]$$

$$k_3[\text{N}_2][\text{M}] \left(\frac{k_{11}[\text{e}^-] + k_5[\text{CO}_2]}{k_{11}[\text{e}^-] + k_5[\text{CO}_2] + k_6[\text{O}] \times \text{Pr}(\text{NaO}^+ \rightarrow \text{Na}^+)} \right) + k_4[\text{CO}_2][\text{M}]$$

$$= k_3[\text{N}_2][\text{M}] \left(\frac{k_{11}[\text{e}^-] + k_5[\text{CO}_2]}{k_{11}[\text{e}^-] + k_5[\text{CO}_2] + k_6[\text{O}] \left(\frac{k_7[\text{O}] + k_9[\text{O}_2]}{k_7[\text{O}] + k_8[\text{N}_2] + k_9[\text{O}_2] + k_{10}[\text{CO}_2] + k_{11}[\text{e}^-]} \right)} \right) + k_4[\text{CO}_2][\text{M}]$$

where $\text{Pr}()$ denotes the branching probability.

Notes:

- Formation of $\text{Na}^+ \cdot \text{CO}_2$ leads irreversibly to Na via DR, because this ion is thermally stable and does ligand-witch with O, N_2 or O_2 [Cox and Plane, 1998].
- Once NaO^+ forms via reaction 6, reactions 7 and 9 convert it back to Na^+ . However, these reactions are in competition with reactions 8, 10 and 11. Reactions 10 and 11 will always produce Na via DR; reaction 8 produces $\text{Na}^+ \cdot \text{N}_2$, so there is a small probability that this will recycle again through NaO^+ to Na^+ and not lead to DR.
- Reactions involving H_2O are not included (analogues to R4, R5, R10 and R11), because $[\text{H}_2\text{O}]$ is around 2 orders of magnitude lower than $[\text{CO}_2]$, and these species have very similar chemistries.

The expression for the first-order conversion rate of Na^+ , $k(\text{Na}^+ \rightarrow \text{Na})$, can easily be computed as a function of height in a spreadsheet using typical values for N_2 , O_2 , O etc., and the electron density from the ionosonde and temperature from the W-T lidar. Discussion of the vertical profile of $k(\text{Na}^+ \rightarrow \text{Na})$ should replace the first part of Section 3.2, up to around line 10 on page 8. The Na^+ concentration required to produce the observed production rate of Na is simply obtained from $d[\text{Na}]/dt = k(\text{Na}^+ \rightarrow \text{Na})[\text{Na}^+]$, and the question is whether this is sensible in terms of the expected fraction of Na^+ ions which make up the total of metallic ions in the E_s layer.

It is still not clear what the role of lightning in this process is. The authors say that the field reversal induced by lightning will increase the electron density below 100 km by causing rapid downward transport of electrons. But does this actually happen? They do not quantify the magnitude of increase in electron density that might occur at 98 km, where the Na_s layer is observed. A more important question is whether it is electrons that are rate-determining in the neutralization process. In the expression for $k(\text{Na}^+ \rightarrow \text{Na})$, the question is whether $k_{11}[\text{e}^-]$ is larger than $k_5[\text{CO}_2]$. I do not believe that it is, so increasing electrons will make little difference to $k(\text{Na}^+ \rightarrow \text{Na})$. An obvious piece of evidence is that Na_s form without lightning being required.

2. The discrepancy between the two lidar records in Figure 1

Apparently there were problems with the USTC lidar shown in Figure 1. It is not clear to me what they were, and I still do not understand how the absolute Na density could vary by a factor of 2. The explanation on page 4 (lines 8 – 18) is unclear. It seems to be something to do with the uncertainty in the Na density retrieved from the broadband lidar. If the authors know what the problem is, they have two options: 1) discard the data, and just show data from the W/T lidar which makes up 3 of the 4 panels in Figure 1; 2) present a proper estimate of the uncertainty in the absolute density retrieved from each system, and show that they are in accord.