Responses to Reviewer # 1

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

Authors: Shican Qiu, Ning Wang et al.

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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 Nas 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 $k[N_2]$. 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	$Na + O_2^+ \rightarrow Na^+ + O_2$	2.7×10^{-9}

2	$Na + NO^+ \rightarrow Na^+ + NO$	8.0×10^{-10}
3	$Na^+ + N_2(+M = N_2\ \&\ O_2) \rightarrow Na^+ \cdot N_2$	$4.8 \times 10^{-30}(T\ /\ 200K)^{-2.2}$
4	$Na^+ + CO_2(+M) \rightarrow Na^+ \cdot CO_2$	$3.7 \times 10^{-29}(T\ /\ 200K)^{-2.84}$
5	$Na^+ \cdot N_2 + CO_2 \rightarrow Na^+ \cdot CO_2 + N_2$	6.0×10^{-10}
6	$Na^+ \cdot N_2 + O \rightarrow NaO^+ + N_2$	4.0×10^{-10}
7	$NaO^+ + O \rightarrow Na^+ + O_2$	1.0×10^{-11}
8	$NaO^+ + N_2 \rightarrow Na^+ \cdot N_2 + O$	1.0×10^{-12}
9	$NaO^+ + O_2 \rightarrow Na^+ + O_3$	5.0×10^{-12}
10	$NaO^+ + CO_2 \rightarrow Na^+ \cdot CO_2 + O$	6.0×10^{-10}
11	$Na^+ \cdot X\ (X = O, N_2, CO_2) + e^- \rightarrow Na + X$	$1.0 \times 10^{-6}(200K\ /\ T)^{0.5}$

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

$$k(Na^+ \rightarrow Na) = k_3[N_2][M] \times Pr(Na^+ \cdot N_2 \rightarrow Na) + k_4[CO_2][M]$$

$$= k_3[N_2][M] \left(\frac{k_{11}[e^-] + k_5[CO_2]}{k_{11}[e^-] + k_5[CO_2] + k_6[O] \times Pr(NaO^+ \rightarrow Na^+)} \right) + k_4[CO_2][M]$$

$$= k_3[N_2][M] \left(\frac{k_{11}[e^-] + k_5[CO_2]}{k_{11}[e^-] + k_5[CO_2] + k_6[O] \left(\frac{k_7[O] + k_9[O_2]}{k_6[O] + k_8[N_2] + k_9[O_2] + k_{10}[CO_2] + k_{11}[e^-]} \right)} \right)$$

$$+ k_4[CO_2][M]$$

where Pr() denotes the branching probability.

Notes:

1. Formation of $Na^+.CO_2$ 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].

2. 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 $Na^+.N_2$, so there is a small probability that this will recycle again through NaO^+ to Na^+ and not lead to DR.

3. Reactions involving H_2O are not included (analogues to R4, R5, R10 and R11), because $[H_2O]$ is around 2 orders of magnitude lower than $[CO_2]$, and these species have very similar chemistries. The expression for the first-order conversion rate of Na^+, $k(Na^+ \rightarrow Na)$, 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 $k(Na^+ \rightarrow Na)$ 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 $d[Na]/dt = k(Na^+ \rightarrow Na)[Na^+]$, 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 Es 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 $k(Na^+ \rightarrow Na)$, the question is whether $k_{11}[e^-]$ is larger than $k_5[CO_2]$. I do not believe that it is, so increasing electrons will make little difference to $k(Na^+ \rightarrow Na)$. An obvious piece of evidence is that Na_S form without lightning being required.

Reply: We would like to note our appreciation for all the contributions that this kind and wise reviewer has made for our manuscript. We apologize for addressing the chemical reactions in such a cursory manner during the previous revision. The first-order rate coefficient for the neutralization rate of Na^+ ions, k ($Na^+ \rightarrow Na$), has been calculated, with the help of WACCM-Na model simulation results from Dr. Wuhu Feng. We have modified section 3.2 substantially following the reviewer's comments.

On the other hand, we admit that we are only broadly sketching the lightnings as

a possible trigger of the electric field overturning. The electric field could turn upward through electrostatic induction by the thunderstorm. The strong lightnings could be regarded as an index of thunderstorm. And the echoes observed by the ionosonde exhibits synchronous activities with the lightnings, indicating a possible link between the lower atmosphere and the ionosphere. We hope to pursue some further study on the candidate triggers, such as lightnings, sprites, and elves. In any case, we would not doubt that the main source of Na_S is E_S. These authors always support the E_S mechanism most. The first author Shican Qiu and Xingjin Wang (her old student) are always dreaming of studying abroad sometime in Plane's group, if and when the concerns on coronal virus ends. For these flimsy reasons, we still hope to retain the contents about lightnings, without further significant new insights, in our manuscript.
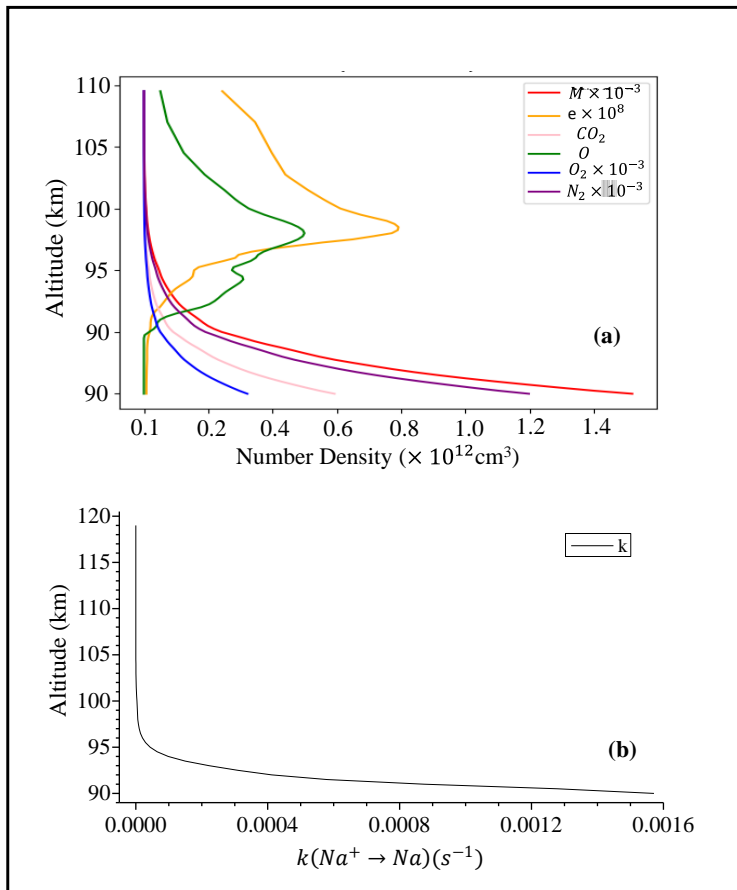

Figure 1** Model simulation results from WACCM-Na. (a) Constituents of the species used for calculating k ($Na^+ \rightarrow Na$). The number densities of CO_2, O_2, O, the total atmosphere density M and $N_2 \approx [M] - [O_2] - [O]$ are derived from Yuan et al., 2019. The number density of electrons equals to $e \approx 1.24 \times 10^4 f_o E_S^2$ (cm^{-3}). (b)

The calculated first-order rate coefficient k (Na$^+$→Na), indicating much more efficient recombination below about 100 km.

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.

Reply: Thanks for this comment. We have checked the original data files carefully again, and found the sodium density by the west beam of T/W lidar would probably be about 8650 cm^{-3}. We have discarded the bad data by the wide band lidar and replaced with a new image for the west beam of T/W lidar. Thus, Fig. 3(a) has been modified accordingly.
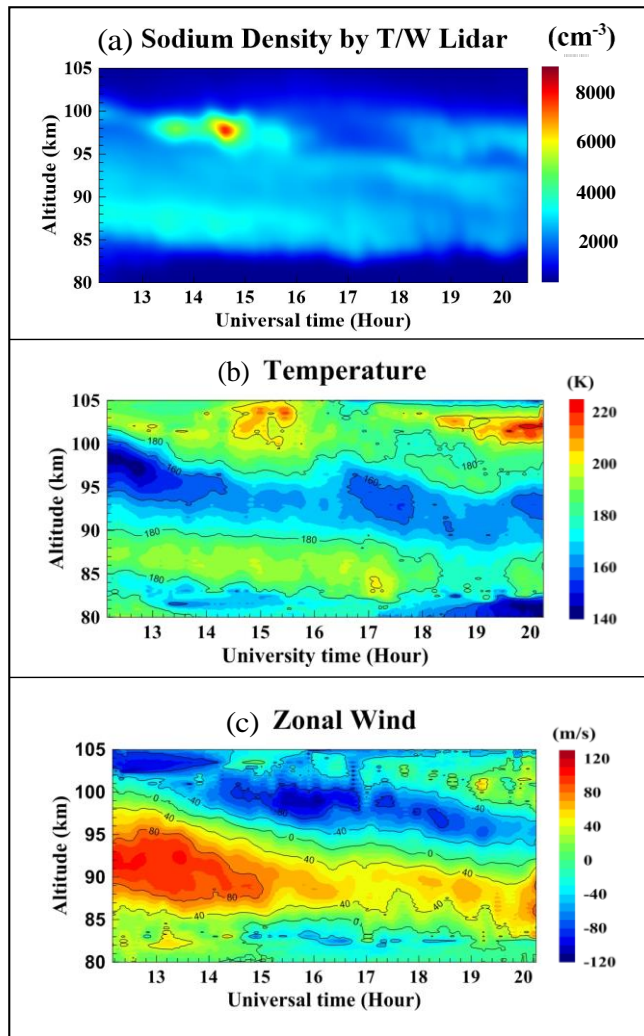
Figure 2** Observations on June 3rd, 2013, by the USTC T/W lidar. (a) The sodium density profile of the west beam by T/W lidar A moderate increase of sodium density appears at about 13:20 UT, while the largest intensity of sodium enhancement begins at about 14:20 UT. The sodium density peaks at 14:37 UT around 97.65 km. (b) Temperature profile observed by the T/W lidar, showing a cold region where the Na_S occurs. (c) The zonal wind detected by the T/W lidar, exhibiting a suitable wind shear for the creation or formation of E_S.

This version has been much improved than the previous one, and the authors gave a more reasonable analysis of the Nas layer enhancement in MLT region generated by lower atmospheric electric field. However, there are still some issues that need to be improved, which are listed as below:

1. Figure 1: Although the author provided inverting method of sodium density from two different kinds of lidar data in detail, the differences of sodium density between Figure 1a and Figure 1b are still quite large. The density of Figure 1a is almost double sizes of that of Figure 1b. And it is impossible to have such a big different result for two lidars which are almost in the same area (maybe less than 1km). Even though the author believes that this was the result of lidar noise affecting the density, but from Figure 3 in the "response to review2" provided by author, the sodium layer peak signal 107 is more than ten times than the noise (7). Although the count rate of this lidar is relatively lower, the density error is equal to the reciprocal of the square root of the signal minus the noise, which is about 1/10. So it is impossible for the signal-to-noise ratio to produce a double error consequently. The author should carefully consider about it, whether the inverted parameters (for example, the scattering cross section) were wrong processed? In addition, in "response to review2", as shown in Figure 2b "east density". Did that mean the density in Figure 1b is not vertical? This really makes me puzzled, I recommend the author to provide the density of the wind lidar in the vertical direction. The sodium densities detected by the oblique direction laser and the vertical direction laser are likely to be much different, as the distance between these two lasers is 40-50km in the height of the sodium layer, which has already been found in other sodium wind lidar data.

Reply: We truly appreciate all the contributions this kind and wise reviewer has made in improving our manuscript. In fact, the wide band lidar provides the vertical sodium density, while the narrowband lidar observes the oblique direction. We have checked the original data files carefully again and found that the sodium density from the west beam of T/W lidar would probably be about 8650 cm^{-3}. So we see the deduced sodium

density are actually different for each lidar beam. Considering both reviewers' comments, we now think it is better to discard the bad data by the wide band lidar, since it operated poorly on that day. We have replaced with a new image with the results taken from the west beam of T/W lidar. Both Fig. 1(a) and Fig. 3(a) have been modified accordingly in the final revised manuscript.
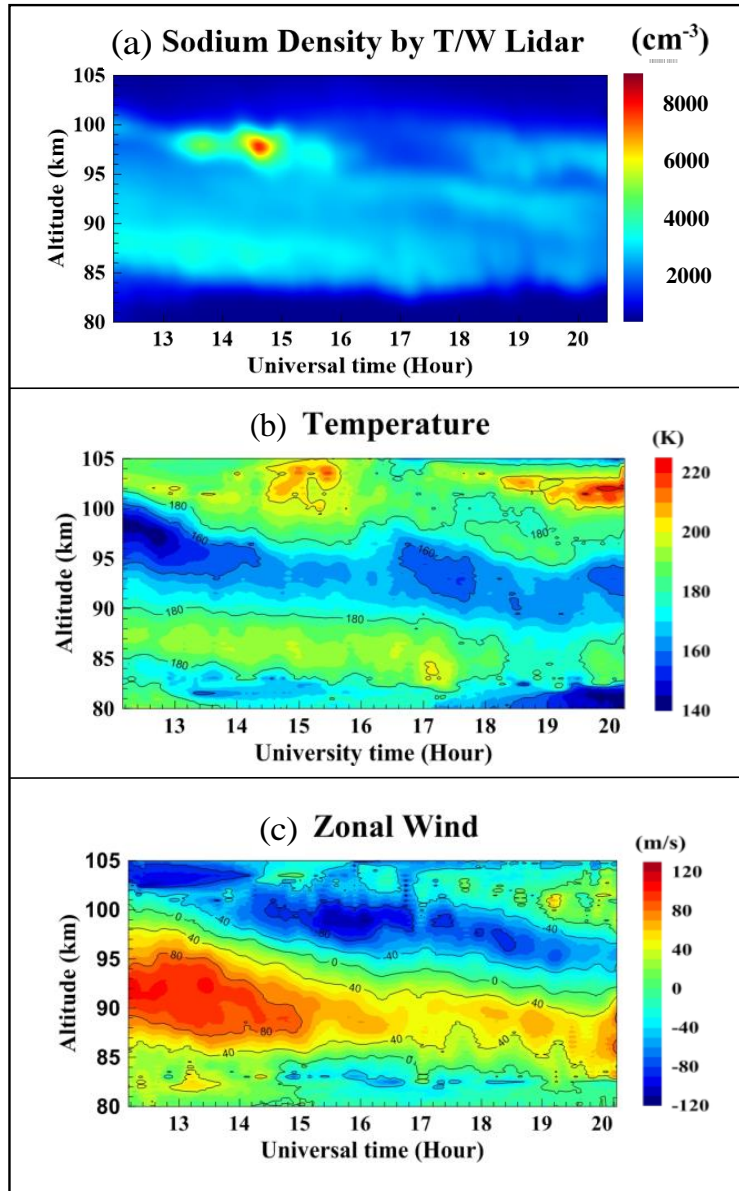

Figure 1** Observations on June 3rd, 2013, by the USTC T/W lidar. (a) The sodium density profile of the west beam by T/W lidar A moderate increase of sodium density appears at about 13:20 UT, while the largest intensity of sodium enhancement begins at about 14:20 UT. The sodium density peaks at 14:37 UT around 97.65 km. (b) Temperature profile observed by the T/W lidar, showing a cold region where the NaS

occurs. (c)The zonal wind detected by the T/W lidar, exhibiting a suitable wind shear for the creation or formation of E_S.

2. In my last review comment, I wrote: "it can be seen from Fig.2a: there is an enhancement in the Es layer from 13:20 to 14:20, and the origin of this enhancement was not explained or discussed in the manuscript. Is it caused by lightning as proposed by Johnson and Davis (GRL, 2006) ? I suggest that Authors could explain or discuss the enhancement in the Es layer from 13:20 to 14:20."
In this revised manuscript, the author believes that: electrons will follow the northward electric field and accumulate, but the ions still move in the same direction due to the difference in collision frequency (At the moment when the electric field reverses, electrons will be rapidly accelerated by the northward electric field, and ions would be regarded as essentially remaining northward or unchanged). This explanation is a little bit vague. The author also said in the previous paragraph: "Since metal ions are much heavier than electrons, the ions would drag electrons in order to move/drift together". Then why the electrons in this place can break away from the bondage of the deionization and accumulation with the movement of the ions? The point that reversal of electric field leads the enhancement of Es was not the crucial work of this article (The idea that the electric field reversal leads to the enhancement of Es has already been proposed by other authors, and the main contribution of this article is to discover and explain the generation of Nas). But I still hope that the author can provide a deeper explanation on this issue according to the previous research.

Reply: Thanks for this comment. The authors have made a primary statistical work, indicating the atmospheric electric field would probably influence the E_S layers. However, the results exhibit complex features as the following images show. For some cases during the overturning of electric field, foE$_S$ may be detected to increase in the data. But during other cases the E_S may disappear. Thus, we cannot draw a conclusion

on the definite pattern currently. The enhancement of E_S during the lightnings was first proposed by Johnson and Davis (2006), without detailed explanation about the mechanism. And those authors do not give further research results on the enhancement of E_S. So, it is still beyond our capability and expertise to explain the mechanism of the enhancement of E_S involved. We propose a further study on the link between electric field, lightnings, and E_S in the future work.
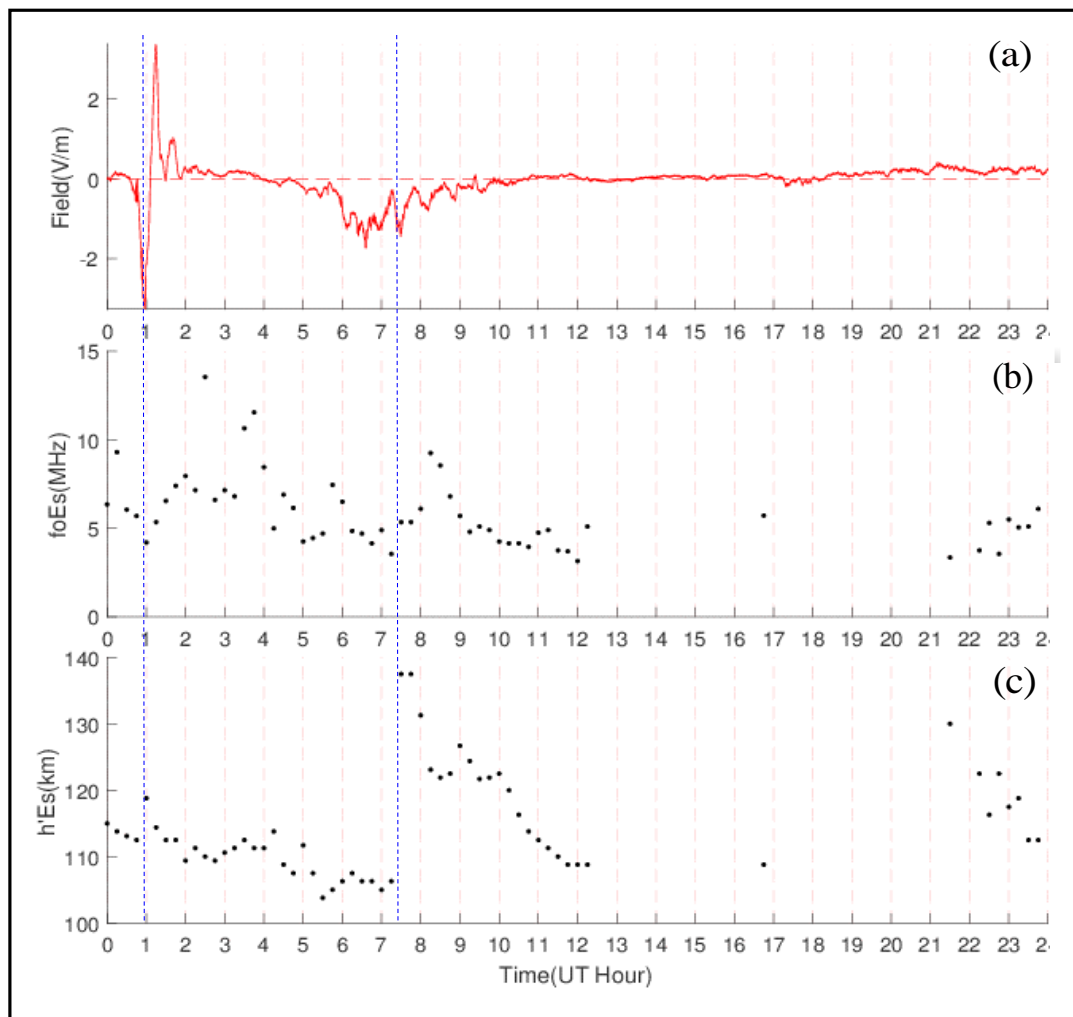

Figure 2** A typical case of foE$_S$ increase and h'E$_S$ rise caused by electric field overturning was observed on June 22, 2012
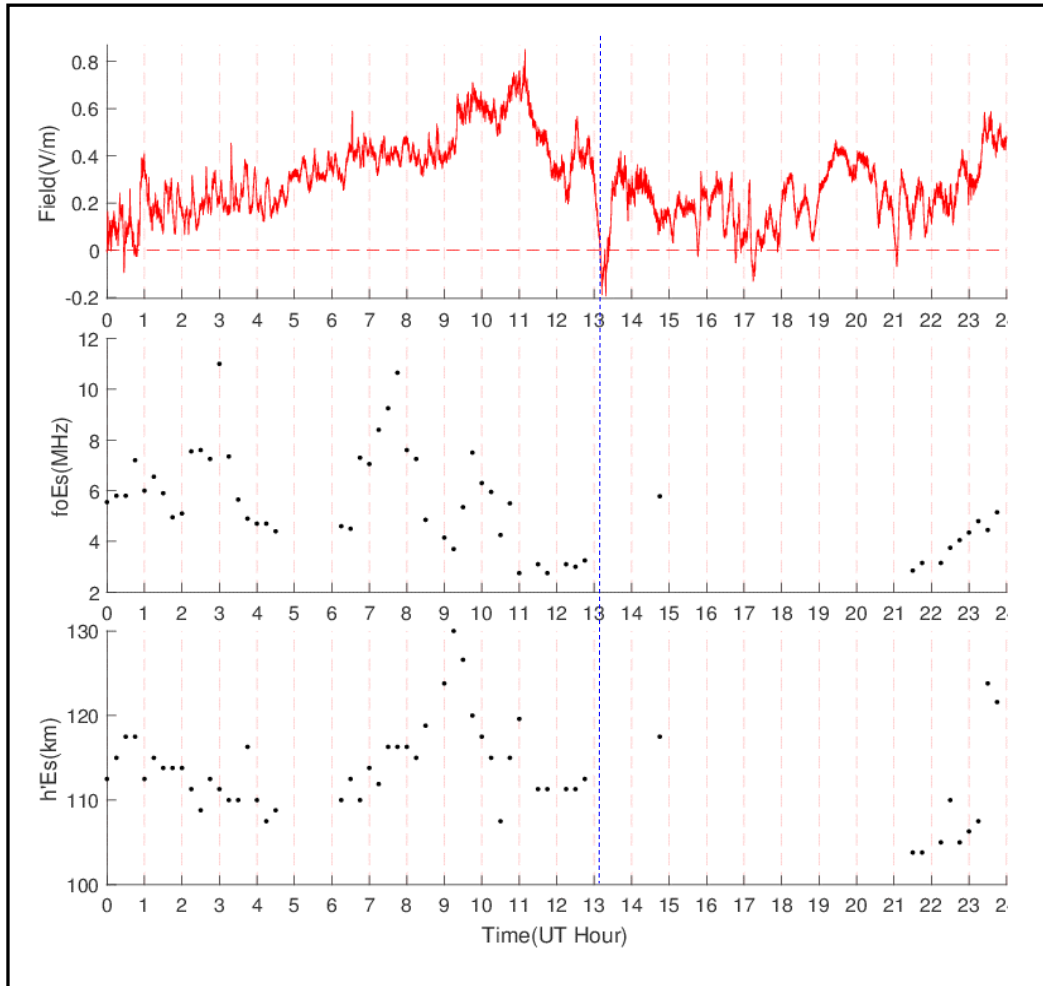
Figure 3** A typical case of E$_S$ disappearance caused by atmospheric electric field inversion was observed on May 21, 2012

On the other hand, under a quasi-equilibrium state, the ions and electrons would move together at least during the initial stage (e.g. the heavier ions dragging the electrons, which is called ambipolar diffusion). So the ions and electrons would move downward during a southward electric field. But in a nonequilibrium condition, e.g., at the point of the electric field overturning, each plasma species has a different relaxation time (the time needed for establishing equilibrium again). The relaxation for the electrons is much shorter than that for the ions, because $\tau = (4\pi\varepsilon_0)^2 \frac{3m^{1/2}T^{3/2}}{4\sqrt{2\pi}nq^4 \ln \Lambda}$ is positively related to the particle mass. This is why the electrons would respond much faster than the ions do during the phase of relaxation. This discrepancy would cause a charge separation temporarily. The electrons move opposite along the electric field,

which means during the upward electric field they would move downward. However, after the relaxation time, the system would reach an equilibrium state again. We have added some more explanations and descriptions for the relaxation time from line 7 to line 32 on page 8.

3. Referring to the generation of Nas at 14:20, the author believes that if the electron concentration in Es increased a lot, it can speed up the neutralization of sodium ions, and leading to the appearance of a new Nas peak. This explanation does really make sense. Since the reactants increase, the products must also increase. But I still stick to that there could be another possible contribution to the formation of Nas: the reversal of the electric field caused the nearby metal ions (including sodium ions) to join into Es, also resulting the increase of Es. And then the sodium ions in Es were neutralized to produce sodium atoms (at the same time Es was weakened). Anyway, though Plane's theory (Cox and Plane, 1998, JGR) indicates that metal ions have a very short lifetime below 100km, actually many calcium ions appeared below 100km and last several hours, which were already reported (Gerding et al., 2001, Annales Geophysicae; Raizada et al., 2012, JGR; Raizada et al., 2020 GRL). Therefore, the metal ions actually exist below 100km in my opinion.

Reply: Thanks for the comment. We have made a simulation of the chemical reactions through the encouragement of the other reviewer. The main reactions and corresponding rate coefficients for the sodium species under the mesopause condition are summarized in the new Table 2 of our revised manuscript (Cox and Plane, 1998; Jiao et al., 2017; Plane et al., 2015; Plane, 2004; Yuan et al., 2019). Application of reaction branching probabilities to reactions 3 to 11 yield the following first-order rate coefficient for the neutralization rate of Na^+ ions (Plane, 2004):

$$k(Na^+ \rightarrow Na) = k_3[N_2][M] \times Pr(Na^+ \cdot N_2 \rightarrow Na) + k_4[CO_2][M]$$

$$= k_3[N_2][M] \left(\frac{k_{11}[e^-]+k_5[CO_2]}{k_{11}[e^-]+k_5[CO_2]+k_6[O] \times Pr(NaO^+ \rightarrow Na^+)} \right) + k_4[CO_2][M]$$

$$= k_3[N_2][M] \left(\frac{k_{11}[e^-] + k_5[CO_2]}{k_{11}[e^-] + k_5[CO_2] + k_6[O] \left(\frac{k_7[O] + k_9[O_2]}{k_6[O] + k_8[N_2] + k_9[O_2] + k_{10}[CO_2] + k_{11}[e^-]} \right)} \right)$$

$$+ k_4[CO_2][M]$$

where *Pr* denotes the branching probability. The first-order conversion rate of

k (Na$^+\rightarrow$Na) can be computed as a function of height using typical values for N_2, O_2,

O, CO_2 from a WACCM-Na model simulation (Yuan et al., 2019). The calculated

results are given by Figure 6. The simulation results show sodium ions could probably

exist below 100 km: the inflection point of k (Na$^+\rightarrow$Na) comes out around 100 km, and

below that altitude, the sodium ions would recombine with electrons efficiently through

cycling chemical under a large k value. So the metal ions might actually exist below
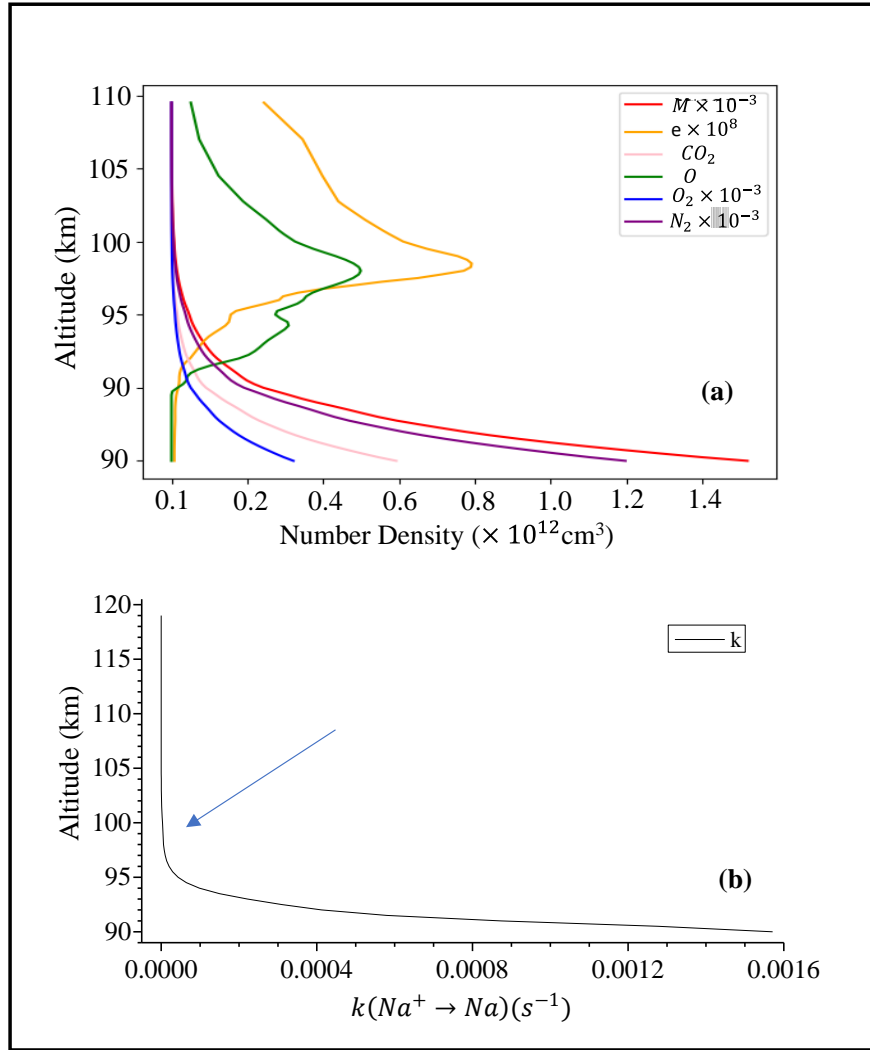
100 km as the reviewer regards.

Figure 4** Model simulation results from WACCM-Na. (a) Constituents of the species used for calculating k (Na$^+\to$Na). The number densities of CO_2, O_2, O, the total atmosphere density M and $N_2 \approx [M] - [O_2] - [O]$ are derived from Yuan et al., 2019. The number density of electrons equals to $e \approx 1.24 \times 10^4 f_o E_S^2 \ (cm^{-3})$. (b) The calculated first-order rate coefficient k (Na$^+\to$Na), indicating much more efficient recombination below about 100 km.

4. Page 5 Line 24: The formula is wrong. Authors double check their calculating results here and elsewhere. The critical frequency foE_S should be given by

$$foE_S = f_{pe} = \frac{\omega_{pe}}{2\pi} = \left(\frac{n_e e^2}{4\pi^2 m_e \varepsilon_0}\right)^{\frac{1}{2}}$$

Reply: Thanks for the comment. We have modified this formula around line 9 on page 5.