Seasonal Variation of the mesospheric Ca layer and Ca+ layer Simultaneously Observation over Beijing (40.41°N, 116.01°E)

Yuchang Xun [1,2], Peng Zhao [1,2], Zelong Wang [2,3], Lifang Du [2], Jing Jiao[2], Zhishan Chen[1,2], Haoran Zheng [2], Shaohua Gong[4], and Guotao Yang [2,*]

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Introduction

In this supporting information, Figure S1 shows the average temperature over Beijing at 80~100km.

Table S1 listed the relevant ion-molecule reactions of Ca [1,2] . These reactions were used to calculate the first-order-neutralization rates of Ca^+ by dissociative recombination and direct (radiative) recombination (Referring to the method of Wu et al. [3] , Qiu et al. [4] , Jiao et al. [5] , and Plane [6]).

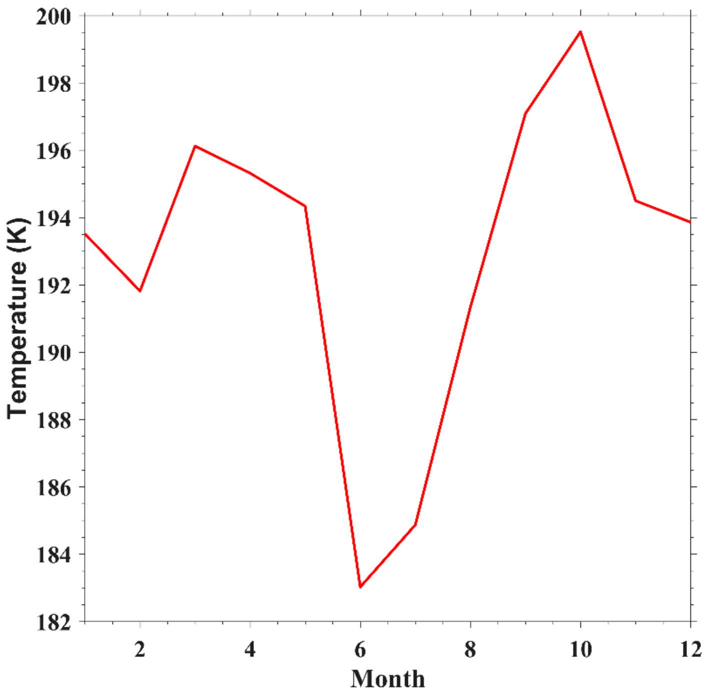

Figure S1. Annual variation of 80~100km mean temperature over Beijing with time (temperature data from WACCM)

Table S1. Ca Ion-Molecule Reactions and Rate Coefficients:

NO.	Reaction	Rate Coefficient
1	$Ca + O_2^+ \rightarrow Ca^+ + O_2$	1.8×10^{-9}

2	$Ca + NO^+ \rightarrow Ca^+ + NO$	4.0×10^{-9}
3	$Ca^+ + O_3 \rightarrow CaO^+ + O_2$	3.9×10^{-10}
4	$CaO^+ + O \rightarrow Ca^+ + O_2$	4.2×10^{-11}
5	$Ca^+ + O_2(+M) \rightarrow CaO_2^+$	$4.2 \times 10^{-29}\left(\frac{T}{200}\right)^{-2.37}$
6	$CaO_2^+ + O \rightarrow CaO^+ + O_2$	1.0×10^{-10}
7	$Ca^+ + N_2 + M \rightarrow Ca \cdot N_2^+ + M$	$2.3 \times 10^{-30}\left(\frac{T}{200}\right)^{-2.49}$
8	$Ca^+ + CO_2(+M) \rightarrow Ca^+ \cdot CO_2$	$4.3 \times 10^{-29}\left(\frac{T}{200}\right)^{-3.09}$
9	$Ca^+ + H_2O(+M) \rightarrow Ca^+ \cdot H_2O$	$1.2 \times 10^{-28}(T/200)^{-2.12}$
10	$Ca \cdot N_2^+ + O_2 \rightarrow CaO_2^+ + N_2$	3×10^{-10}
11	$Ca^+ \cdot CO_2 + O_2 \rightarrow CaO_2^+ + CO_2$	1.2×10^{-10}
12	$Ca^+ \cdot CO_2 + H_2O \rightarrow Ca^+ \cdot H_2O + CO_2$	1.3×10^{-9}
13	$Ca^+ \cdot H_2O + O_2 \rightarrow CaO_2^+ + H_2O$	4.0×10^{-10}
14	$CaX^+ + e^- \rightarrow Ca + X\ (X = O, O_2, N_2, CO_2, H_2O)$	$3 \times 10^{-7}(T/295)^{-\frac{1}{2}}$
15	$Ca^+ + e^- \rightarrow Ca + hv$	$3.8 \times 10^{-12}(T/200)^{-0.9}$

the first-order rate coefficient k($Ca^+ \rightarrow Ca$) for the neutralization of Ca^+ was calculated as follows:

$$k(Ca^+ \rightarrow Ca) = k_3[O_3] \times \Pr(CaO^+ \rightarrow Ca) + k_5[O_2][M] \times \Pr(CaO_2^+ \rightarrow Ca) + k_7[N_2][M] \times \Pr(CaN_2^+ \rightarrow Ca) + k_8[CO_2][M] \times \Pr(Ca^+CO_2 \rightarrow Ca) + k_9[H_2O][M] \times \Pr(Ca^+H_2O \rightarrow Ca)$$

where Pr() denotes the branching probability:

$$1. k_3[O_3] \times \Pr(CaO^+ \rightarrow Ca) = k_3[O_3] \cdot \left(\frac{k_{14}[e^-]}{k_{14}[e^-] + k_4[O]}\right)$$

$$2. k_5[O_2][M] \times \Pr\,(CaO_2^+ \rightarrow Ca) = k_5[O_2][M] \times \{\Pr(CaO_2^+ \rightarrow Ca\ direct) + \Pr(CaO_2^+ \rightarrow CaO^+) \times \Pr(CaO^+ \rightarrow Ca)\}$$

$$k_5[O_2][M] \times \Pr(CaO_2^+ \rightarrow Ca) = k_5[O_2][M] \cdot \left\{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_6[O]} + \frac{k_6[O]}{k_{14}[e^-]+k_6[O]} \cdot \frac{k_{14}[e^-]}{k_{14}[e^-]+k_4[O]}\right\}$$

$$3. k_7[N_2][M] \times Pr(CaN_2^+ \rightarrow Ca) = k_7[N_2][M] \times \{\Pr\,(CaN_2^+ \rightarrow Ca\ \ direct) + \Pr\,(CaN_2^+ \rightarrow CaO_2^+) \times \Pr\,(CaO_2^+ \rightarrow Ca)\}$$

$$k_7[N_2][M] \times Pr(CaN_2^+ \to Ca) = k_7[N_2][M] \times \left\{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_{10}[O_2]} + \frac{k_{10}[O_2]}{k_{14}[e^-]+k_{10}[O_2]} \cdot \left\{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_6[O]} + \frac{k_6[O]}{k_{14}[e^-]+k_6[O]} \cdot \frac{k_{14}[e^-]}{k_{14}[e^-]+k_4[O]}\right\}\right\}$$

4. $k_8[CO_2][M] \times Pr(Ca^+CO_2 \to Ca) = k_8[CO_2][M] \times \{Pr(Ca^+CO_2 \to Ca\ direct) + Pr(Ca^+CO_2 \to CaO_2^+) \times \Pr(CaO_2^+ \to Ca) + Pr(Ca^+CO_2 \to Ca^+H_2O) \times Pr(Ca^+H_2O \to Ca)\}$

$$k_8[CO_2][M] \times Pr(Ca^+CO_2 \to Ca) = k_8[co_2][M] \times \{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_{11}[O_2]+k_{12}[H_2O]} + \frac{k_{11}[O_2]}{k_{14}[e^-]+k_{11}[O_2]+k_{12}[H_2O]} \times \Pr(CaO_2^+ \to Ca) + \frac{k_{12}[H_2O]}{k_{14}[e^-]+k_{11}[O_2]+k_{12}[H_2O]} \cdot \{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_{13}[O_2]} + \frac{k_{13}[O_2]}{k_{14}[e^-]+k_{13}[O_2]} \times \Pr(CaO_2^+ \to Ca)\}\}$$

$$k_8[CO_2][M] \times Pr(Ca^+CO_2 \to Ca) = k_8[co_2][M] \times \{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_{11}[O_2]+k_{12}[H_2O]} + \frac{k_{11}[O_2]}{k_{14}[e^-]+k_{11}[O_2]+k_{12}[H_2O]} \cdot \left\{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_6[O]} + \frac{k_6[O]}{k_{14}[e^-]+k_6[O]} \cdot \frac{k_{14}[e^-]}{k_{14}[e^-]+k_4[O]}\right\} + \frac{k_{12}[H_2O]}{k_{14}[e^-]+k_{11}[O_2]+k_{12}[H_2O]} \cdot \{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_{13}[O_2]} + \frac{k_{13}[O_2]}{k_{14}[e^-]+k_{13}[O_2]} \cdot (\frac{k_{14}[e^-]}{k_{14}[e^-]+k_6[O]} + \frac{k_6[O]}{k_{14}[e^-]+k_6[O]} \cdot \frac{k_{14}[e^-]}{k_{14}[e^-]+k_4[O]})\}\}$$

5. $k_9[H_2O][M] \times \Pr(Ca^+H_2O \to Ca) = k_9[H_2O][M]) \times \{\Pr(Ca^+H_2O \to Ca\ direct) + Pr(Ca^+H_2O \to CaO_2^+) \times (Pr(CaO_2^+ \to Ca)\}$

$$k_9[H_2O][M] \times \Pr(Ca^+H_2O \to Ca) = k_9[H_2O][M] \times \{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_{13}[O_2]} + \frac{k_{13}[O_2]}{k_{14}[e^-]+k_{13}[O_2]} \cdot \{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_6[O]} + \frac{k_6[O]}{k_{14}[e^-]+k_6[O]} \cdot \frac{k_{14}[e^-]}{k_{14}[e^-]+k_4[O]}\}\}$$

As $[CO_2]$ is three orders of magnitude smaller than $[O_2]$, k5 and k8 are one order of magnitude smaller, $[H_2O]$ is five orders of magnitude smaller than $[O_2]$, and k9 is only one order of magnitude larger than k5, ignore terms 4 and 5 [3].

So:

$$k(Ca^+ \to Ca) = k_3[O_3] \times Pr(CaO^+ \to Ca) + k_5[O_2][M] \times Pr(CaO_2^+ \to Ca) + k_7[N_2][M] \times Pr(CaN_2^+ \to Ca)$$

$$= k_3[O_3] \cdot \left(\frac{k_{14}[e^-]}{k_{14}[e^-]+k_4[O]}\right) + k_5[O_2][M] \cdot \left\{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_6[O]} + \frac{k_6[O]}{k_{14}[e^-]+k_6[O]} \cdot \frac{k_{14}[e^-]}{k_{14}[e^-]+k_4[O]}\right\} + k_7[N_2][M] \cdot \left\{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_{10}[O_2]} + \frac{k_{10}[O_2]}{k_{14}[e^-]+k_{10}[O_2]} \cdot \left\{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_6[O]} + \frac{k_6[O]}{k_{14}[e^-]+k_6[O]} \cdot \frac{k_{14}[e^-]}{k_{14}[e^-]+k_4[O]}\right\}\right\}$$

$$= k_3[O_3] \cdot \left(\frac{k_{14}[e^-]}{k_{14}[e^-]+k_4[O]}\right) + (k_5[O_2][M] + k_7[N_2][M] \cdot \frac{k_{10}[O_2]}{k_{14}[e^-]+k_{10}[O_2]}) \cdot$$

$$\left\{\frac{k_{14}[e^-]}{k_{14}[e^-]+k_6[O]}+\frac{k_6[O]}{k_{14}[e^-]+k_6[O]}\cdot\frac{k_{14}[e^-]}{k_{14}[e^-]+k_4[O]}\right\}+k_7[N_2][M]\cdot\frac{k_{14}[e^-]}{k_{14}[e^-]+k_{10}[O_2]}$$

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