Key ionic reactions affecting stratospheric O_3 and HNO_3 changes caused by the Halloween solar proton event†

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High-energy protons emitted during solar proton events (SPEs) penetrate into the middle atmosphere. They can induce an increase in concentrations of odd-hydrogen (HO_x) and odd-nitrogen (NO_x) through ionization and dissociation of oxygen and nitrogen. These chemical species are known to cause variations of O_3. When the "Halloween" SPE occurred in 2003, O_3 and HNO_3 changes were observed in the polar stratosphere by the MIPAS onboard ENVISAT satellite.[1)] In this study, we aim to identify the key ionic reactions by comparing the MIPAS observations and numerical results with/without ionic reactions.

Previous studies[1–3)] have shown that it is important to incorporate not only neutral but also ionic reactions into models to reproduce the observed *short-term* changes, which lasted for about 10 days. However, very few models include as many ionic reactions as the SIC model[2)] when simulating trace gas variations in the stratosphere. We have developed a box-model with the largest number of chemical reactions in homogeneous gas phase, but no transport processes. We adopted 90 chemical species and 752 reactions, including 605 ionic reactions in this model.

Figure 1 shows the result for changes in the number densities of area-weighted average from 70°N to 90°N of O_3 (top) and HNO_3 (bottom) since October 21, 2003 at a 50 km altitude. The *short-term* O_3 decrease and HNO_3 increase observed during the Halloween event were well reproduced in the box-model including full (ion and neutral) chemistry, but not in the model excluding ionic reactions. The cause of the difference between the observed and calculated O_3 concentrations after about 10 days from the event is unclear, but it may be due to the lack of transport processes in the model.

We identified that sequential reaction pathways that form hydrated clusters, starting from $O_2^+ + H_2O + M \rightarrow O_2^+(H_2O) + M$, are crucial to understand these short-term changes. This is because the hydrated clusters are the primary ions that generate OH and HNO_3. The reaction network including these ionic pathways is shown in Fig. 2. We see that the ionic reactions releases a new reaction window that allows the destruction of O_3 and production of HNO_3.

In summary, our study shows the importance of ionic reactions that produce hydrated clusters when simulating stratospheric O_3 and HNO_3 variations in the presence of strong ionization processes.

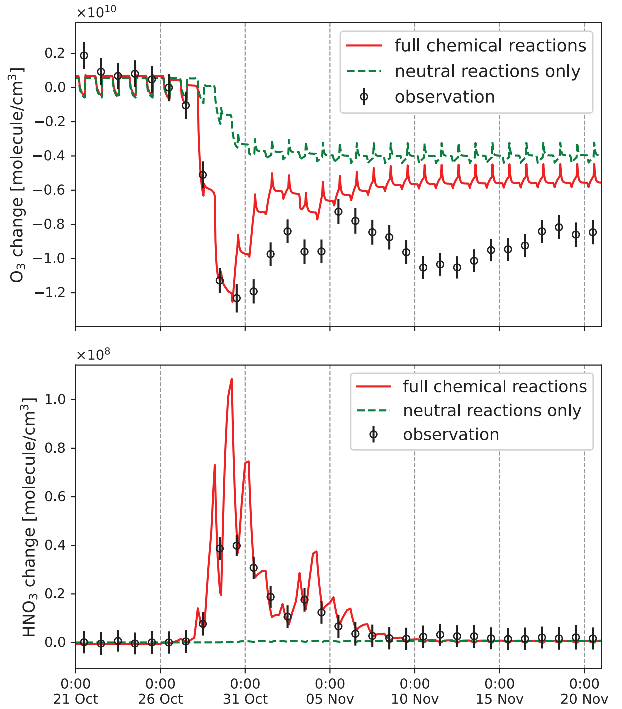

Fig. 1. Changes in the number densities of area-weighted average from 70°N to 90°N of O_3 (top) and HNO_3 (bottom) since October 21, 2003, for the Halloween event at a 50 km altitude.

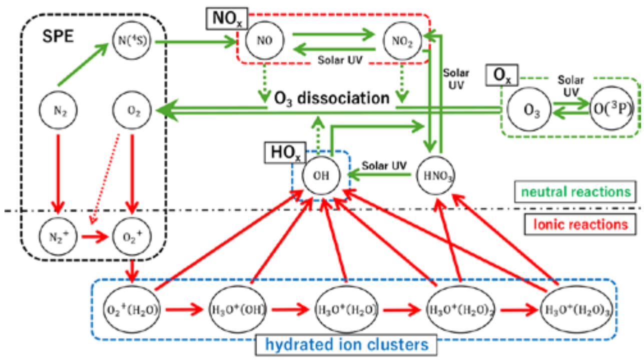

Fig. 2. A partial reaction network of ion and neutral chemistry caused by a SPE.

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