

Stratospheric Trace Gas Detection by Chemical Ionization: Application and Comparison of different Ion-molecule Reaction Schemes

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INTRODUCTION

The reservoir gases HNO_3 , N_2O_5 and ClONO_2 have a crucial part in the ozone destruction process [1]. Presently the majority of the techniques to measure the concentration of these substances is based on remote sensing, either from balloon platforms or satellites. For the previously mentioned three gases, in situ measurement in the stratosphere by Chemical Ionization Mass Spectrometry (CIMS) has only been performed so far for nitric acid [2]. It is in the aim of the MACSIMS project to extend the CIMS technique for the three gases and possibly HCl. Within this effort different ion-molecule reaction schemes are investigated in the laboratory and tested in flight.

The present paper reports on the results obtained for HNO_3 measurements through the use of four different ion-molecule reaction schemes. The detection of other gases by CIMS is also considered.

EXPERIMENTAL SETUP

The CIMS technique is based on the formation of specific product ions, resulting from the reaction of atmospheric trace gases with specific source ions, produced by an ion source. The source ions are injected in a flow tube in which stratospheric air is aspirated by a small turbine. These ions are transported by the air flow to a double focusing Mattauch-Herzog magnetic mass spectrometer and react on their way selectively with trace gases. Measurement of the relative abundances of source and product ions, of the time of flight and knowledge of the reaction rate coefficients allows the deduction of the trace gas mixing ratios.

Up to now four ion sources have been installed in the MACSIMS experiment, which are operated in an alternating order during the descent phase of the balloon flight:

- a) a capillary discharge ion source (DIS-A) producing Cl_n^- ($n = 1, 3$) from a gas mixture of Cl_2 in Ar (30 to 1000 ppm);
- b) a similar ion source (DIS-B) producing I_n^- ($n = 1, 3$) from a gas mixture of CH_3I in Ar (1000 ppm);
- c) a photo electron ion source (PEIS-A). Photo electrons, created by impact of UV photons on the flow tube wall, attach to atmospheric oxygen and consecutive ion-molecule reactions with atmospheric ozone and CO_2 result in the formation of CO_3^- ;
- d) a similar source (PEIS-B) producing CF_3O^- by dissociative electron attachment to $\text{CF}_3\text{OOF}_3\text{C}$ (2500 ppm in Ar).

RESULTS

The trace gas concentration $[X]$ is derived by means of the following formula:

$$[X] = \frac{1}{(k_A - k_B)\tau} \ln \left[1 + \frac{k_A - k_B}{k_A} R \right] \quad (1)$$

with R the ratio of product to source ions. k_A is the rate coefficient of the ion-molecule reactions with X resulting in the formation of the product ions, k_B is the rate for the reactions with X , which cause a loss of product ions, and τ represents the time of flight in the flow tube. The HNO_3 concentration can be obtained from the data of the DIS-A source in two different ways. The first method (DIS-A-1) is based on the reaction of Cl_3^- with HNO_3 and the subsequent reaction of the product ion $\text{NO}_3^- \cdot \text{HCl}$ with nitric acid. The HNO_3 concentration is given by equation (1) with $R = [\text{NO}_3^- \cdot \text{HCl}] / [\text{Cl}_3^-]$ and $k_A = 2.44 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$. The loss rate k_B of the product ion $\text{NO}_3^- \cdot \text{HCl}$ equals $1.33 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$ [3]. In the second method (DIS-A-2) all the ions of the chlorine family (Cl_n^- ($n = 1, 3$), $\text{Cl}^- \cdot \text{H}_2\text{O}$ and $\text{Cl}^- \cdot \text{HCl}$) are considered as source ions, while all NO_3^- -core ions constitute the product ions. In formula (1) k_A equals $2.44 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$ (the reaction rate of the most abundant ion, i.e. Cl_3^-) and k_B is put to zero.

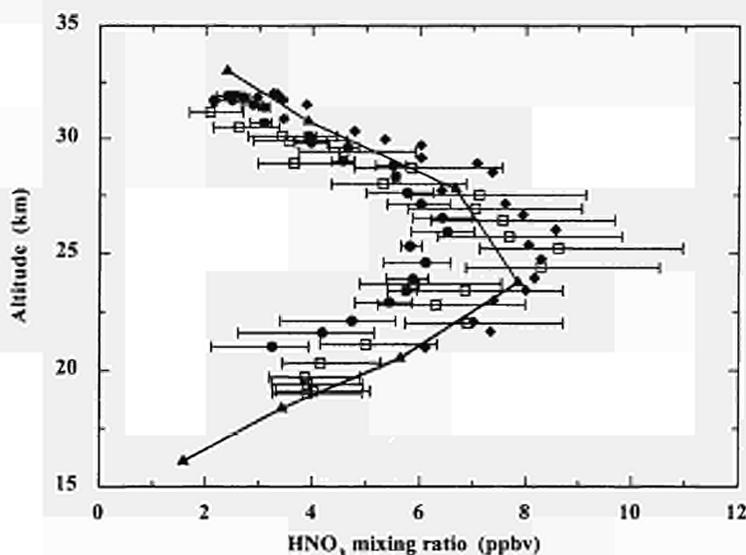


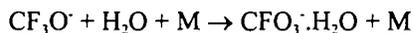
Figure 1: HNO_3 height profile, obtained with the DIS-A and the PEIS-A ion source (León, November 23rd 1995), and previously measured values by LIMS. (●): DIS-A-1; (◆): DIS-A-2; (□): PEIS-A; (▲): LIMS.

The concentration of the trace gas HNO_3 can also be derived from the measurements with the PEIS-A source. In this case the major source ions are CO_3^- and $\text{CO}_3^- \cdot \text{H}_2\text{O}$. The reaction of both these ions leads to the formation of $\text{CO}_3^- \cdot \text{HNO}_3$. In equation (1) k_A is given by the reaction rate of CO_3^- with HNO_3 , since CO_3^- is the most abundant source ion ($k_A = 1.6 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$ [4]). The loss reaction $\text{CO}_3^- \cdot \text{HNO}_3 + \text{HNO}_3 + \text{M} \rightarrow \text{CO}_3^- \cdot (\text{HNO}_3)_2 + \text{M}$ is characterized by $k_B > 6 \times 10^{-10} \text{cm}^3 \text{s}^{-1}$. For a more detailed discussion of the methods described above, we refer to [5].

HNO₃ height profiles, obtained with these methods, are shown in figure 1 for the flight on November 23rd 1995 in León, Spain (42°35'N, 05°38'W). In view of the assumptions made and the representation on linear scale the agreement with previously reported measured values [6] is good.

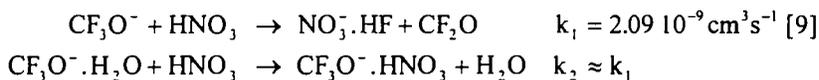
The DIS-B ion source was originally developed for the determination of the N₂O₅ height profile, based on the assumption that I⁻ only reacts with N₂O₅ to form NO₃⁻. However Huey [7] showed that ClONO₂ also reacts with I⁻ resulting in the same product ion, so that only the weighted concentration of N₂O₅ + ClONO₂ can be derived from the measurements with the DIS-B source. The deduced height profile is too large by a factor 3 or more. This discrepancy is due to an oversimplification of the chemistry involved. Firstly the ion source produces next to I⁻ also I₃⁻ for which the reaction products with N₂O₅ and ClONO₂ are unknown for the moment. Furthermore recent laboratory experiments have shown that I⁻ reacts with ozone resulting in IO₃⁻, which on turn reacts with HNO₃ leading to NO₃⁻ [8]. It is clear that further extensive laboratory studies are necessary for the interpretation of the data from the DIS-B source.

According to Huey [9] the source ion CF₃O⁻ is very well suited for the derivation of the height profiles of trace gases, such as HNO₃, ClONO₂ and HCl with the CIMS method. A new ion source was developed (PEIS-B), which was used for the first time during the flight of June 17th 1997 in Gap, France (44°27'N, 06°02'W). Two source ions are observed: CF₃O⁻ and CF₃O⁻.HF. The latter is not formed by reaction with stratospheric HF, since it was also observed in the same relative proportion during laboratory tests for the development of the ion source. The most abundant precursor ion is however CF₃O⁻.H₂O, which is formed in situ. The large hydration can be caused either by a totally unexpected temperature dependence of the 3-body reaction



for which Huey [9] found a reaction rate of $3 \times 10^{-14} \text{cm}^3 \text{s}^{-1}$ at ambient temperature, or it is caused by the presence of contaminating H₂O in the flow tube, in the ion source or in the immediate vicinity of the instrument. Experiments are undertaken to clarify the presence of CF₃O⁻.H₂O.

A variety of product ions are observed from the reaction of CF₃O⁻ and CF₃O⁻.H₂O with HNO₃, ClONO₂ and HCl. Despite the presence of CF₃O⁻.H₂O we are able to derive the HNO₃ concentration, according to the following reaction scheme:



According to Huey [9] the reaction of CF₃O⁻ with nitric acid proceeds at the collision limit. Assuming that the same is true for the reaction of CF₃O⁻.H₂O with HNO₃ and taking into account that collisional rate coefficients scale linearly with the inverse square of the reduced mass of the ion-molecule system [10], the rate coefficient k₂ is at most 5% different from k₁. Formula (1) is used with k_A = k₁ and k_B put to zero. The family of source ions consists of CF₃O⁻ and CF₃O⁻.H₂O. Next to NO₃⁻.HF and CF₃O⁻.HNO₃ the secondary reaction products NO₃⁻.(HNO₃)_n (n = 1, 2), CF₃O⁻.(HNO₃)₂ and NO₃⁻.HF.H₂O constitute the family of product ions. The resulting mixing ratio is shown in figure 2 (preliminary). The agreement with interpolated LIMS data [6] is satisfactory.

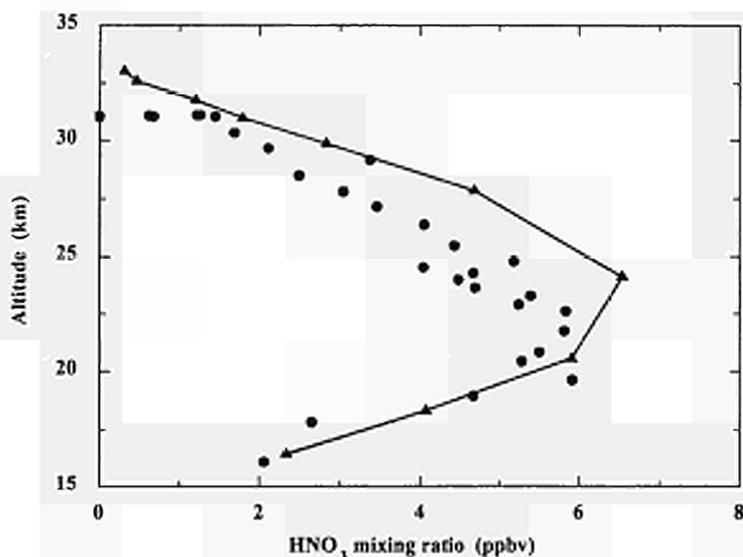


Figure 2: preliminary HNO_3 height profile derived from the measurements with the PEIS-B source (Gap, June 17th 1997). (●): PEIS-B; (▲): LIMS.

The derivation of the ClONO_2 and HCl height profiles is hampered by the occurrence of $\text{CF}_3\text{O}\cdot\text{H}_2\text{O}$, which disturbs the originally developed reaction scheme. Detector problems at the location of some specific product ions are also encountered. Laboratory measurements of the reaction of $\text{CF}_3\text{O}\cdot\text{H}_2\text{O}$ with ClONO_2 and HCl are needed to finalize the reaction schemes and are planned in the near future. Furthermore, if the presence of $\text{CF}_3\text{O}\cdot\text{H}_2\text{O}$ is due to contaminating H_2O , suitable modifications to the instrument will be carried out in order to eliminate the formation of this ion.

This work was supported by the European Commission (contracts EV5V-CT92-0062 and ENV4-CT95-0042), the DWTC (Diensten voor Wetenschappelijke, Technische en Culturele Aangelegenheden, Belgium), the CNRS (Centre National de Recherches Scientifiques, France), the CNES (Centre National d'Etudes Spatiales, France), the Conseil Regional du Centre, France and the SNF (Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung).

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