Mid-latitude CIMS-based Measurements of Stratospheric Trace Gas Concentrations

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1. Introduction

Chemical Ionisation Mass Spectrometry (CIMS) is a sensitive analytical tool, which allows the in situ determination of stratospheric trace gas concentrations [1], provided that suitable reaction schemes are available. Reaction schemes for the derivation of the concentration of stratospheric HNO_3, HCl and $ClONO_2$, based upon a new ion source mainly producing CF_3O^-, were applied. The results of two flights of our balloon borne chemical ionisation mass spectrometer (MACSIMS) equipped with this new ion source are shown and discussed.

2. Method

The CIMS technique is based upon the reaction of atmospheric trace gases with specific source ions resulting in the formation of specific product ions. The source ions S are injected into a flow tube through which a flow of stratospheric air is established by means of a small turbine and are transported by the flow of air to a double focusing Mattauch-Herzog magnetic mass spectrometer. During the transport specific product ions P_X^- are formed by the reaction of these source ions with the atmospheric trace gas constituent X. Simultaneous measurement of the abundance of the specific source and product ions allows the determination of the concentration of the trace gas X through the following equations:

$$S^- + X \rightarrow P_X^- + \text{neutral products} \qquad (1)$$

$$S^- + Y \rightarrow P_Y^- + \text{neutral products} \qquad (2)$$

$$[X] = \frac{1}{k\tau}\left(1 + \frac{[\sum P_Y^-]}{[P_X^-]}\right)^{-1} \ln\left(1 + \frac{[P_X^-] + [\sum P_Y^-]}{[S^-]}\right) \qquad (3)$$

where k is the rate constant for the ion-molecule reaction (1) and τ is the residence time of the ions in the flow tube. In (3) $\Sigma[P_Y^-]$ represents the relative abundance of all product ions P_Y^- formed by the reaction of the source ions S^- with trace gases Y other than X (ion-molecule reaction (2)).

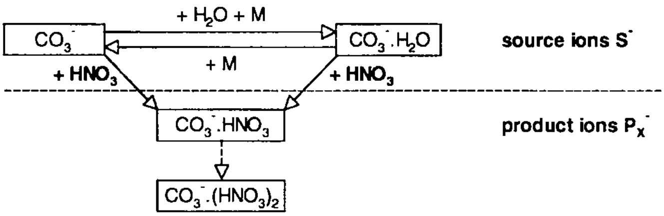
During the balloon flights of June 17th 1997 and June 17th 1999 in Gap Tallard, France (44°27'N, 06°02'E), the MACSIMS experiment was equipped with four separate ion sources of which two will be discussed in this paper:

- Photo-electron ion source PEIS-A: photo-electrons generated by illumination of the stainless steel flow tube wall by a Kr capillary discharge lamp attach to atmospheric oxygen and consecutive ion-molecule reactions with atmospheric O_3, CO_2 and H_2O result in the formation of CO_3^- and $CO_3^-.H_2O$.

Photo-electron ion source PEIS-B: in this source photo-electrons are created by illumination of the metallic body of this source by a second UV discharge lamp and CF_3O^- ions are formed by dissociative attachment of these photo-electrons to CF_3OOF_3C (2500 ppm in Ar). These ions are partially converted in the flow tube to $CF_3O^-.H_2O$ by reaction with stratospheric water vapour, and to $CF_3O^-.HF$ probably by reaction with impurities in the parent gas mixture.

As these hydrates and $CF_3O^-.HF$ react with approximately the same rate constant as the core ions CO_3^- and CF_3O^- (see further on), they are lumped together with the latter as source ions S^- in equation (3).

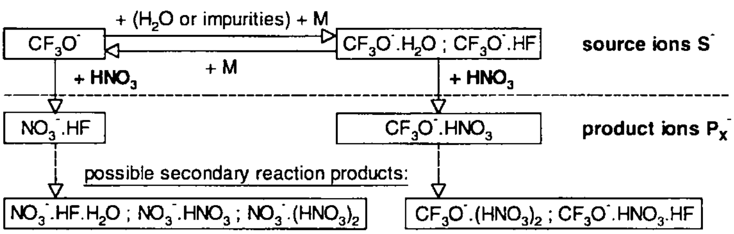
Nitric acid concentrations are inferred from the results obtained with the PEIS-A ion source according to the following reaction scheme:



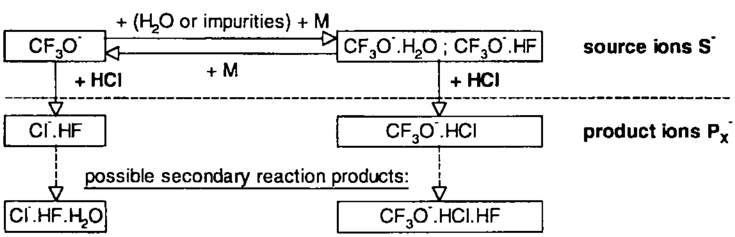
The average of the rate constants of CO_3^- and $CO_3^-.H_2O$ with HNO_3 (respectively $2.4 \times 10^{-9} cm^3 s^{-1}$[2] and $2.04 \times 10^{-9} cm^3 s^{-1}$), weighted by their abundance, is used for the value of the rate constant k in equation (3).

For the PEIS-B ion source the following reaction schemes are used for the derivation of the concentration of HNO_3, HCl and $ClONO_2$:

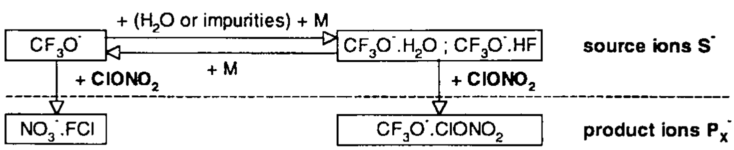
- HNO_3:



- HCl:



- $ClONO_2$:



The rate constants of the reactions of CF_3O^-, $CF_3O^-.H_2O$ and $CF_3O^-.HF$ with HNO_3 and HCl have been measured in our laboratory [3]. Since the reaction rate constants of these three source ions with HNO_3, respectively with HCl, are equal within the error bars for each neutral species, their mean value has been used in formula (3). For the derivation of the $ClONO_2$ concentration it is assumed that the reaction rate of $CF_3O^-.H_2O$ and $CF_3O^-.HF$ with $ClONO_2$ equals the one of CF_3O^- with $ClONO_2$, which has been measured by Huey et al. [4].

3. Results and discussion

In Figure 1 the $[HNO_3]$ height profile, derived from the night-time measurements with the PEIS-B ion source, are shown for two balloon flights of the MACSIMS experiment in Gap (June 17th 1997 and June 17th 1999). Typical error bars on these profiles range from 30% to 40%. Also shown in this figure are the results obtained with the PEIS-A ion source for the last balloon flight and the results of the MIPAS night-time balloon flight on July 2nd 1997 in Gap [5]. Taking into account the error bars on the different profiles the agreement between these profiles is satisfactory. The difference with the results of Sen et al. [6] (sunset measurements with a balloon borne FTIR instrument at 35°N on September 25th 1993) is somewhat larger.

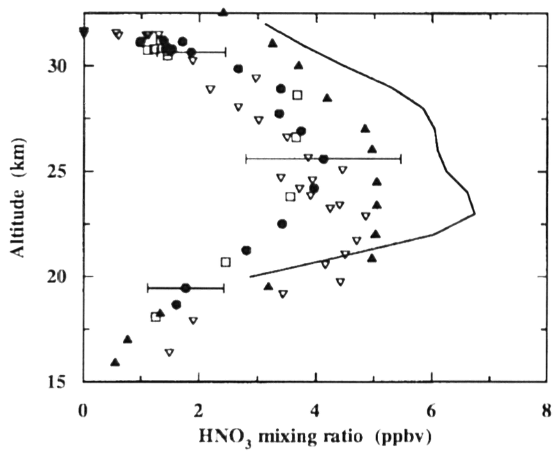


Figure 1. $[HNO_3]$ height profile obtained with

a) the MACSIMS PEIS-B ion source: (●): Gap, June 17th 1999; (∇): Gap, June 17th 1997

b) the MACSIMS PEIS-A ion source: (□): Gap, June 17th 1999.

Comparison with the results of the MIPAS balloon flight in Gap on July 2nd 1997 (▲) and with data from [6] (—)

Figures 2 and 3 show respectively the [HCl] and the $[ClONO_2]$ height profiles, obtained with the PEIS-B ion source for the flight in Gap on June 17th 1999. With respect to recent literature data [7] these profiles have the right shape but are too low. A possible explanation might be that we underestimate the product ions $CF_3O^-.X$, due to reverse reactions of the type $CF_3O^-.X + H_2O \rightarrow CF_3O^-.H_2O + X$ (X = HCl or $ClONO_2$), which may occur at a non-negligible rate due to the relatively high water vapour concentration in the stratosphere. A rate constant of $\approx 1 \times 10^{-11} cm^3 s^{-1}$ for this reverse reaction already shifts the $[ClONO_2]$ profile by a factor of two. Additionally it should be noted that we would expect a higher abundance than the measured one for the reaction products of CF_3O^- with HCl and $ClONO_2$, as reported in literature [4], if we take into account the abundance of the different source ions and the above proposed reaction schemes. Therefore further laboratory experiments are required to simulate and to understand the complicated chemistry taking place in the flow tube reactor in order to deduce consistent and detailed reaction schemes.

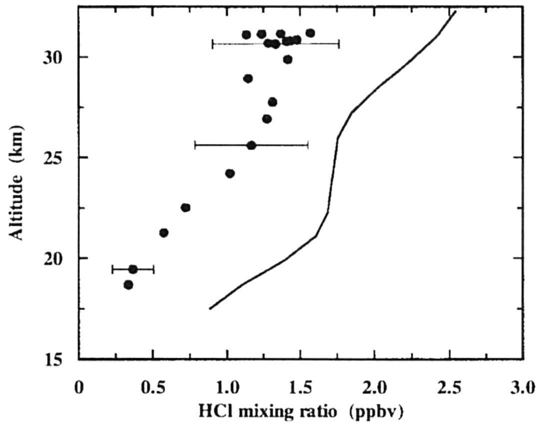


Figure 2. [HCl] height profile obtained with the MACSIMS PEIS-B ion source for the balloon flight in Gap on June 17th 1999 (●). Comparison with data from [7] (—).

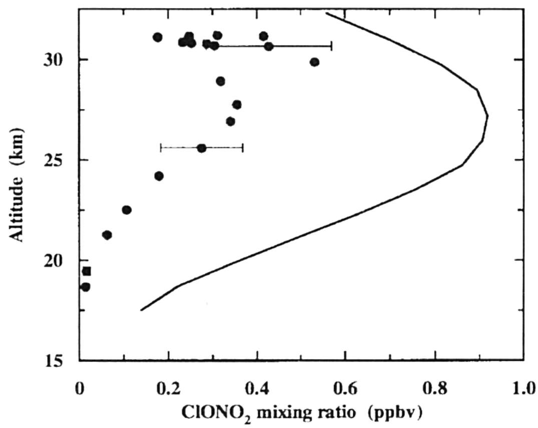


Figure 3. [$ClONO_2$] height profile obtained with the MACSIMS PEIS-B ion source for the balloon flight in Gap on June 17th 1999 (●). Comparison with data from [7] (—).

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