

I N S T I T U T D ' A E R O N O M I E S P A T I A L E D E B E L G I O U E

3 - Avenue Circulaire  
B - 1180 BRUXELLES

# AERONOMICA ACTA

A - N° 271 - 1983

Positive ion composition measurements  
between 33 and 20 km altitude

by

E. ARIJS, D. NEVEJANS, J. INGELS and P. FREDERICK

B E L G I S C H I N S T I T U U T V O O R R U I M T E - A E R O N O M I E

3 - Ringlaan  
B - 1180 BRUSSEL

## FOREWORD

The paper "Positive ion composition measurements between 33 and 20 km altitude", has been presented at the symposium SW 18 (Ions in the Middle Atmosphere) of the "European Geophysical Society Assembly" held in Leeds, August 1982. This contribution will appear in *Annales Geophysicae*, 1, 1983.

## AVANT-PROPOS

L'article : "Positive ion composition measurements between 33 and 20 km altitude" a été présenté au Symposium SW 18 (Ions in the Middle Atmosphere) du "European Geophysical Society Assembly" tenu à Leeds en août 1982. Cette contribution sera publiée dans *Annales Geophysicae*, 1, 1983.

## VOORWOORD

De tekst : "Positive ion composition measurements between 33 and 20 km altitude" werd voorgedragen tijdens het Symposium SW 18 (Ions in the Middle Atmosphere) van de "European Geophysical Society Assembly", gehouden te Leeds in augustus 1982. Deze bijdrage zal gepubliceerd worden in *Annales Geophysicae*, 1, 1983.

## VORWORT

Die Arbeit : "Positive ion composition measurements between 33 and 20 km altitude" wurde zum Symposium SW 18 (Ions in the Middle Atmosphere) von der "European Geophysical Society Assembly", Leeds, August 1982, vorgestellt. Dieser Text wird in *Annales Geophysicae*, 1, 1983 herausgegeben werden.

POSITIVE ION COMPOSITION MEASUREMENTS BETWEEN  

---

33 AND 20 KM ALTITUDE  

---

by

E. ARIJS, D. NEVEJANS, J. INGELS and P. FREDERICK

Abstract

Recent data on the positive stratospheric ion composition between 33 and 20 km obtained during two valve controlled balloon flights are presented.

Apart from  $H^+(H_2O)_n$  and  $H^+X_l(H_2O)_m$  cluster ions (with X being most probably  $CH_3CN$ ) other types of ions were observed, in particular very heavy ones. The influence of signal instabilities and contamination on the interpretation of data is discussed. From the relative abundances of the ions obtained during these and previous flights the mixing ratio of X ( $\equiv CH_3CN?$ ) is deduced in the altitude range from 35 km to 24 km.

## Résumé

Des données récentes sur la composition des ions positifs stratosphériques entre 33 et 20 km d'altitude obtenues durant deux vols de ballon à clapet, sont présentées.

Les agglomérats  $H^+(H_2O)_n$  et  $H^+X_\ell(H_2O)_m$  mis à part (X étant probablement  $CH_3CN$ ), d'autres types d'ions ont été observés, notamment des espèces très lourdes. L'influence de l'instabilité des signaux et de la contamination sur l'interprétation de données est discuté. Des abondances relatives des ions obtenues durant ces présents vols et les vols antérieurs, le rapport de mélange de X ( $\equiv CH_3CN?$ ) est déduit dans le domaine d'altitude allant de 35 à 24 km.

## Samenvatting

De resultaten van recente metingen van het positieve ionenbestand in de stratosfeer tussen 33 en 20 km, bekomen gedurende 2 ballonvluchten met ventiel gecontroleerde ballons, worden voorgesteld.

Behalve de cluster ionen van de gedaante  $H^+(H_2O)_n$  en  $H^+X_\ell(H_2O)_m$  [waarbij X hoogst waarschijnlijk  $CH_3CN$  is] werden ook nog andere ionen waargenomen, in het bijzonder zeer zware ionen. De invloed van signaal onstabilliteiten en contaminatie op de interpretatie der gegevens wordt besproken.

Uit de relatieve intensiteiten van het signaal bij verschillende ionenmassa's, waargenomen gedurende deze en vroegere ballonvluchten, wordt de mengverhouding van X ( $\equiv CH_3CN?$ ) afgeleid in het hoogtegebied van 35 tot 24 km.

## Zusammenfassung

Rezente Daten über der Zusammensetzung stratosphärischer positiver Ionen zwischen 33 and 20 km Höhe, bekommen während zwei Ventilkontrollierten Ballonflüge, werden vorgestellt. Neben den Clusterionen  $H^+(H_2O)_n$  und  $H^+X_\ell(H_2O)_m$  wurden auch sehr massareiche geladene Teilchen beobachtet. Der Einfluss von Signalunbeständigkeiten und von Kontamination auf der Interpretation von Daten wird besprochen. Von der relative Ionenhäufigkeit bekommen während dieser und voriger Flüge wird die Mischungsverhältnisse von  $X(\equiv CH_3CN ?)$  deduziert im Höhenbereich zwischen 35 und 24 km.

## 1. INTRODUCTION

In-situ measurements with rocket-borne and balloon-borne mass spectrometers (Arnold *et al.*, 1977; Arijs *et al.*, 1978; Arnold *et al.*, 1978) have shown that the major positive ions in the stratosphere belong to either of two families. The first, called proton hydrates [ $H^+(H_2O)_n$ -PH hereafter], was expected on the basis of models (Ferguson, 1974), whereas the unexpected second one, termed non proton hydrates (NPH hereafter), contains ions of the form  $H^+X_\ell(H_2O)_m$ . High resolution in-situ composition measurements (Arijs *et al.*, 1980) as well as careful inspection of ion abundances (Arnold *et al.*, 1981) have shown that the molecule X has a mass of 41 amu and most likely is  $CH_3CN$ . This suggestion was reinforced by laboratory measurements of Smith *et al.* (1981) and Böhringer and Arnold (1981).

In the meantime measurements have been extended from 41 down to 24 km (Henschen and Arnold, 1981a; Arnold and Henschen, 1982) and have been used to derive number densities of X in the stratosphere.

Apart from the major ions, various minor charged species having masses comparable to those of the PH and NPH (below 150 amu) have been detected (Henschen and Arnold, 1981b; Arijs *et al.*, 1982a). These ions are formed by ion-molecule reactions of high proton affinity trace gases (such as  $CH_3OH$ ), with PH and NPH.

On the other hand, the detection of very heavy positive ions (masses larger than 327 amu) has also been reported (Arnold and Henschen, 1981), but no identification was possible. It was suggested that these heavy ions were multiple ion complexes, which were supposed to play an important role in the aerosol formation processes (Arnold, 1980). These electrically charged condensation nuclei appeared to be layered around 30 km altitude, where they made up about 80% of the total ion count rate. The data were obtained during the ascending phase of a balloon flight.

In the present paper we will propose and discuss data, obtained during the ascent and/or descent phase of two valve controlled balloon flights. Heavy mass ions, as well as PH and NPH will be discussed.

## 2. EXPERIMENTAL METHOD AND MEASUREMENTS CONDITIONS

The balloon-borne instrument, used here, has been described before (Arijs et al., 1980). It consists of a liquid helium cooled cryo-pump (Ingels et al., 1978) and a quadrupole mass filter with associated microprocessor controlled electronics, allowing a flexible choice of many different measuring programs with selectable resolutions, mass domains a.s.o. (Nevejans et al., 1983).

The data shown and discussed hereafter were obtained during two different balloon flights, performed on 12 June 1981 and on 16 June 1982 from the CNES launching base at Gap-Tallard (southern France). In both flights a 100,000 m<sup>3</sup> valve controlled balloon was used, allowing slow descending from float altitude at a rate of 1 m.s<sup>-1</sup>. In the first case, the ion sampling hole of the mass spectrometer was pointing upwards (to the balloon). Spectra from positive as well as negative ions were measured during daytime (Arijs et al., 1982b) while descending from 33 down to 20 km .

During the second flight, two similar mass spectrometers, with downward pointing sampling apertures, were flown together. One was measuring positive ions and the other negative ions. The results of the negative ion measurements will be reported elsewhere.

During ascent (nighttime) positive ions were only measured in the total ion mode (no DC on the quadrupole rods) while during descent (daytime) series of multiple scans with moderate resolution ( $m/\Delta m \cong 17$ ) alternated with single scans in the total ion mode. In this way data between 33.8 and 24 km were obtained. At float altitude (33.8 km) spectra were recorded in the constant peak width mode, allowing an unambiguous mass identification of the detected ions.



During both flights the ambient pressure, required to derive the altitude, was measured by a high precision Baratron gauge.

### 3. RESULTS AND DISCUSSION

#### 3.1. Measurements in the total ion mode

The mass analyzer used in our spectrometer, is a quadrupole mass filter, the theory of which is well established (Dawson, 1976). This filter normally is supplied with DC and RF voltages. When the RF voltage is modulated by a linear ramp function a linear mass versus time relation evolves and mass peaks appear with a resolution, determined by the DC to RF ratio. If however, the DC is put to zero, the quadrupole acts as a high pass filter and at a given RF value  $V$ , corresponding to a mass  $m$  at high resolution, all masses above  $(0.706 \times m/0.908)$  are transmitted. In this mode however, a high transmission virtually independent of the ion mass, is obtained. The so-called "integral spectra" obtained in this way, can be used to determine the total abundance of all ions having a mass larger than a given value, determined by the maximum RF value applied on the quadrupole. A typical spectrum obtained in this way is shown in figure 1. As can be seen large signal fluctuations occur for curve 1, the "integral spectrum" as measured. In order to smooth these fluctuations the raw data are transformed into a histogram, where the signal has been averaged over 20 atomic mass units. Thus curve 2 of figure 1 is obtained. To calculate the fractional abundance of all ions having a mass larger than 238 amu, the amplitude of the last but one histogram bar is divided by the amplitude of that histogram bar where signal is maximum. The results obtained in this way for the different spectra, recorded at different altitudes for both flights, described above, are shown in figure 2 and 3.

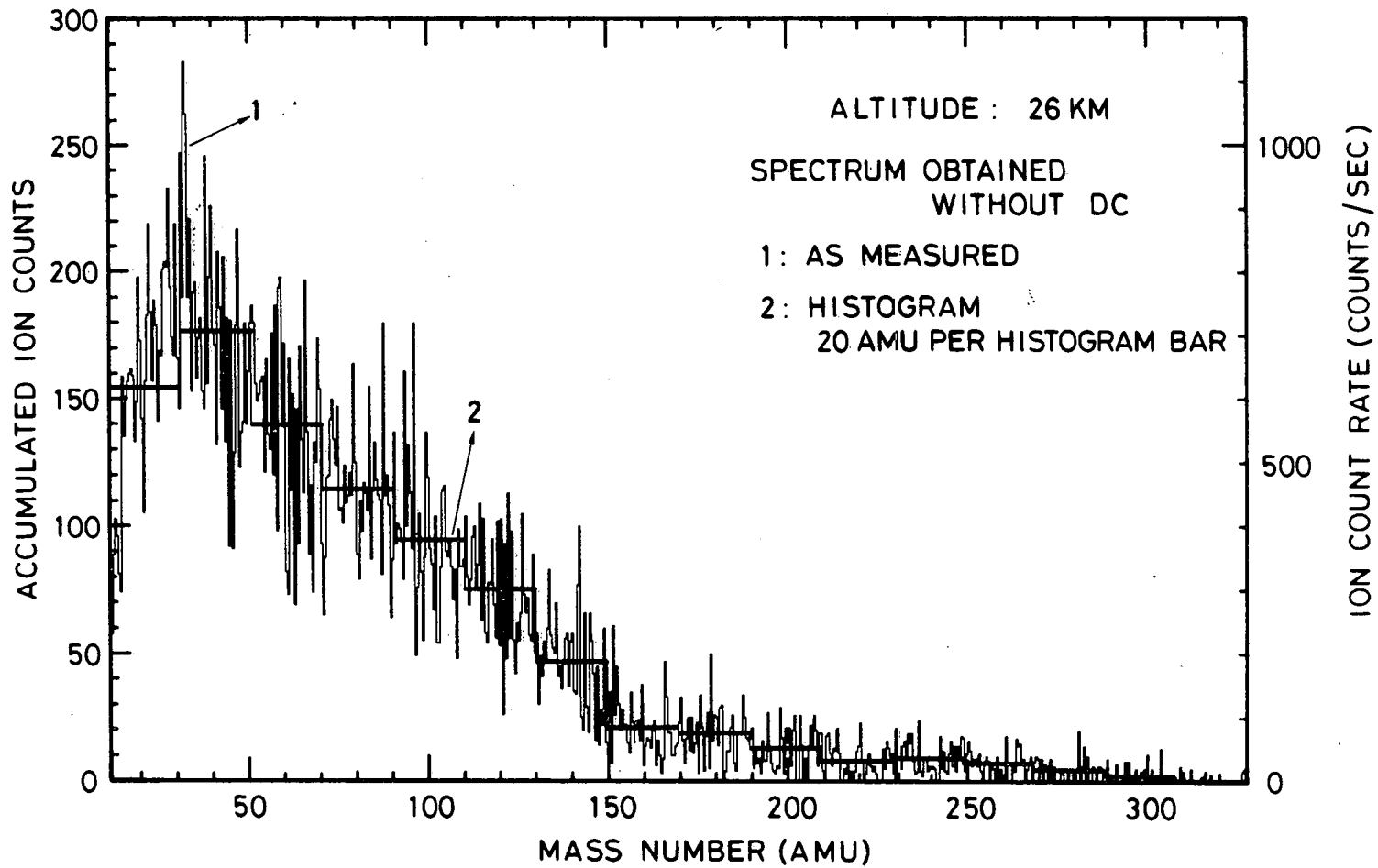


Fig. 1.- Typical spectrum obtained in the integral mode (no DC on the quadrupole rods). The mass scale indicated is only valid for high resolution and should be divided by 1.29 to obtain the scale for trailing edges.

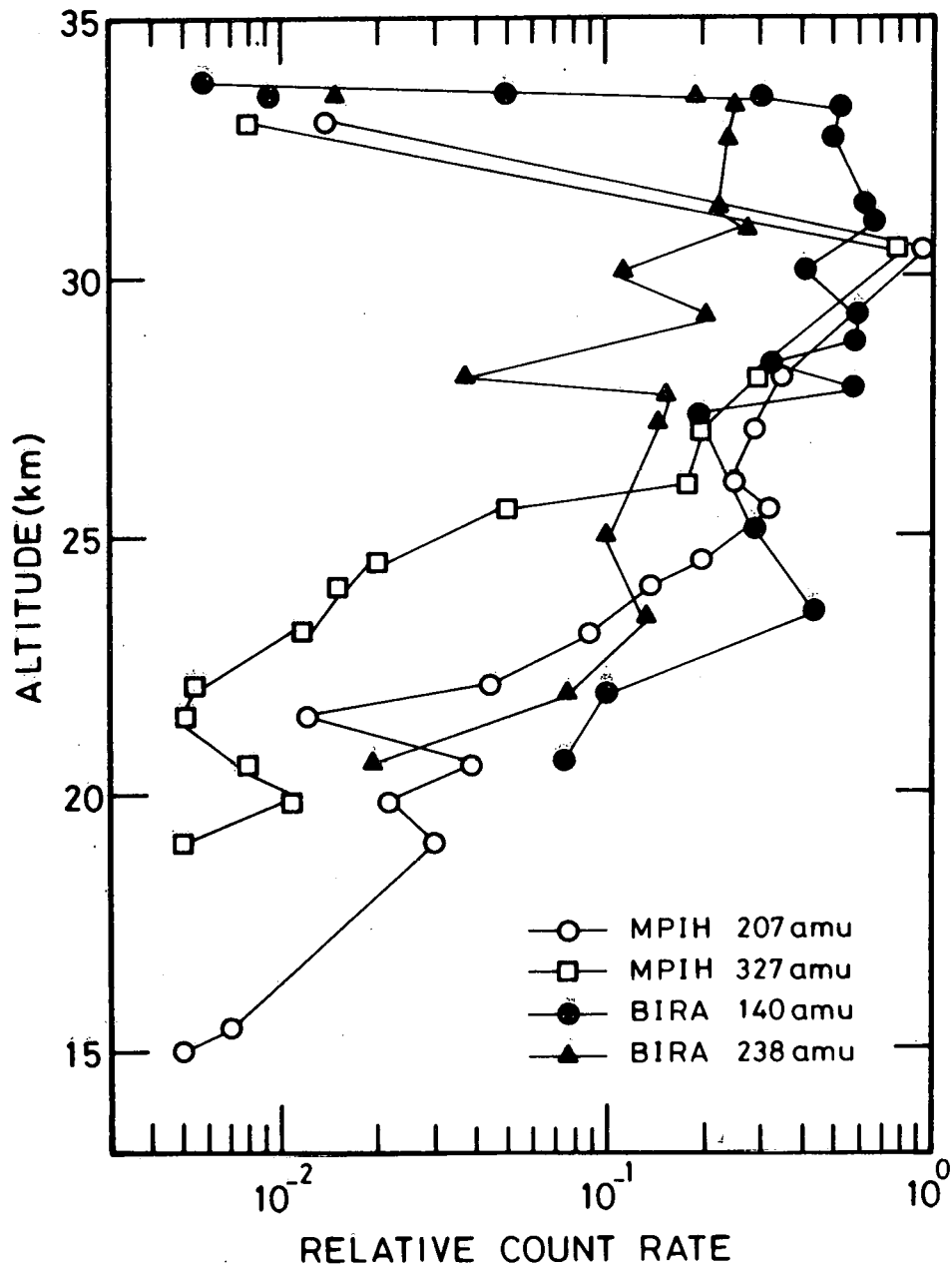


Fig. 2.- Relative count rate of heavy positive ions at different altitudes.

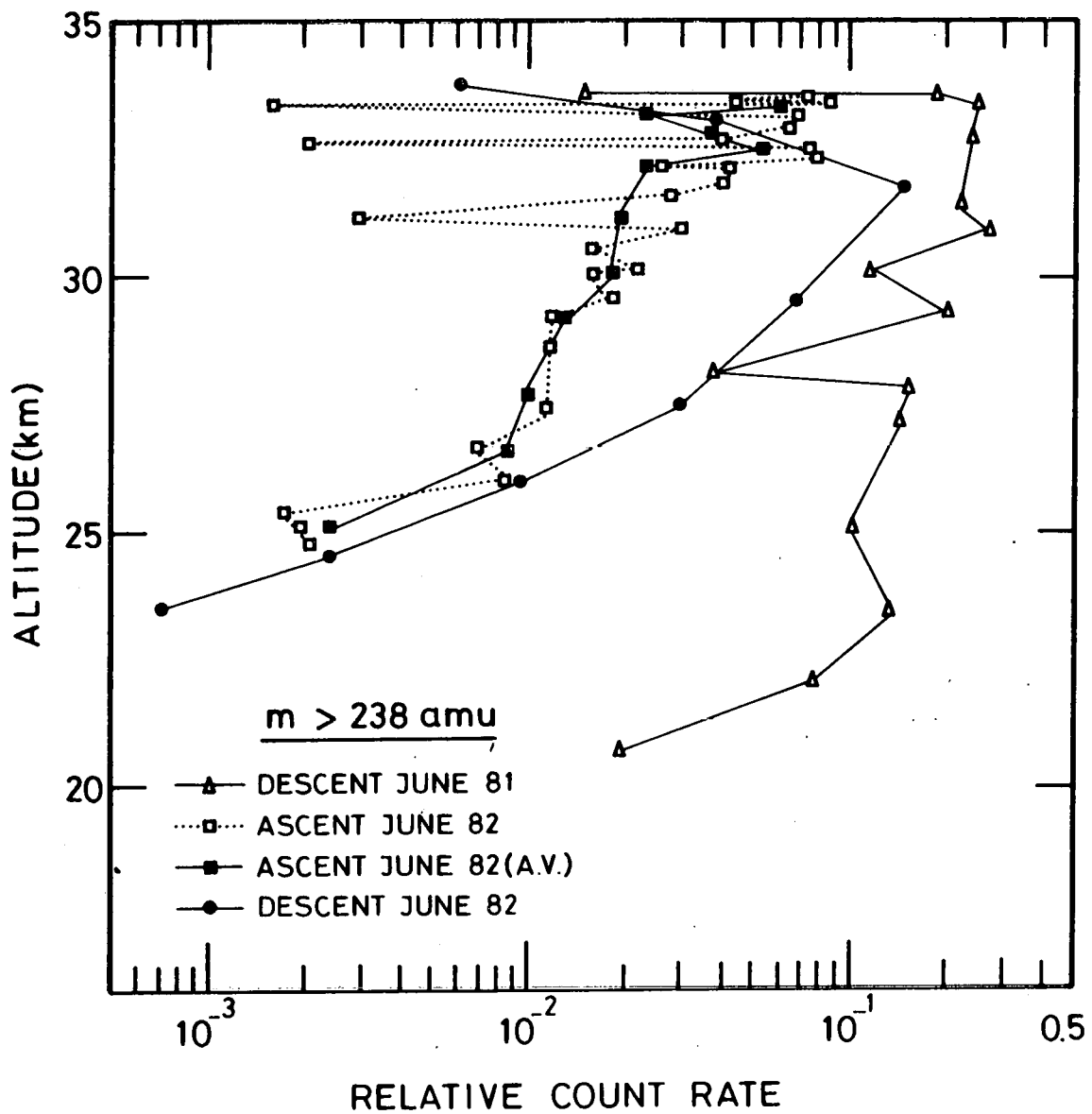


Fig. 3.- Fractional count rate of positive ions with mass larger than 238 amu versus altitude, as obtained under different conditions.

In figure 2 the results of the June 1981 flight are compared to those of the Heidelberg group (MPIH) as reported by Arnold and Henschen (1981), while in figure 3 our June 1981 and June 1982 data are intercompared.

There are some striking differences between the results of the two groups and those of our two flights. We feel that this has little to do with the difference in time at which the results were obtained, but that the discrepancies are merely related to the different instrument configurations and flight conditions.

Comparing the data of our June 1981 flight with those of the MPIH-group, it is noticed that the relative count rate of heavy ions above 25 km reported by our group, is always lower than that measured by Arnold and Henschen (1981) and certainly never reaches 80% as in the Heidelberg data. Apart from the sudden increase just below float altitude (around 34 km), no evidence is found for the so-called layering. It should be mentioned that such a sudden relative count rate increase for heavy ions seems to be typical at the beginning of a balloon descent. Indeed a similar increase is noticed in figure 2 at 28 km altitude, where the balloon was kept for 1 hour (intermediate ceiling altitude) and then allowed to descend again. The same tendency is seen in figure 3 for the descent curve.

Very strong signal fluctuations are also observed in this figure for the ascent data. The fact that these fluctuations increase at higher altitudes, suggest that they might be due to an increased outgassing of the payload (and balloon ?) due to lower ambient pressure. Such an outgassing can severely disturb the ion chemistry since contaminant gases may give rise to ion-molecule reactions, yielding heavy ions. Preliminary results obtained in our laboratory have shown that the positive ion reaction chain may be affected seriously indeed by contaminants released by gondola construction materials and mostly give rise to heavy positive ions.

Although one would expect a smaller contamination effect during the descent than during the ascent of the June 1982 flight (where the sampling hole is pointing downwards), the opposite effect is found. This however must not necessarily be interpreted as a controversy. Since ascent data were obtained at night and descent data during daytime, heating up of the payload due to solar radiation might have increased the outgassing rate considerably. The clean air flow due to the descending motion of the balloon is than only partially compensating for this effect. Two facts are supporting this suggestion. First at lower altitudes the difference between ascent and descent data in the June 1982 flight is much smaller, due to more intensive air flow and to the lower outgassing during descent. Secondly the relative abundance of heavy ions is much higher for the June 1981 flight where air flushing is not so effective because the sampling hole is pointing upwards.

In view of the foregoing comments the interpretation of the heavy ions as multi-ion complexes becomes very disputable. Although it may not be excluded that part of the observed massive charged particles are indeed of natural origin, it seems rather unlikely that natural ions should vary so much in time and space as is observed. Furthermore, the fact that the results of the "integral spectra" are dependent upon instrument configurations and differ for ascent and descent in the same flight reinforces the contamination hypothesis. Recent data obtained by the Heidelberg group (Schlager and Arnold, 1982) also indicate that the relative count rates of heavy ions are much lower than originally believed and suggest that most of them are due to contamination.

### 3.2. High and moderate resolution measurements

At float altitude, where sufficient integration time is available to measure at high resolution, spectra were built up in the constant peak width mode. A typical example of such spectra, used to identify ions unambiguously, is shown in figure 4. The major observed ions belong

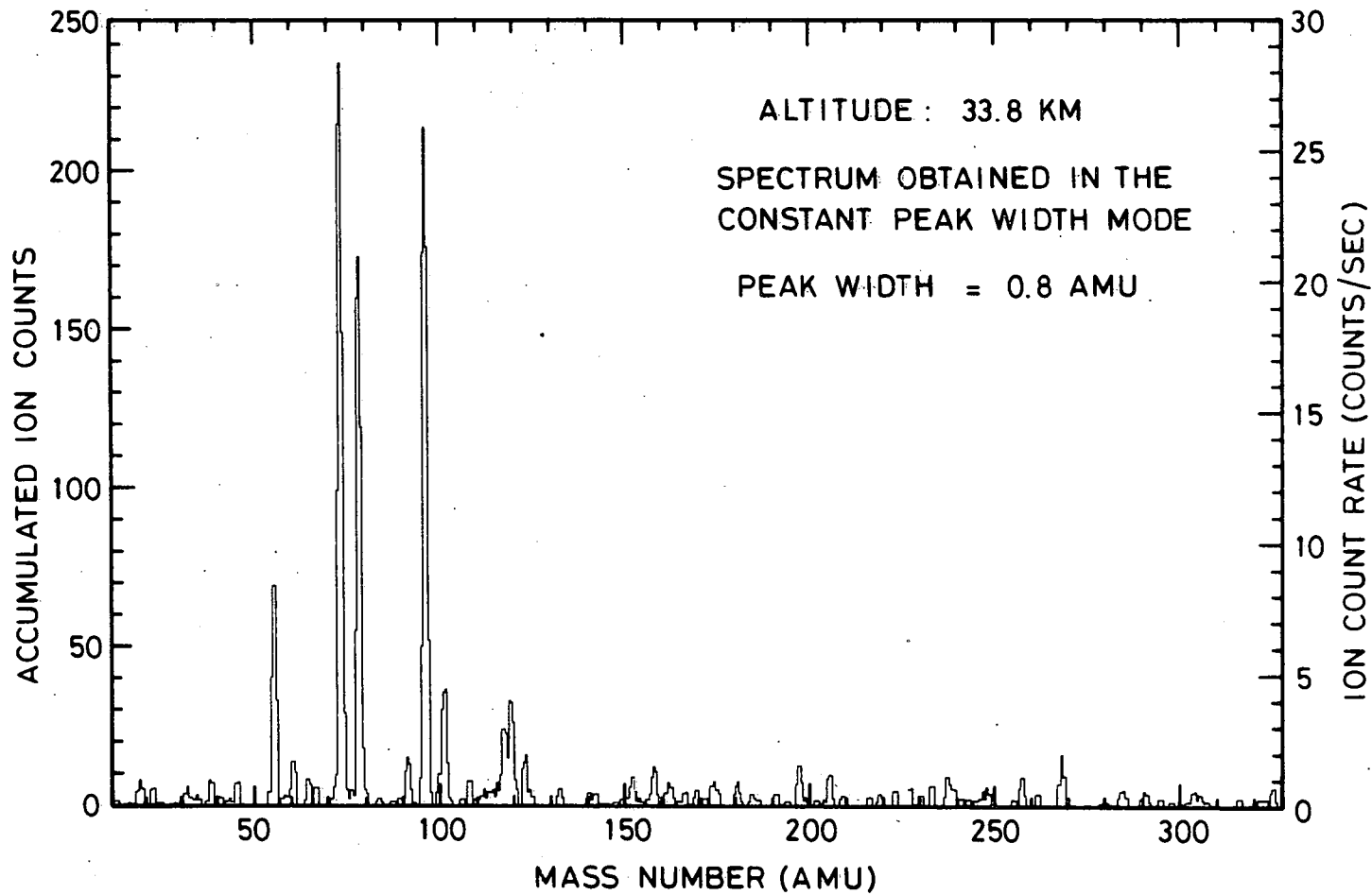


Fig. 4.- Typical mass spectrum of positive stratospheric ions as recorded in the constant peak width mode (sum of 33 scans). The data have been smoothed by a three point smoothing technique (Arijs *et al.*, 1982b).

to the PH family or to the NPH group  $H^+X_\ell(H_2O)_n$ , X having mass 41. However, other minor NPH ions among which those due to  $CH_3OH$ , are also present. A more detailed analysis of these minor mass peaks is still going on and will be presented elsewhere.

During the slow descent of the balloon however high mass filter resolution modes, associated with low quadrupole transmission, would lead to long spectrum integration times and poor altitude resolution. Therefore moderate constant resolutions are adopted during this phase. As can be seen from figure 5 the obtained spectra are still adequate to resolve the major peaks. Spectra remain of almost the same quality down to 24 km altitude. The spectrum at 33.8 km is shown intentionally, because it is obtained just after the start of the balloon descent in the June 1982 flight and shows a peak at mass  $183 \pm 5$  amu, probably due to contamination, that disappears later on. From similar spectra as those shown in figure 5, the relative abundance of NPH containing X is deduced. The results for the June 82 flight are shown in figure 6, together with the results obtained from other flights and those of the MPIH-group. As can be seen reasonable agreement is found between the different results.

Assuming that the NPH ions are lost by ion-ion recombination the mixing ratio {X} can be deduced from the steady state continuity equation :

$$\{X\} = \frac{[H^+X_\ell(H_2O)_m]}{[H^+(H_2O)_n]} \cdot \frac{\alpha[n_-]}{k[M]} \quad (1)$$

where square brackets denote number densities.

The recombination coefficient is calculated from

$$\alpha = 6 \times 10^{-8} (300/T)^{0.5} + 1.25 \times 10^{-25} [M] (300/T)^4 \text{ cm}^3 \text{ s}^{-1} \quad (2)$$

and the total number density [M] from the ideal gas law :

$$[M] = 9.656 \times 10^{18} (p/T) \text{ cm}^{-3} \quad (3)$$



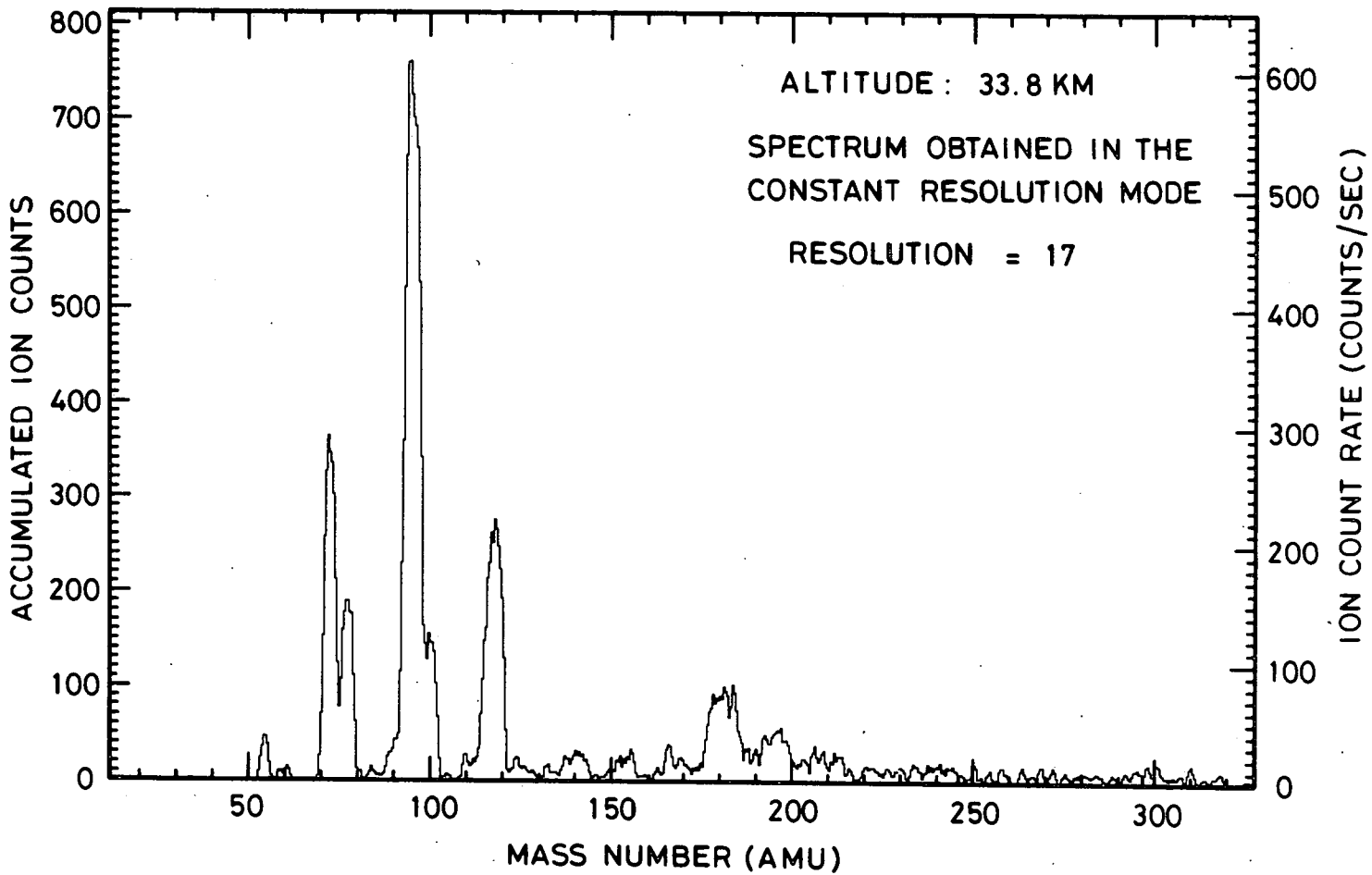


Fig. 5.- Sample positive ion spectrum obtained in the moderate resolution mode. The same smoothing technique as in fig. 4 is applied. The spectrum is the sum of 5 scans.

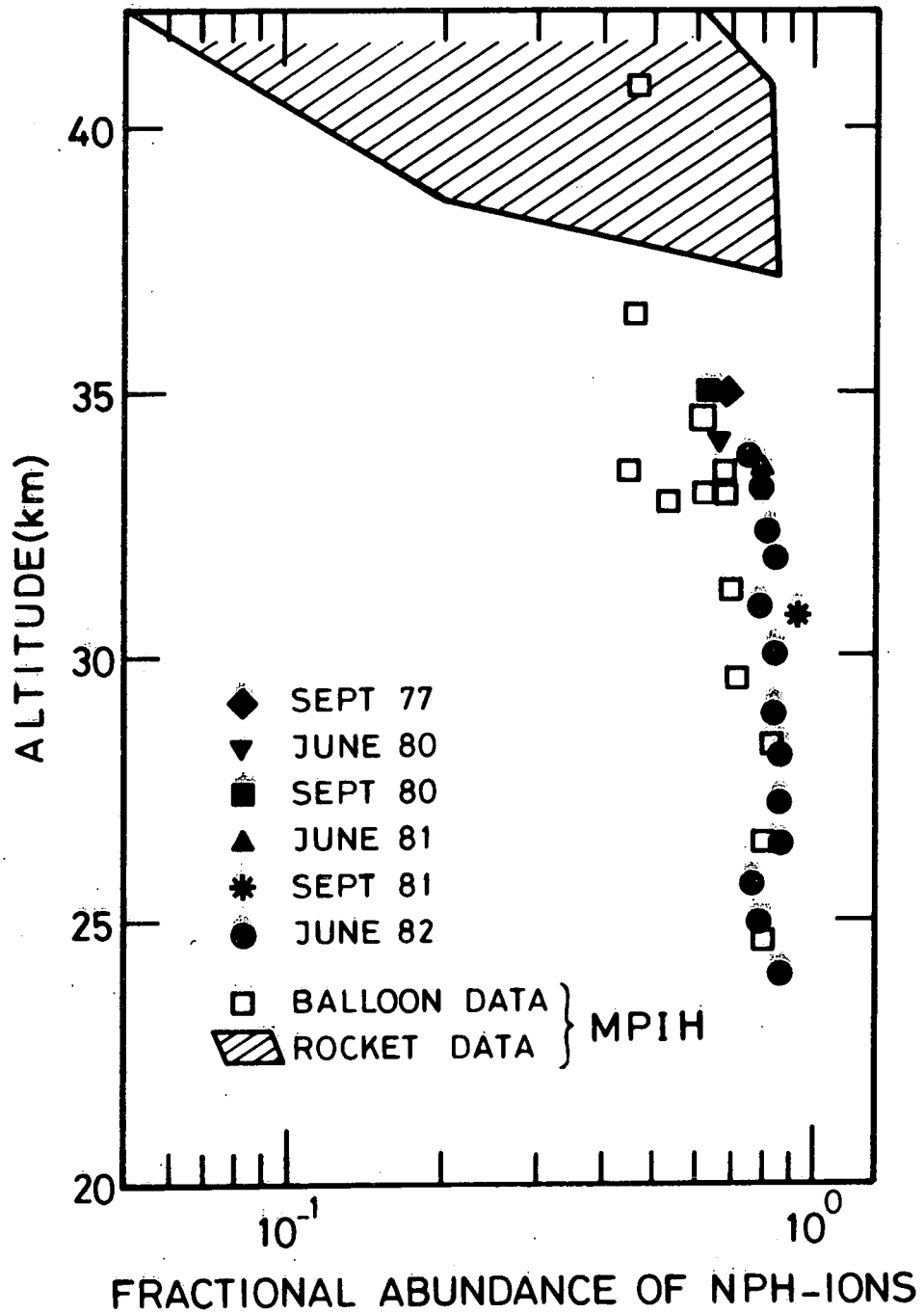


Fig. 6.- Fractional abundance of NPH ions containing X versus altitude for different balloon flights.

where  $p$  is the measured ambient pressure in torr and  $T$  the ambient temperature in Kelvin; derived from the US Standard Atmosphere. Although not representing the expected theoretical temperature dependence, formula (2) gives values for the recombination coefficient, in reasonable agreement with most recent data (Rosen and Hofman, 1981; Smith and Adams, 1982 and Bates, 1982). The total negative ion density  $[n_-]$  used in formula (1) is deduced from

$$[n_-] = (Q/\alpha)^{0.5} \quad (4)$$

The ion production  $Q$  is calculated with the parametrization formulae of Heaps (1978)

$$Q = (A + B \sin^4 \phi) [M] \quad (5)$$

for altitudes above 30 km and

$$Q = (A + B \sin^4 \phi) N_o^{(1-n)} [M]^n \quad (6)$$

below 30 km.

$$\text{With } A = 1.74 \times 10^{-18} \quad (7)$$

$$n = 0.6 + 0.8 \cos \phi \quad (8)$$

$$\text{and } N_o = 3.03 \times 10^{17} \quad (9)$$

For  $\phi$ , a geomagnetic latitude of  $46.6^\circ$  N has been chosen, which is the mean value of the geomagnetic latitudes of Gap-Tallard ( $46.31^\circ$ N) and of Aire-sur-l'Adour ( $46.88^\circ$ N). In view of the motion of the balloon, this looks a realistic choice. For the parameter  $B$ , which depends on the solar activity, a parametrization of the form :

$$B = [2.385 - 0.455 \cos \frac{2\pi}{11} (y - 1969)] 10^{-17} \quad (10)$$

has been adopted, where  $y$  is the year of the flight.

For the reaction rate coefficient  $k$ , used in formula (1) a value of  $3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  was taken, according to the laboratory measurements of Smith et al. (1981).

The volume mixing ratios thus obtained for X are shown in figure 7, together with the recently MPIH data published (Henschen and Arnold, 1982), corrected for the same values of  $\alpha$  and  $[n_-]$  as those used in this work.

In view of the uncertainties on the various parameters used in formula (1), the error on the mixing ratio {X} is estimated to be a factor of two. Within these error limits, the results obtained in the different experiments for {X} are in reasonable agreement and suggest a constant mixing ratio of about  $3 \times 10^{-12}$  below 30 km. Above this altitude a tendency for a slow decrease with increasing altitude is noticed.

Such an altitude profile would suggest a source of X below 30 km, as already pointed out by Henschen and Arnold (1981). If X were  $\text{CH}_3\text{CN}$ , such a source term might be surface production by biomass burning (Crutzen, 1981) or industrial releases, followed by upward diffusion. On the other hand, an in-situ production mechanism for  $\text{CH}_3\text{CN}$  has recently been proposed (Murad and Swider, 1982).

The rather slow decrease of X with altitude indicates that the photochemical destruction of X is not very efficient below 35 km. This seems consistent with an identification of X as being  $\text{CH}_3\text{CN}$ . Recent laboratory work by Harris et al. (1981) has shown a rate coefficient smaller than  $10^{-14} \text{ cm}^3 \text{ s}^{-1}$  for the reaction of  $\text{CH}_3\text{CN}$  with the hydroxyl radical, which is the main removal process for trace gases in the stratosphere.

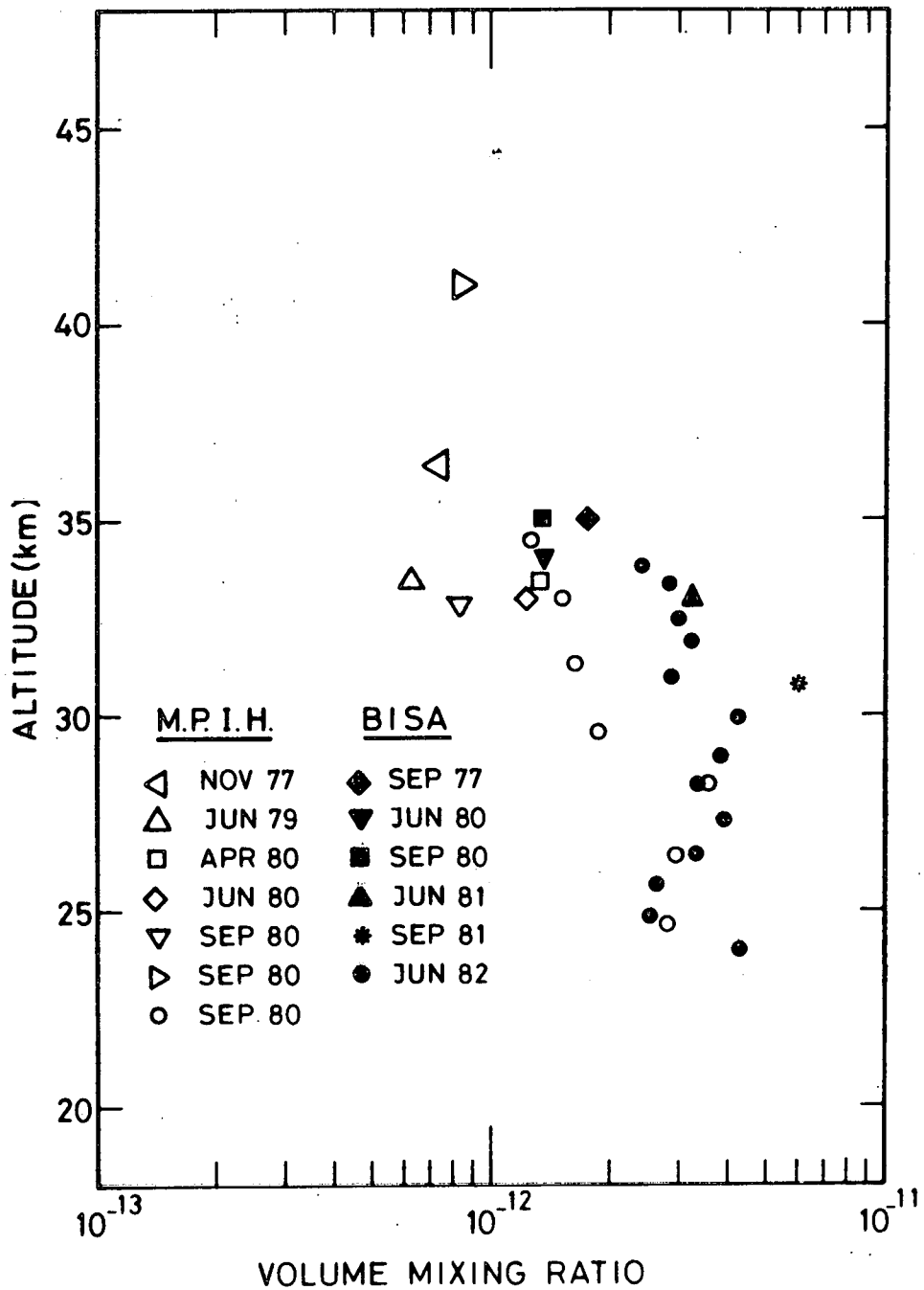
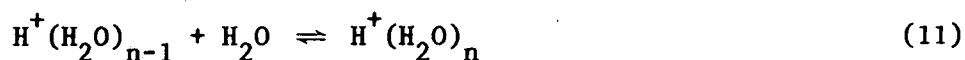


Fig. 7.- Volume mixing ratio of X versus altitude as calculated from ion abundances.

It is clear however that more laboratory work is needed to elucidate the sources and sinks of  $\text{CH}_3\text{CN}$  in the stratosphere and that the in-situ composition data need to be extended above 40 km and below 20 km to obtain a more complete mixing ratio profile of X and to test whether the identification of X as acetonitrile is consistent with the laboratory data.

So far, we have only considered the total fractional abundances of the PH and NPH families. We will now discuss the fractional abundances of the different ions belonging to both groups.

Figure 8 shows the fractional abundance of the major PH ions. Black symbols in this graph represent the data as measured in the June 1982 flight, whereas open symbols are calculated values for summer standard atmosphere and a constant water mixing ratio of 4.5 ppm. These were obtained by assuming an equilibrium distribution of the PH ions and using the most recent thermochemical data of Lau et al. (1982) for the gas phase reactions :



For the reduction of the calculated PH distribution it was assumed that the total fractional abundance of all PH was constant from 35 to 25 km. For this number a value of 0.18 was adopted, which is the average of the observed abundances at different altitudes.

Comparing the measured and calculated abundances for mass 73 [ $\text{H}^+(\text{H}_2\text{O})_4$ ] it is noticed that, down to 30 km, the general trend of the theoretical curve is fairly well followed by the data, although their values are somewhat smaller than expected. This is due to collisional induced dissociation in the mass spectrometer, but as was expected this effect is not dramatic above 30 km (Arijs et al., 1982). Below this altitude however the deviations between theory and observations become larger. Above the cross-over point between the calculated curves for

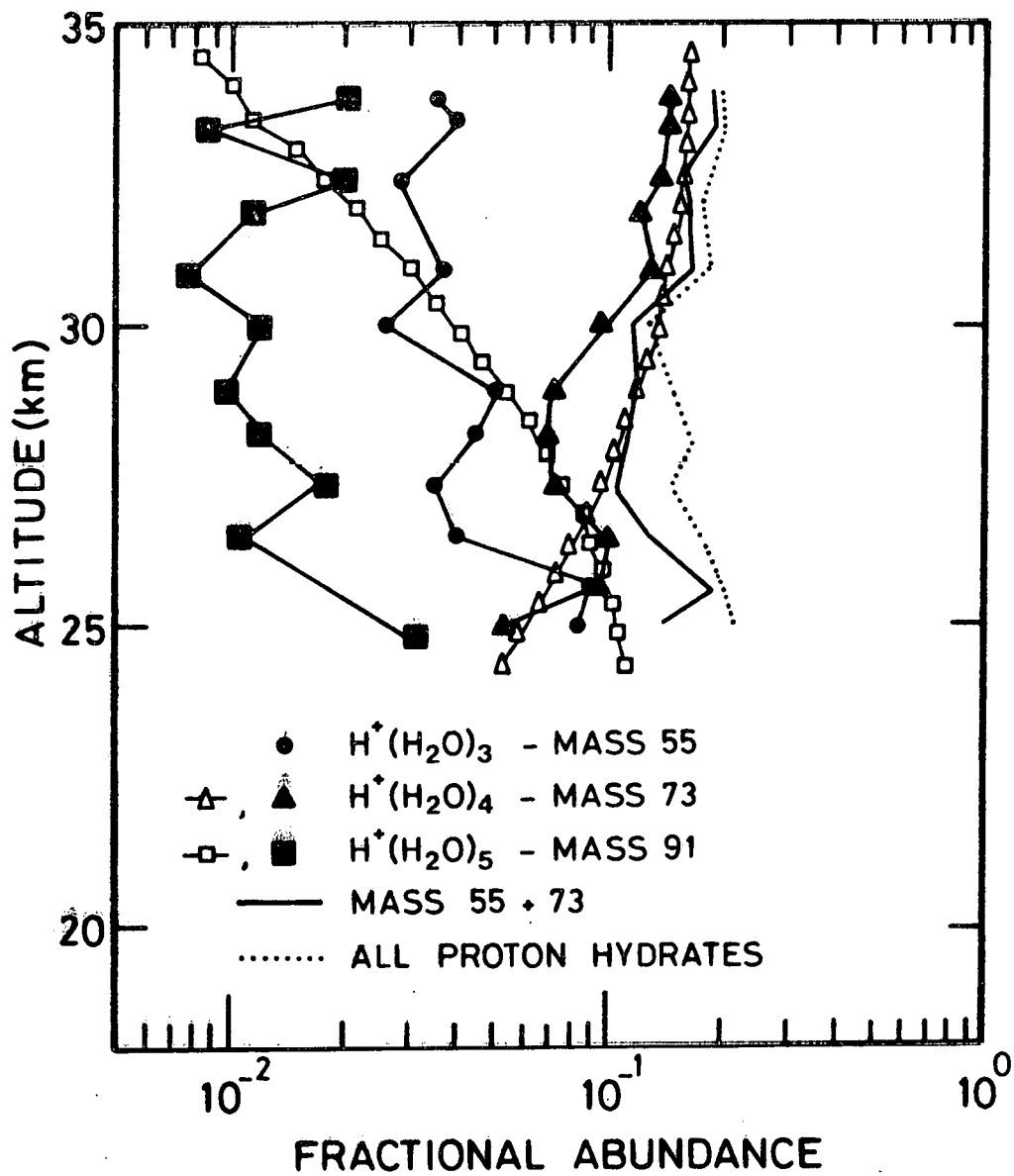


Fig. 8.- Fractional abundances of  $H^+(H_2O)_n$  ions versus altitude.

mass 73 and 91 (at 27 km) the observed abundances for  $H^+(H_2O)_4$  are smaller than the calculated ones. This is due to an increased effect of cluster break-up of  $H^+(H_2O)_4$  ions, resulting from the higher pressure in the mass spectrometer at lower altitudes. Below 27 km however, the signal at mass 73 becomes larger than theoretically expected. This coincides with the calculated increase the abundance of mass 91 and can therefore be explained by break-up of  $H^+(H_2O)_5$  ions. These contribute to the signal at mass 73 by losing one ligand. This is consistent with the fact that the measured abundance of mass 91 is far below the expected one. It also indicates that cluster break-up is more pronounced for mass 91 and becomes already effective at higher altitudes because of the lower binding energy of  $H_2O$  in the  $H^+(H_2O)_5$  clusters. The most remarkable discrepancy however is noticed for mass 55. Calculations predict that the fractional abundance should be  $10^{-3}$  at 35 km and should decrease to  $10^{-5}$  at 27 km. According to figure 8, the measured values are a factor of 10 to 1000 (depending on the altitude) too high. This is caused completely by cluster break-up of mass 73, as already pointed out previously (Arnold et al., 1981; Arijs et al., 1982).

The fractional abundances of the various NPH ions as observed in the June 1982 flight are shown in figure 9. At present it is difficult to compare these data with calculations, because reliable thermochemical data for the NPH ions are lacking. However general trends can be inferred, such as the increase of  $H^+X_2(H_2O)_n$  clusters at lower altitudes, as was expected already (Henschen and Arnold, 1981). The increase of mass 60 with decreasing altitude clearly shows that cluster break-up is severely disturbing the measurements. Therefore the use of the data for deriving thermochemical quantities is at present still hampered by collisional induced cluster dissociation, a phenomenon to be studied in detail in the laboratory.



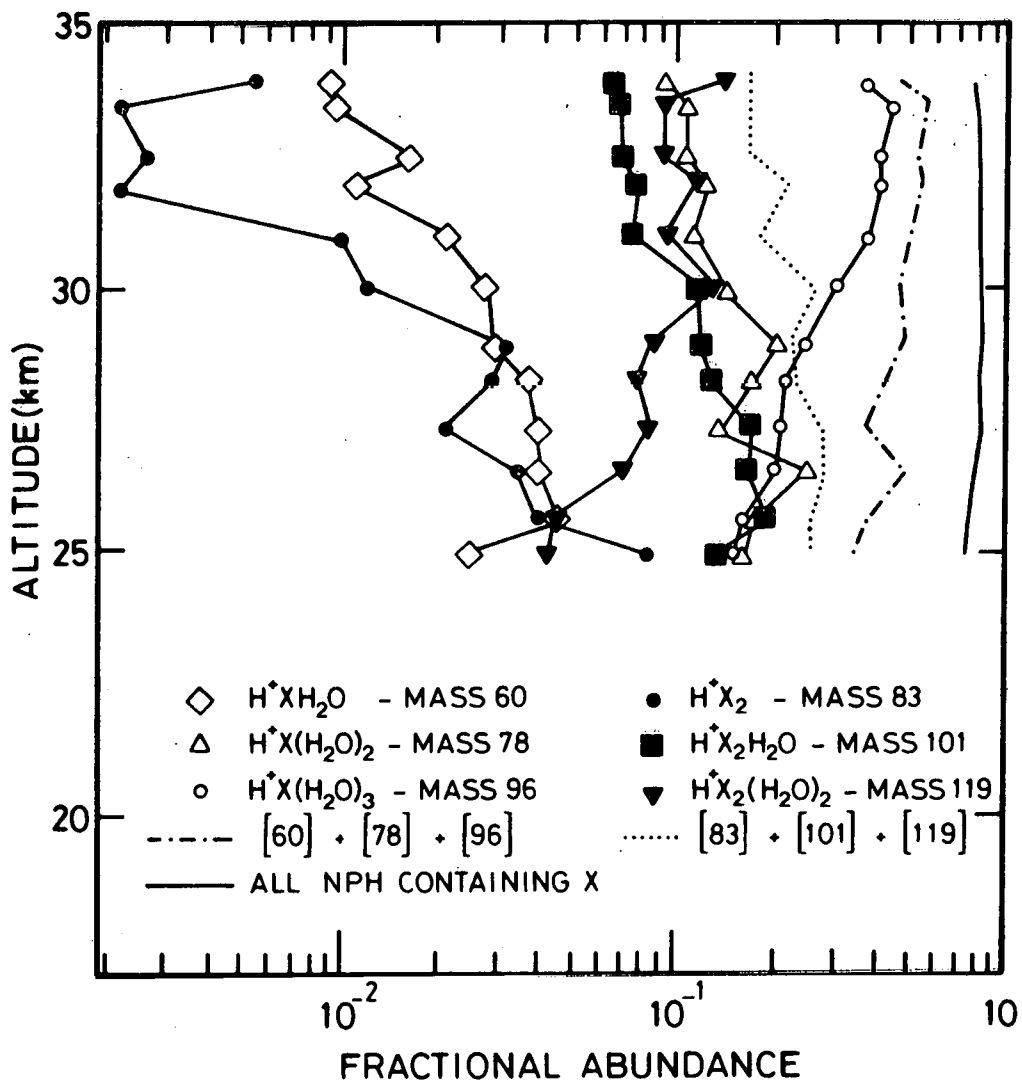


Fig. 9.- Fractional abundances of  $H^+X_\ell(H_2O)_n$  ions versus altitude.

#### 4. SUMMARY AND CONCLUSIONS

A comparison of spectra acquired in the "integral mode", obtained during different flights and during descent and ascent in one flight, shows that signal instabilities and contamination are seriously influencing the data. An interpretation of heavy ion mass peaks as multi-ion complexes is certainly disputable. It is much more likely that these ions, are less abundant than was believed originally and are caused by contamination.

The volume mixing ratio profile for the molecule X, obtained from the relative abundances of PH and NPH ions, suggests a source for X in the lower stratosphere and a slow destruction at higher altitudes of this molecule. In order to verify whether X can be identified as  $\text{CH}_3\text{CN}$ , the measurements need to be extended to higher and lower altitudes and laboratory studies of the possible reactions leading to formation and destruction of acetonitrile in the stratosphere are needed.

It has also been shown that the ion mass spectra at altitudes below 30 km are seriously disturbed by cluster break-up. More laboratory work about this phenomenon should be undertaken to allow a more complete interpretation of the data.

#### ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the technical staffs of the Belgian Institute for Space Aeronomy and the CNES launching base, which made the experiments possible.

They are also indebted to the NFWO (Belgian National Science Foundation), which financed part of this project.

## REFERENCES

- ARIJS, E., J. INGELS and D. NEVEJANS, Mass spectrometric measurements of the positive ion composition in the stratosphere, *Nature*, 271, 642-644, 1978.
- ARIJS, E., D. NEVEJANS and J. INGELS, Unambiguous determination of major stratospheric positive ions, *Nature*, 288, 684-686, 1980.
- ARIJS, E., D. NEVEJANS and J. INGELS, Stratospheric positive ion composition measurements, ion abundances and related trace gas detection, *J. Atm. Terr. Phys.*, 44, 43-53, 1982a.
- ARIJS, E., D. NEVEJANS, J. INGELS and P. FREDERICK, Stratospheric negative ion composition measurements, ion abundances and related trace gas detection, *J. Atm. Terr. Phys.*, 44, 681-694, 1982b.
- ARNOLD, F., Multi-ion complexes in the stratosphere - Implications for trace gases and aerosols, *Nature*, 284, 610-611, 1981.
- ARNOLD, F., H. BÖHRINGER and G. HENSCHEN, Composition measurements of stratospheric positive ions, *Geophys. Res. Lett.*, 5, 653-656, 1978.
- ARNOLD, F. and G. HENSCHEN, Mass spectrometric detection of precondensation nuclei in the stratosphere - Evidence for a stratospheric gas to particle conversion mechanism, *Geophys. Res. Lett.*, 8, 83-86, 1981.
- ARNOLD, F. and G. HENSCHEN, Positive ion composition measurements in the upper stratosphere - Evidence for an unknown aerosol component, *Planet. Space Sci.*, 30, 101-108, 1982.
- ARNOLD, F., G. HENSCHEN and E.E. FERGUSON, Mass spectrometric measurements of fractional abundances in the stratosphere - Positive Ions, *Planet. Space Sci.*, 29, 185-193, 1981.
- ARNOLD, F., D. KRANKOWSKY and K.H. MARIEN, First mass spectrometric measurements of positive ions in the stratosphere, *Nature*, 267, 30-32, 1977.
- BATES, D.R., Recombination of small ions in the troposphere and lower stratosphere, *Planet. Space Sci.*, in press, 1982.

- BOHRINGER, H. and F. ARNOLD, Acetonitrile in the stratosphere - Implications from laboratory studies, *Nature*, 290, 321-322, 1981.
- CRUTZEN, P., Personal communication, 1981.
- DAWSON, P.H., in "Quadrupole mass spectrometers and applications", Elsevier, Amsterdam, 1976.
- FERGUSON, E.E., in "The natural Stratosphere of 1974", CIAP Monogr., 1, 5.42-5.54, 1974.
- HARRIS, G.W., T.E. KLEINDIENST and J.N. PITTS, Jr., Rate constants for the reaction of OH radicals with CH<sub>3</sub>CN, C<sub>25</sub>CN and CH<sub>2</sub>CNCN in the temperature range 298-424 K, *Chem. Phys. Lett.*, 80, 479-483, 1981.
- HEAPS, M.G., Parametrization of the cosmic ray ion-pair production rate above 18 km, *Planet. Space Sci.*, 26, 513-517, 1978.
- HENSCHEN, G. and F. ARNOLD, Extended positive ion composition measurement in the stratosphere - Implications for neutral trace gases, *Geophys. Res. Lett.*, 8, 999-1001, 1981a.
- HENSCHEN, G. and F. ARNOLD, New positive ion species in the stratosphere, *Nature*, 291, 211-213, 1981b.
- INGELS, J., ARIJS, E., D. NEVEJANS, FORTH, H.J. and G. SCHAEFER, Liquid helium cryopump and reliable opening device for a balloon borne mass spectrometer, *Rev. Sci. Instr.*, 49, 782-784, 1978.
- LAU, Y.K., S. IKUTA and P. KEBARLE, Thermodynamics and kinetics of the gas-phase reactions:  $H_3O^+(H_2O)_{n-1} + H_2O = H_3O^+(H_2O)_n$ , *J. Am. Chem. Soc.*, 104, 1462-1469, 1982.
- MURAD, E. and W. SWIDER, On the formation of organic stratospheric ions, Abstracts of the A.G.U. Spring Meeting, Philadelphia, p. 47, 1982.
- NEVEJANS, D., FREDERICK, P. and E. ARIJS, Microprocessor based data acquisition and control system for a balloon borne quadrupole mass spectrometer, *Bull. Acad. Roy. Belges*, in press, 1983.
- ROSEN, J.M. and D.J. HOFMAN, Balloon borne measurements of electrical conductivity, mobility and the recombination coefficient, *J. Geophys. Res.*, 86, 7406-7420, 1981.

SCHLAGER, H. and F. ARNOLD, Extended stratospheric positive ion composition measurements, E.G.S. meeting - Abstracts, p. 116, 1982.

SMITH, D. and N.G. ADAMS, Ionic recombination in the stratosphere, Geophys. Res. Lett., 9, 1085-1087, 1982.

SMITH, D., N.G. ADAMS and E. ALGE, Ion-ion mutual neutralization and ion-neutral switching reactions of some stratospheric ions, Planet. Space Sci., 4, 449-454, 1981.