

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

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**Positive ion composition measurements and acetonitrile
in the upper stratosphere**

by

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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

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FOREWORD

A more concise version of this paper "Positive ion composition measurements and acetonitrile in the upper stratosphere" will be published in Nature.

AVANT-PROPOS

Une version abrégée de cet article : "Positive ion composition measurements and acetonitrile in the upper stratosphere" sera publiée dans Nature.

VOORWOORD

Een verkorte versie van deze tekst : "Positive ion composition measurements and acetonitrile in the upper stratosphere" zal verschijnen in Nature.

VORWORT

Eine verkürzte Version von dieser Arbeit : "Positive ion composition measurements and acetonitrile in the upper stratosphere" wird in Nature herausgegeben werden.

POSITIVE ION COMPOSITION MEASUREMENTS AND ACETONITRILE

IN THE UPPER STRATOSPHERE

by

E. ARIJS, D. NEVEJANS and J. INGELS

Abstract

The first measurements of the positive ion composition between 42 and 46 km altitude are reported. From the relative ion abundances the mixing ratio of an unknown molecule X is deduced in the upper stratosphere. Assuming X to be acetonitrile (CH_3CN), the density of OH is calculated between 35 and 45 km from the known reaction rate of OH with CH_3CN and from the X-profile. The agreement between the OH-profile thus obtained and previous measured and calculated OH densities supports the suggestion of X being acetonitrile.

Résumé

Les premières mesures de la composition des ions stratosphériques entre 42 et 46 km d'altitude sont présentées. Le rapport de mélange d'un gaz X est déduit des abondances relatives des ions. En supposant que X est acetonitrile (CH_3CN), la densité de OH est calculée à partir du profil de concentration de X et la vitesse connue de la réaction entre OH et CH_3CN . La ressemblance du résultat obtenu avec les observations et calculs de OH, rapportés dans la littérature, supporte la suggestion que X serait CH_3CN .

Samenvatting

De eerste metingen van het positieve ionenbestand tussen 42 en 46 km hoogte worden hier voorgesteld. Uit de relatieve signaalsterkten der ionen wordt de mengverhouding van een onbekende verbinding X afgeleid in de hogere stratosfeer. De dichtheid van OH wordt berekend in de veronderstelling dat X acetonitrile (CH_3CN) is, uit het dichtheidsprofiel van X en de bekende reactiecoëfficiënt van CH_3CN met OH. De goede overeenkomst van dit resultaat met vroegere metingen en berekeningen omtrent OH steunt de suggestie dat X CH_3CN zou zijn.

Zusammenfassung

Die erste Massenspectra erhalten im Höhegebiet von 42 bis 46 km sind hier vorgestellt. Die Dichte einer Verbindung X wurde abgeleitet aus den Häufigkeiten der verschiedenen Ionen. Annehmend dass X Methylcyanide (CH_3CN) ist, wurde die Dichte von OH verechnet aus der bekannte Reaktionsgeschwindigkeitskoeffizient zwischen OH und CH_3CN und aus der Teilchenanzahldichte von X. Die Ergebnisse unterstützen der Vorschlag dass X Methylcyanide ist.

1. INTRODUCTION

Although previous ion chemistry models (Mohnen, 1971; Ferguson, 1974) predicted proton hydrates (PH) i.e. ions of the form $H^+(H_2O)_n$, as major positive ions in the stratosphere, the first in-situ mass spectrometric measurements (Arnold et al., 1977; Arijs et al., 1978; Arnold et al., 1978) revealed an additional ion family, called non proton hydrates (NPH). As was shown by observations (Arnold et al., 1977; Arijs et al., 1978; Henschen and Arnold, 1981; Arijs et al., 1983), the fractional abundance of these NPH, represented by $H^+X_\ell(H_2O)_m$, increases from 1% to 90% from 55 down to 23 km. Several proposals were made in the literature (Arnold et al., 1978; Ferguson, 1978; Murad and Swider, 1979) for the identity of the molecule X, but high resolution spectra (Arijs et al., 1980) and ion abundance measurements (Arnold et al., 1981; Arijs et al., 1982) suggested that X should be acetonitrile (CH_3CN).

This suggestion was reinforced by laboratory measurements of Smith and colleagues (1981) and Böhringer and Arnold (1981) and in-situ data between 20 and 42 km, allowing a determination of the concentration profile of X in this altitude region (Henschen and Arnold, 1981; Arijs et al., 1983).

Here we report the first positive ion composition data obtained with a balloon borne instrument between 42 and 46 km altitude. These data extend the density profile of X and give supplementary indications about its identity.

The data presented and discussed hereafter were obtained with a mass spectrometer flown on 23 September 1982 with a 1,000,000 m³ stratospheric balloon at the CNES launching base of Aire-sur-l'Adour (44°N). Also included in the payload, and mounted above the mass spectrometer, were : a gondola containing photographic equipment for the detection of aerosol layers (Ackerman et al., 1981) and an instrument to measure ozone by means of UV absorption.

The instrument was launched at 12.38 UT and the flight lasted about 7h. A float altitude of 46 km was reached at 16.00 UT and after sunset the balloon descended slowly to 42 km. The altitude was determined independently from a pressure measurement with a high precision Baratron gauge and from high resolution radar tracking. The difference between both results was smaller than 300 m. A typical result of the balloon altitude determination is shown in figure 1.

Spectra of positive as well as negative ions have been obtained from 46 down to 42 km. The negative ion composition data will be reported elsewhere.

The instrument used to obtain the spectra has been described in detail before (Arijs et al., 1980). It consists of a microprocessor controlled (Nevejans et al., 1982) quadrupole ion mass spectrometer with a mass range of 10 to 330 amu built into a liquid helium cooled cryopump (Ingels et al., 1978). In order to obtain a greater sensitivity at high altitudes, a larger ion sampling hole (0.4 mm diameter) was used in the flight discussed here.

Since no other major ion groups than PH and NPH were detected, all positive ion spectra used here were recorded in a moderate resolution mode ($m/\Delta m \cong 17$), adequate to resolve the major ions and their fractional abundance. At some times spectra were recorded in the total ion mode (no DC on the quadrupole rods) or with low resolution, which allowed an estimation of the abundance of ions having a mass larger than 256 amu (Arijs et al., 1983). To minimize the possible effects of contamination (Arijs et al., 1983), all useful data were recorded either at float altitude or during the descent part of the flight, with the ion sampling hole pointing downward.

A typical positive ion spectrum obtained at float altitude is shown in figure 2. As can be seen all major mass peaks below 150 amu can be

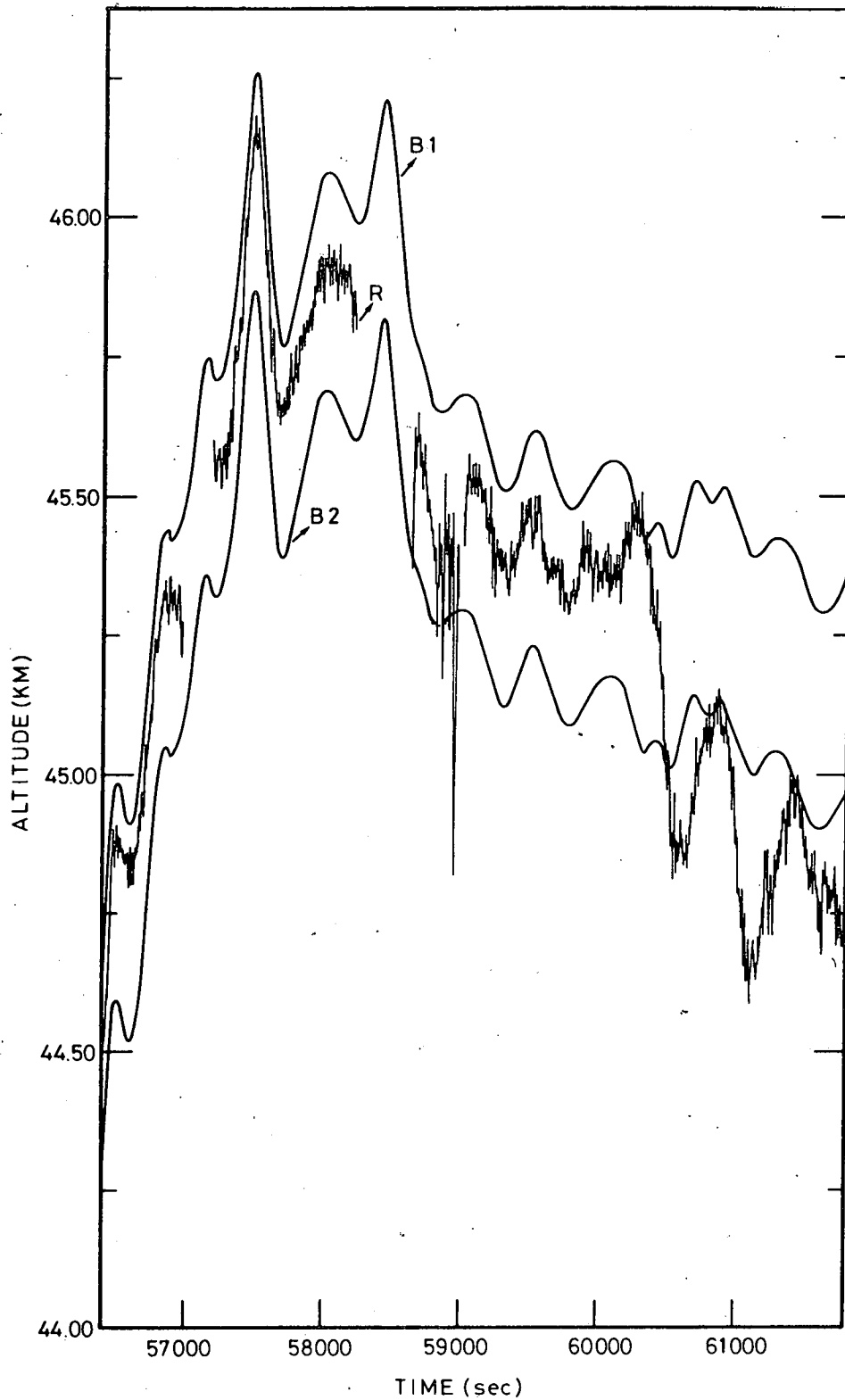


Fig. 1.- Typical altitude oscillations of the balloon during flight. The curve labeled R was obtained by radar tracking. The curves B1 and B2 are the result of a pressure measurement with the high precision Baratron (upper and lower limits). Time axis starts at 00:00 UT.

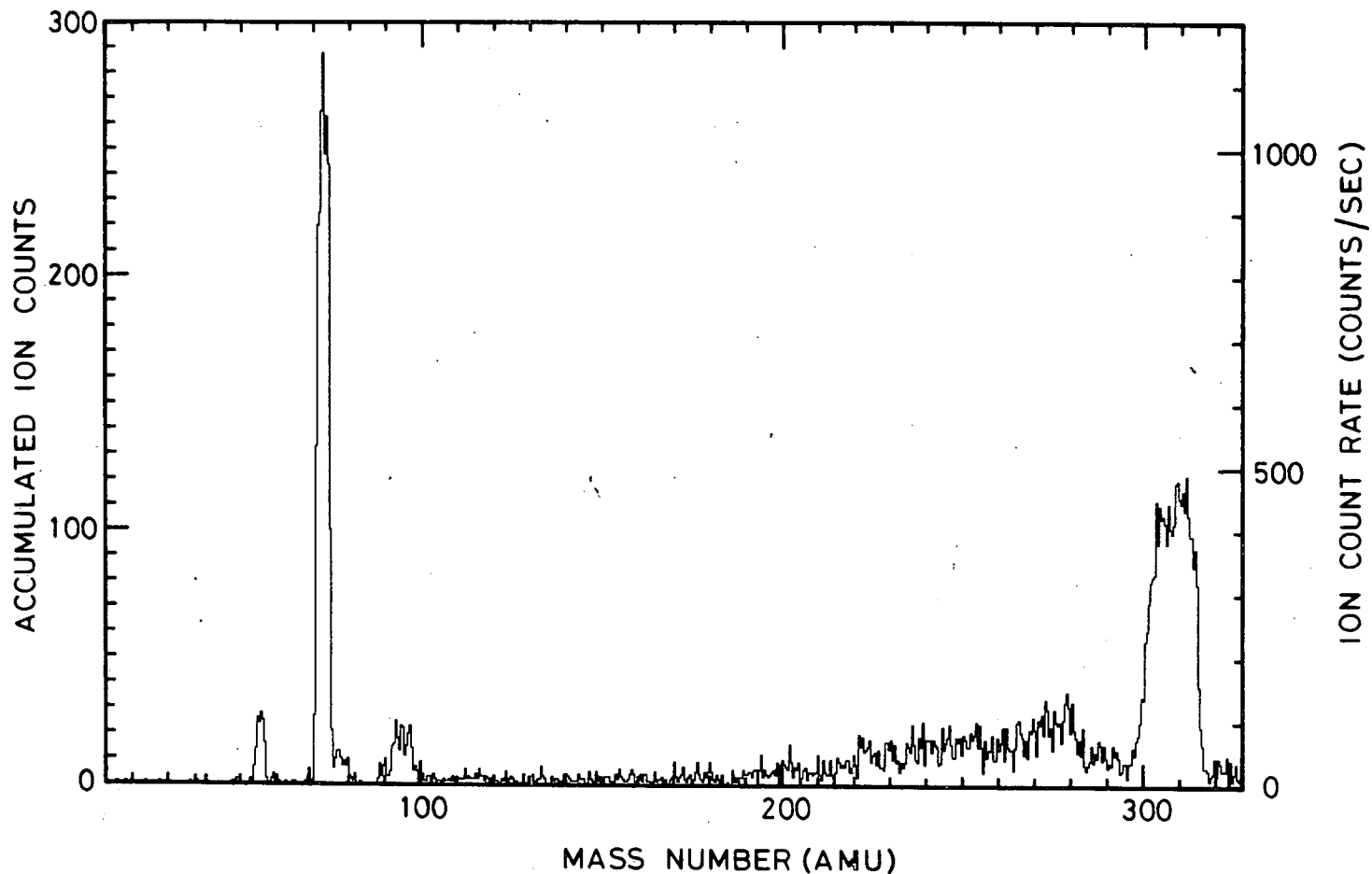


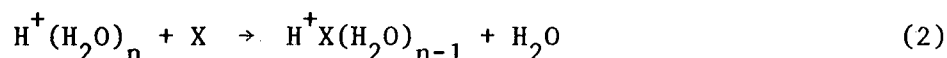
Fig. 2.- Typical positive ion spectrum obtained around 45.6 km altitude in the moderate resolution mode ($m/\Delta m \cong 17$). The spectrum has been obtained after 1 scan of 160 s for the mass domain 10 -330 amu. This spectrum has been chosen on purpose to show clearly the presence of contaminant ions (mass 278 and 310 amu). The first part of this spectrum was obtained during a descending phase of the balloon excursion whereas the second half was recorded during ascent.

attributed to either PH ions (masses 55,73 and 91) or to NPH clusters (masses 78,96,...). Two groups of mass peaks are also present around 278 and 310 amu. The intensity of these peaks fluctuated with altitude and increased during ascending phases of the balloon altitude oscillations. In spectra recorded during the descent of the balloon, these mass peaks due to contamination were much less pronounced. Laboratory studies in our institute have shown that these ions originated from gases desorbing from the painted surfaces of the photographic payload, heated by solar radiation. These gases appeared to be mainly dibutylphthalate and butylbenzylphthalate vapours, two solvents present in the paint.

As was already pointed out by Arnold *et al.* (1978) the number density of X can be derived from the observed fractional ion abundances through the continuity equation for NPH :

$$k_1 [\text{PH}][\text{X}] = \alpha [n_-][\text{NPH}] \quad (1)$$

where $[n_-]$ the total negative ion density α is the ion-ion recombination coefficient and k_1 the rate coefficient for ion-molecule reactions of the type



The total fractional abundances of NPH ions and PH ions, $[\text{NPH}]$ and $[\text{PH}]$, can be deduced directly from the ion mass spectra, assuming that ion count rates are reflecting ion abundances. It is believed that this assumption is acceptable in view of the moderate resolution used, resulting in low mass discrimination effects.

For k_1 a value of $3 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ was chosen, according to the laboratory measurements of Smith and colleagues (1981). The total negative ion concentration $[n_-]$ was calculated with the parametrization formula of Heaps (1978).

For α a parametrization of the form

$$\alpha = 6.10^{-8} \left(\frac{300}{T} \right)^{1/2} + 1.25 \times 10^{-25} [M] \left(\frac{300}{T} \right)^4 \text{ cm}^3 \text{ s}^{-1} \quad (3)$$

was adopted where T is the temperature in Kelvin and $[M]$ the total neutral number density in cm^{-3} . The recombination coefficient calculated with formula (3) compromises for the different values of α as obtained by recent in-situ measurements (Rosen and Hofman, 1981), laboratory experiments (Smith and Adams, 1982) and theoretical studies (Bates, 1982).

The concentrations of X , thus obtained from spectra similar to figure 2 are converted to mixing ratios and represented in figure 3 for the different altitudes covered by the present flight.

In the foregoing derivations of $[X]$ with the continuity equation (1), it was assumed that the contaminant gases giving rise to heavy ions (around mass 278 and 310 amu) do not affect the ambient ion chemistry. To investigate the possible role of contamination on our calculations, we will represent the real number density of X by

$$[X]_R = [X](1 + \varepsilon) \quad (4)$$

where $[X]$ is the number density inferred from equation (1). The relative error ε can now be calculated for two extreme reaction schemes, which could modify the simple ion chemistry leading to equation (1). In the first one we assumed that the contaminants react with both PH and NPH and give rise to heavy ions CI, which subsequently disappear by recombination. The continuity equation for NPH and CI leads to :

$$\varepsilon = k_3 [CI] (k_2 [PH] + k_3 [NPH])^{-1} \quad (5)$$

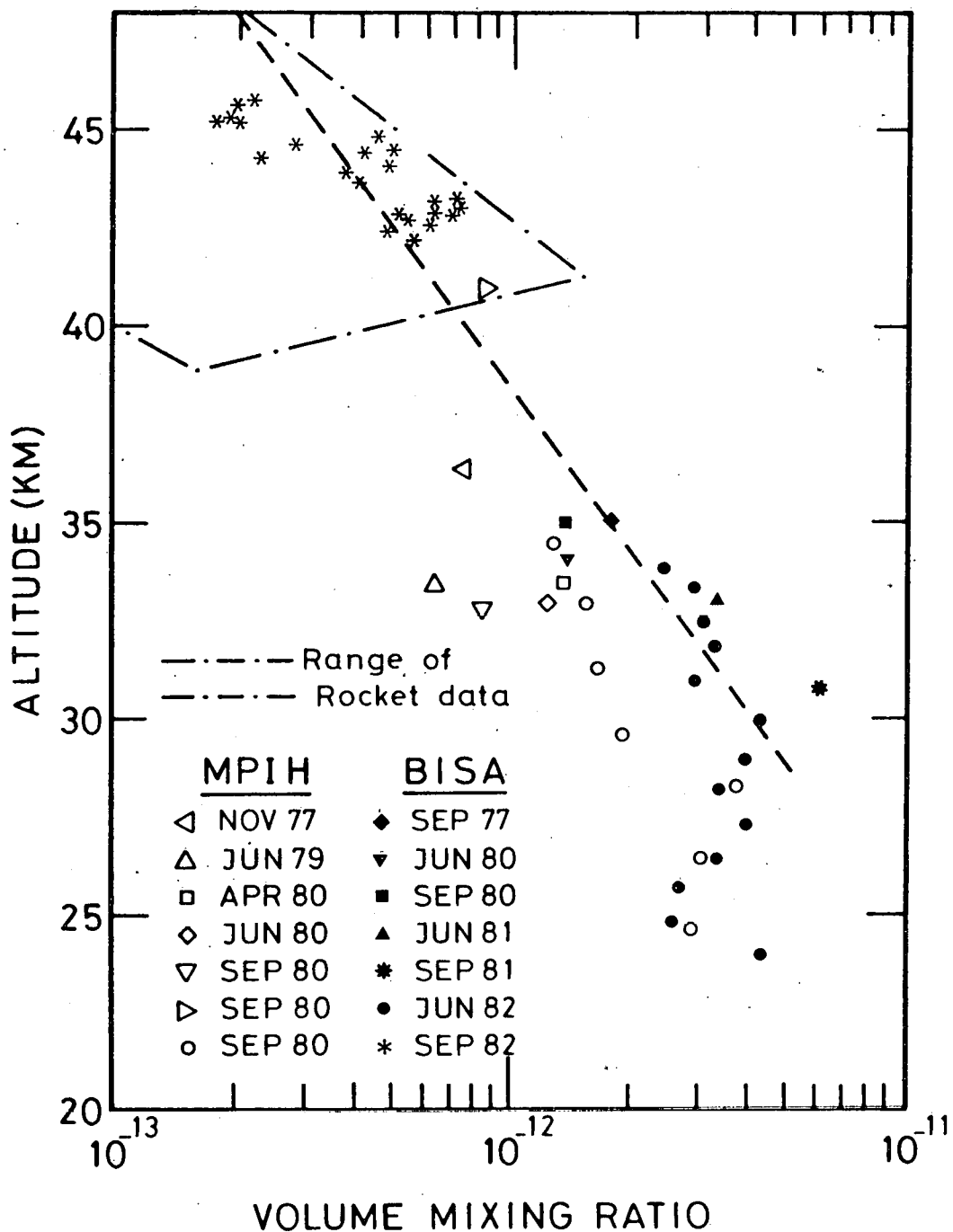


Fig. 3.- Volume mixing ratio of X as calculated from ion abundances. The data labeled MPIH are those obtained by the group of the Max-Planck-Institut of Heidelberg. The points called BISA are from Belgian Institute for Space Aeronomy. The range of rocket data, obtained by Arnold and colleagues (1977) has been taken from a compilation by Henschen and Arnold (1981). The dotted straight line represents an approximation of the form $f(\text{CH}_3\text{CN}) = 6 \times 10^{-10} \exp(-z/6)$, with z expressed in km.

where k_2 and k_3 are common rate constants for the reactions of contaminants with PH and NPH respectively. This implies that the values of $[X]$ would be too low by a factor $(1+\epsilon)$. The relative error ϵ reduces to zero if the contaminants react with PH only ($k_3 = 0$). When $k_2 \cong k_3$ the error ϵ is estimated to be at maximum 1 in the most contaminated spectra, used for the derivation of $[X]$. This is concluded from estimations of $[CI]/([PH] + [NPH])$ in spectra obtained at very low resolution or in the total ion mode, where few or no errors are induced due to the limited mass range of the instrument. When the contaminants are reacting with NPH only ($k_2 = 0$), ϵ can become very large. This would mean that for high values of $[CI]$ lower values of $[X]$ should be found. However spectra obtained during ascending phases of the balloon and showing high $[CI]$ values seem to indicate the opposite (these spectra were not used for $[X]$ -derivations!). This leads us to believe that the first proposed reaction scheme is rather unlikely.

Another modification of the continuity equation for NPH arises when the contaminant gases react with PH and the resulting CI subsequently react with X to form extra NPH. Continuity considerations now result in :

$$\epsilon = - k_4 [CI] (k_1 [PH] + k_4 [CI])^{-1} \quad (6)$$

where k_4 is the reaction rate coefficient of X with CI. Assuming $k_1 \cong k_4$ (which is an extreme case, in view of the large value of k_1) the values of $[X]$ should be reduced by a factor of 2 in the worst case of contamination for the spectra used, when $[CI] \cong [PH]$.

As a general conclusion we feel that it is safe to accept an error of a factor of 2 due to contamination for the values of $[X]$ as derived in this work. In fact below 44 km where the balloon descended at a rate of 1.3 ms^{-1} , we believe that this error is much smaller, due to the lower outgassing of the optical payload after sunset and due to the induced air flow. This is also confirmed by a total ion mode spectrum,

obtained below 44 km during descent, which shows a total abundance of [CI] less than 10%. Furthermore the reasonable agreement of our data points with the rocket data, as observed in figure 3, strengthens our faith in their reliability.

Considering the previous remarks and the uncertainty on the quantities α , k_1 and $[n_-]$ used in formula (1), the maximum total error on the data is estimated to be a factor of 3.

When combined with results of previous balloon flights a more complete mixing ratio profile of the molecule X is now obtained. This profile, showing a slow decrease of the mixing ratio of X above 30 km, suggests as was already pointed out (Henschen and Arnold, 1981; Arijs et al., 1983) a source of X below 30 km.

If X were CH_3CN such a source might be surface production by industrial releases or biomass burning, followed by wash-out, diffusion and photochemical destruction. Recent observations by Becker and Ionescu (1982) indicate that the concentration of CH_3CN at ground level ranges from 2 to 7 ppbv, which support the hypothesis of surface emission, followed by strong heterogeneous removal.

For CH_3CN , the emission factors of which are not known yet, the loss processes one expects are reaction with OH and photodissociation. Since however light absorption by CH_3CN and resulting photolysis only starts in the far UV (Mc. Elcheran et al., 1958), the main loss happens through reaction with the hydroxyl radical. Reactions with $\text{O}(^1\text{D})$ and Cl may also contribute to the destruction of CH_3CN , although due to the low concentrations of these species and the expected slower reactions this loss term can probably be neglected here. In such a case the steady state continuity equation for CH_3CN can be simplified to

$$\frac{\partial \phi(\text{CH}_3\text{CN})}{\partial z} + k [\text{OH}] [\text{M}] f(\text{CH}_3\text{CN}) = 0 \quad (7)$$

with
$$\phi(\text{CH}_3\text{CN}) = - K[M] \frac{\partial f(\text{CH}_3\text{CN})}{\partial z} \quad (8)$$

where [OH] is the number density of hydroxyl radicals, k the reaction rate coefficient of CH₃CN with OH, f(CH₃CN) the mixing ratio and K the eddy diffusion coefficient.

The reaction rate coefficient k, as recently measured by Harris et al. (24), is given by

$$k = 5.86 \times 10^{-13} \exp(-750/T) \text{ cm}^3 \text{ s}^{-1} \quad (9)$$

The total density [M] can be easily calculated from the ideal gas law and the U.S Standard Atmosphere. If then we take according to Brasseur et al. (1982)

$$K = 1019 \exp(z/9.43) \text{ cm}^2 \text{ s}^{-1} \quad (10)$$

(z in km), and approximate the mixing ratio f(CH₃CN) in the altitude region 33 to 45 km by

$$f = 6 \times 10^{-10} \exp(-z/6) \quad (11)$$

which is the dotted straight line in figure 2, the set of equations (7) and (8) can be solved analytically and the OH mixing ratio can be calculated from the approximated CH₃CN profile.

The result of such a calculation is shown in figure 4 for U.S. Standard Atmosphere fall temperature conditions. The obtained OH profile is compared to recent measurements, performed by different authors (Anderson, 1976, 1981; Heaps, 1981).

As can be seen the OH mixing ratios of this work are considerable lower than the measurements. It should be kept in mind however that the measurements represent instantaneous values of [OH], whereas the

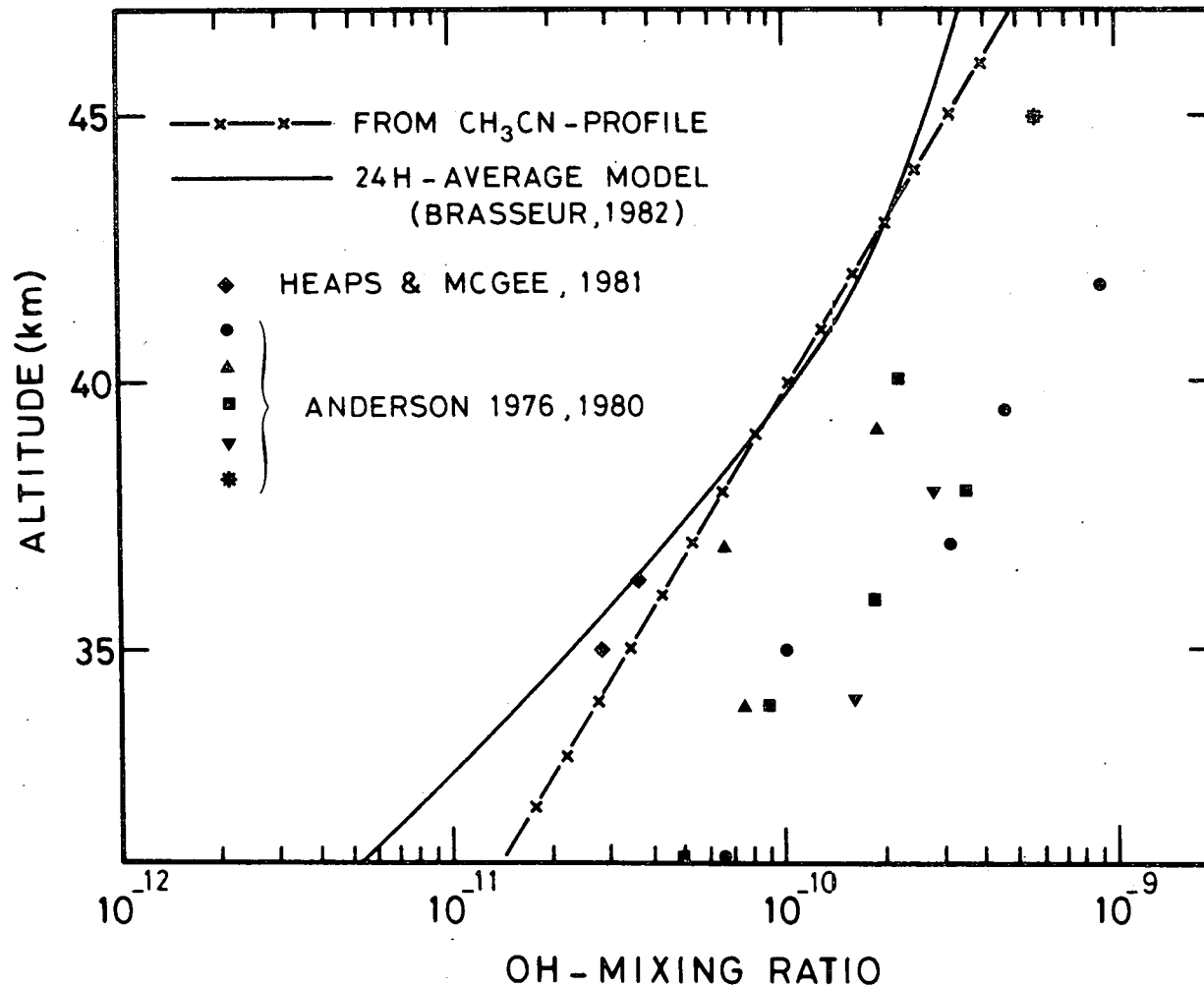


Fig. 4.- OH volume mixing ratio profile calculated assuming that X were CH₃CN, and compared to measurements and model calculations.

data calculated here are 24 h averages, regarding the long lifetime of CH_3CN versus the OH reactions (between 400 and 1000 h for the altitude region under consideration).

In fact a comparison of the OH-profile calculated from the CH_3CN profile with a recent model calculation of the 24 hour average of OH according to Brasseur (1982) turns out to be quite satisfactory, in view of the simple CH_3CN profile assumed (a straight line on semi-log plot).

The reasonable agreement of these OH data with previous works can be considered as additional evidence for the identification of X as CH_3CN .

It is clear however that a more complete model of CH_3CN , taking into account possible surface sources, wash-out in the troposphere, diffusion and photochemical destruction is needed to elucidate this problem.

At present however, all data acquired so far seem to indicate that the molecule X is indeed CH_3CN .

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