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Vertical distribution of acetonitrile in the atmosphere

by

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## FOREWORD

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## AVANT-PROPOS

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## VOORWOORD

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## VORWORT

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# VERTICAL DISTRIBUTION OF ACETONITRILE IN THE ATMOSPHERE

by

J. INGELS, D. NEVEJANS and E. ARIJS

## Abstract

The presence of acetonitrile in the atmosphere has been confirmed by results of both surface and stratospheric investigations. Stratospheric measurements gave mixing ratios typically decreasing with height from about 3 ppt at 25 km to about 0.5 ppt at 40 km. Measurements at the earth's surface are less unanimous, although a ground level background mixing ratio of a few times 10 ppt seems realistic. Recent measurements are compatible with a small global surface source of acetonitrile and a small tropospheric loss.

Therefore, a vertical distribution of acetonitrile as known and presented here, is likely to be consistent with our general knowledge of composition and chemistry of the atmosphere.

## Résumé

La présence d'acétonitrile dans l'atmosphère a été confirmée à la fois par des observations au sol et dans la stratosphère. Les mesures stratosphériques conduisent à des rapports de mélange décroissant avec l'altitude approximativement entre 3 ppt à 25 km et 0.5 ppt à 40 km. Les mesures à la surface de la terre sont moins concordantes, bien qu'une valeur de quelques 10 ppt semble être un rapport de mélange réaliste. Des mesures récentes sont compatibles avec une faible source globale d'acétonitrile à la surface de la terre et une faible perte troposphérique.

Dès lors, la distribution verticale d'acétonitrile telle qu'elle est connue et présentée ici, est probablement compatible avec notre connaissance générale de la composition et de la chimie de l'atmosphère.

## Samenvatting

De aanwezigheid van acetonitrile in de atmosfeer werd bevestigd door de resultaten van onderzoeken aan het aardoppervlak en in de stratosfeer. Stratosferische metingen leveren typische mengverhoudingen op, die met de hoogte verminderen van 3 ppt op 25 km tot ongeveer 0,5 ppt op 40 km. Metingen in de onderste luchtlagen geven minder eensgezinde resultaten, alhoewel mengverhoudingen van enkele tientallen ppt realistisch schijnen te zijn. Recente metingen wijzen op een kleine, wereldwijde bron van acetonitrile aan het aardoppervlak en op een geleidelijke afname in de troposfeer.

Daarom is de verticale distributie van acetonitrile zoals ze nu bekend is en zoals wij ze hier voorstellen, verenigbaar met de algemene kennis van de samenstelling van, en de scheikundige verschijnselen in de atmosfeer.

## Zusammenfassung

Die Anwesenheit des Methanzyanides in der Atmosphäre wurde bestätigt durch die Ergebnisse von Messungen an der Erdoberfläche und in der Stratosphäre. Stratosphärische Messungen ergeben typische Mischungsverhältnisse, in der Höhe abnehmend zwischen 3 ppt an 25 km und 0,5 ppt an 40 km. Messungen in den unteren Luftschichten ergeben weniger einmütige Ergebnisse, obschon Mischungsverhältnisse von einzigen 10 ppt wahrscheinlich realistisch sein werden. Rezente Messungen ergeben eine kleine, weltumfassende Quelle des Methanzyanides an der Erdoberfläche und eine allmähliche Abnahme in der Troposphäre.

Deshalb ist die vertikale Distribution des Methanzyanides wie sie nun bekannt ist und hier dargestellt wird, vereinbar mit der allgemeinen Kenntnis der atmosphärischen Zusammenstellung und Chemie.

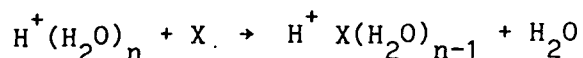
Mass spectrometric measurements of the stratospheric ion composition with balloon-borne and rocket-borne instruments showed the presence of so-called non proton hydrates (NPH), i.e.  $H^+X_l(H_2O)_m$  (Arnold et al., 1977; Arijs et al., 1978; Arnold et al., 1978). Arnold et al. (1978) suggested acetonitrile as a possibility for the molecule X. This hypothesis has been the subject of controversial discussions (Ferguson, 1978; Murad and Swider, 1979), but high resolution mass spectra (Arijs et al., 1980) and laboratory investigations (Böhringer and Arnold, 1981; Smith et al., 1981) seem to support this hypothesis.

Since 1978, positive ion composition measurements between 20 and 45 km have been performed with balloon-borne instruments (Arnold, 1980, 1982; Henschen and Arnold, 1981; Arijs, 1983; Arijs et al., 1983a,b), to determine fractional ion abundances of proton hydrates (PH) and NPH.

As pointed out by Arnold et al. (1978), the number density of  $CH_3CN$  can be calculated from the observed fractional ion abundances through the continuity equation for NPH

$$k_1 [PH][CH_3CN] = \alpha [n_-][NPH]$$

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



The total fractional abundances of NPH and PH ions,  $[NPH]$  and  $[PH]$ , can be deduced from ion mass spectra, assuming that ion count rates reflect ion abundances.

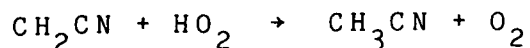
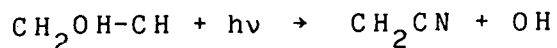
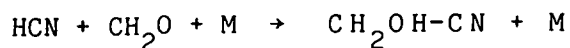
For  $k_1$ , a value of  $3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  was chosen, according to laboratory measurements of Smith et al. (1981). The  $[n_-]$  was calculated with the parametrization formula of Heaps (1978). For  $\alpha$ , a parametrization of the form

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

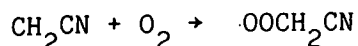
was adopted, where T is the temperature in Kelvin and [M] the total neutral number density in  $\text{cm}^{-3}$ . This parametrization is a compromise for the different values of  $\alpha$  as obtained by recent in-situ measurements (Rosen and Hofman, 1981), laboratory experiments (Smith and Adams, 1982) and theoretical studies (Bates, 1982).

The volume mixing ratios of acetonitrile, obtained with our most recent mass spectra are shown in figure 1. These results are compared with data of the MPIH group (Max-Planck-Institut für Kernphysik, Heidelberg, B.R.D.), which have been re-calculated with the values of  $\alpha$  and  $[n_]$  explained here.

Two different hypotheses have been advanced to explain the presence of acetonitrile in the stratosphere. Murad et al. (1984) propose an in-situ formation mechanism based on the following reactions :



Probably, the first reaction may be much slower than supposed by Murad et al. (1984). However, if fast enough to explain the data of figure 1, it should represent a major sink for HCN, and the HCN values measured by Cicerone and Zellner (1983) should be very difficult to explain. Furthermore, the reaction



may be fast enough to destroy all  $\text{CH}_2\text{CN}$ , before any acetonitrile is formed (Brasseur et al., 1984).

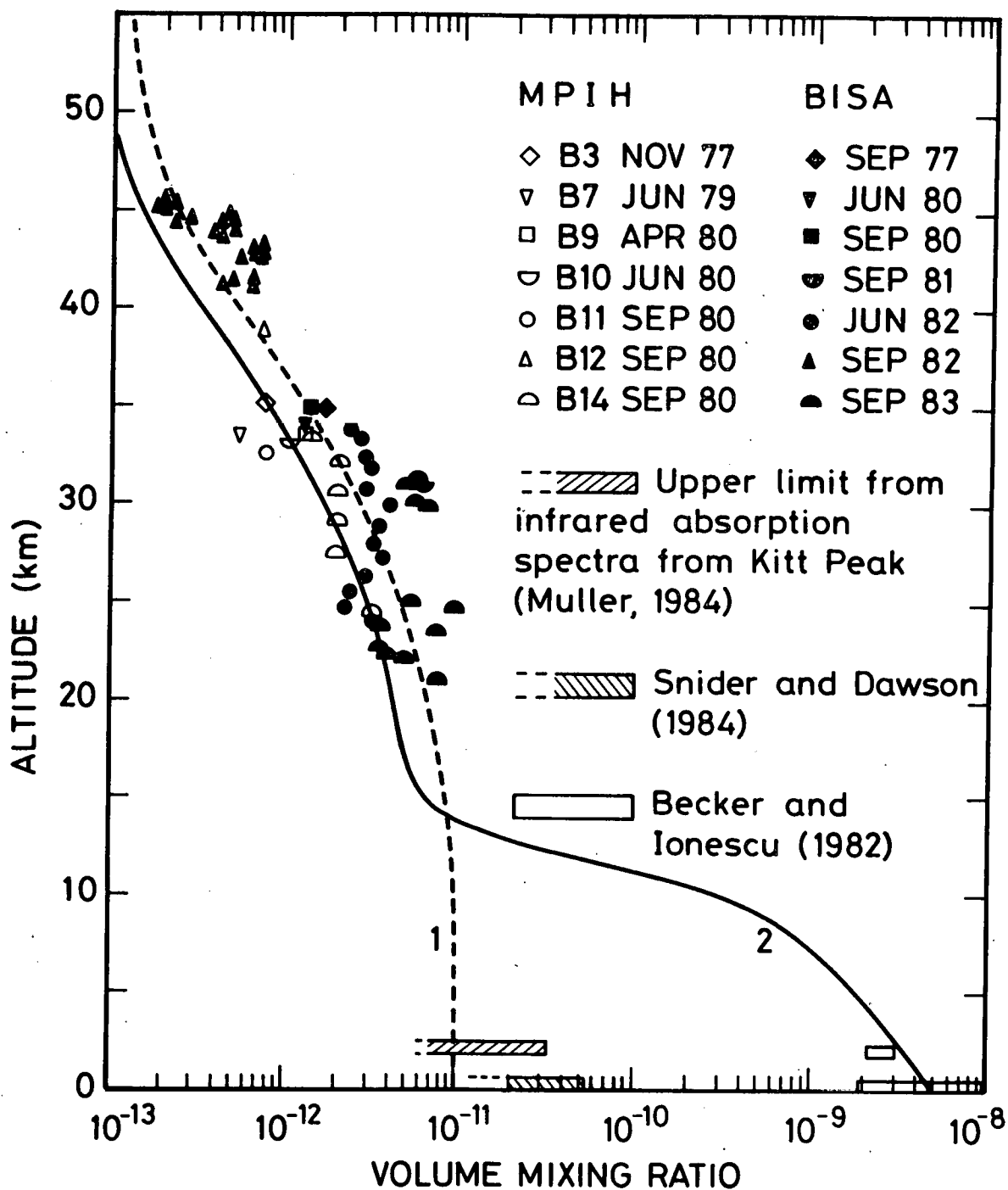
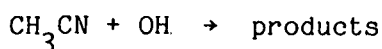


Fig. 1.- Vertical distribution of acetonitrile ( $\text{CH}_3\text{CN}$ ) in the atmosphere.

Therefore, it appears more likely to accept the proposal suggested by Brasseur et al. (1983), which assumes that acetonitrile is released at the earth's surface and that it diffuses into the atmosphere, where it is destroyed by reaction with OH radicals mainly.

Recently, measurements of CH<sub>3</sub>CN near the earth's surface have supported this hypothesis. The two measurements reported in literature (Becker and Ionescu, 1982; Snider and Dawson, 1984) are also shown in figure 1. As can be seen, both data sets differ by about a factor of 100.

Also given in figure 1, are two curves obtained through model calculations by Brasseur et al. (1983), obtained by taking a fixed surface concentration and a zero flux at 100 km altitude as boundary conditions. The only chemical loss reaction introduced was



for which a reaction rate coefficient as measured by Harris et al. (1981) was adopted. Curve 1 assumes a mixing ratio at ground level of 10 pptv and no wash out. Curve 2 was obtained with a surface mixing ratio of 5 ppbv and a wash out coefficient of  $2 \times 10^{-6} \text{ s}^{-1}$ . As can be seen, both curves can reproduce the data obtained by ion mass spectrometry. However, the main problem remains a determination of the loss due to wash out. If the data of Becker and Ionescu (1982) are representative for a background atmosphere, a large loss due to rain out has to be introduced.

According to Heicklen (1981), the lifetime due to wash out can be calculated with

$$\tau_s = \left(1 + \frac{k}{f}\right) \times \tau_0$$

where  $f$  is the fractional volume of air occupied by liquid water,  $\tau_0$  the average lifetime with which droplet removal occurs in the troposphere (about  $10^6$  s) and  $k$  Henry's law constant (ratio of the molecule number density in the vapour phase and the molecule number density in the liquid phase). From a compilation of available data on the acetonitrile - water liquid-vapor equilibrium, a value of  $k = 9 \times 10^{-5}$  can be found for an



average tropospheric temperature of 245 K (Arijs and Brasseur, 1986). Taking for  $f = 10^{-6}$  (about  $1 \text{ g m}^{-3}$  liquid water in the air), a  $\tau_0$  of  $9 \times 10^7$  s is found. This value is in good agreement with the residence time for rain out recently found by Hamm et al. (1984).

It is therefore concluded that curve 1 is a better approximation of reality and that the measurements of Snider and Dawson (1984) seem more realistic than those of Becker and Ionescu (1982), which apparently are more representative for polluted areas.

Recent investigations of infrared spectra indicating that an upper limit for  $\text{CH}_3\text{CN}$  at 2000 m altitude is about 32 pptv (Muller, private communication) seem to support this supposition.

Curve 1 corresponds to a global emission of 0.023 MT/yr. This emission can be explained easily by sources such as biomass burning, car exhaust gases and direct release of  $\text{CH}_3\text{CN}$  from industrial processes. It is expected that the actual emission calculated with a small wash out loss will be somewhat larger, although we do not expect changes larger than a factor of 3.

In fact, new model calculations taking into account loss terms such as reaction with atomic oxygen and chlorine atoms (which seems to be very low; Olbregts et al., 1984) and photodissociation are needed, as well as a systematic investigation of possible emission sources.

And although the vertical distribution of acetonitrile as known and presented here, is likely to be consistent with our general knowledge of its atmospheric chemistry, more in-situ measurements (especially below 20 km) are needed to clarify the remaining problems.

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## REFERENCES

- ARIJS, E., Positive and negative ions in the stratosphere, *Annales Geophysicae*, 1, 149-160, 1983.
- ARIJS, E. and BRASSEUR, G., Acetonitrile in the stratosphere and implications for positive ion composition, accepted for publication in *J. Geophys. Res.*, 1986.
- ARIJS, E., INGELS, J. and NEVEJANS, D., Mass spectrometric measurement of the positive ion composition in the stratosphere, *Nature*, 271, 642-644, 1978.
- ARIJS, E., NEVEJANS, D. and INGELS, J., Unambiguous determination of major stratospheric positive ions, *Nature*, 288, 684-686, 1980.
- ARIJS, E., NEVEJANS, D., INGELS, J. and FREDERICK, P., Positive ion composition measurements between 33 and 20 km altitude, *Annales Geophysicae*, 1, 161-166, 1983a.
- ARIJS, E., NEVEJANS, D. and INGELS, J., Positive ion composition measurements and acetonitrile in the upper stratosphere, *Nature*, 303, 314-316, 1983b.
- ARNOLD, F., Multi-ion complexes in the stratosphere, implications for trace gases and aerosols, *Nature*, 284, 610-611, 1980.
- ARNOLD, F., Ion nucleation, a potential source for stratospheric aerosols, *Nature*, 299, 134-136, 1982.
- ARNOLD, F., BOHRINGER, H. and HENSCHEN, H., Composition measurements of stratospheric positive ions, *Geophys. Res. Lett.*, 5, 653-656, 1978.
- ARNOLD, F., KRANKOWSKY, D. and MARIEN, K.H., 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.*, 30, 1275-1282, 1982.
- BECKER, K.H. and IONESCU, A., Acetonitrile in the lower troposphere, *Geophys. Res. Lett.*, 9, 1349-1351, 1982.
- BOHRINGER, H. and ARNOLD, F., Acetonitrile in the stratosphere - implications from laboratory studies, *Nature*, 290, 321-322, 1981.
- BRASSEUR, G., ARIJS, E., DE RUDDER, A., NEVEJANS, D. and INGELS, J., Acetonitrile in the atmosphere, *Geophys. Res. Lett.*, 10, 725-728, 1983.

- BRASSEUR, G., ZELLNER, R., DE RUDDER, A. and ARIJS, E., Is hydrogen-cyanide (HCN) a progenitor of acetonitrile ( $\text{CH}_3\text{CN}$ ) in the stratosphere ?, *Geophys. Res. Lett.*, 12, 117-120, 1985.
- CICERONE, R.J. and ZELLNER, R., The atmospheric chemistry of hydrogen cyanide (HCN), *J. Geophys. Res.*, 88, 10689-10696, 1983.
- FERGUSON, E.E., Sodium hydroxyde ions in the stratosphere, *Geophys. Res. Lett.*, 5, 1035-1038, 1978.
- HAMM, S., HAHN, J., HELAS, G. and WARNECK, P., Acetonitrile in the troposphere : residence time due to and uptake by the oceans, *Geophys. Res. Lett.*, 11, 1207-1210, 1984.
- HARRIS, G.W., KLEINDIENST, T.E. and PITTS Jr. J.N., Rate constants of OH radicals with  $\text{CH}_3\text{CN}$ ,  $\text{C}_2\text{H}_5\text{CN}$  and  $\text{CH}_2=\text{CH}-\text{CN}$  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.
- HEICKLEN, J., The removal of atmospheric gases by particulate matter, *Atmosph. Environment*, 15, 781-785, 1981.
- HENSCHEN, G. and ARNOLD, F., Extended positive ion composition measurements in the stratosphere. Implication for neutral trace gases, *Geophys. Res. Lett.*, 8, 999-1001, 1981.
- MURAD, E. and SWIDER, W., Chemistry of meteor metals in the stratosphere, *Geophys. Res. Lett.*, 6, 929-932, 1979.
- MURAD, E., SWIDER, W., MOSS, R.A. and TOBY, S., Stratospheric sources of  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{OH}$ , *Geophys. Res. Lett.*, 11, 147-150, 1984.
- OLBREGTS, J., BRASSEUR, G. and ARIJS, E. Reaction of acetonitrile and chlorine atom, *J. Photochem.*, 24, 315-322, 1984.
- ROSEN, J.M. and HOFMAN, D.J., Balloon-borne measurements of electrical conductivity, mobility and the recombination coefficient, *J. Geophys. Res.*, 86, 7406-7420, 1981.
- SMITH, D., ADAMS, N.G. and ALGE, E., Ion-ion mutual neutralization and ion-neutral switching reactions of some stratospheric ions. *Planet. Space Sci.*, 29, 449-454, 1981.
- SMITH, D. and ADAMS, N.G., Ion recombination in the stratosphere, *Geophys. Res. Lett.*, 9, 1085-1087, 1982.
- SNIDER, J.R. and DAWSON, G.A., Surface acetonitrile near Tucson, Arizona, *Geophys. Res. Lett.*, 11, 241-242, 1984.