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**Acetonitrile in the earth's atmosphere : an upper
limit deduced from infrared solar spectra**

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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ACETONITRILE IN THE EARTH'S ATMOSPHERE : AN UPPER

LIMIT DEDUCED FROM INFRARED SOLAR SPECTRA

by

Christian MULLER

Abstract

An upper limit to the atmospheric acetonitrile mixing ratio of 3.2×10^{-11} is deduced from the high resolution Kitt Peak infrared atlas of the solar spectrum. The survey of the spectral region of CH_3CN main absorption shows only stratospheric ozone lines and one water vapor line and does not permit any positive identification of acetonitrile.

Résumé

Une limite supérieure de la fraction molaire du cyanure de méthyle atmosphérique de 3.2×10^{-11} est déduite de l'atlas infrarouge du spectre solaire à haute résolution de Kitt Peak. L'examen du domaine spectral des absorptions les plus fortes de CH_3CN ne montre que des raies de l'ozone stratosphérique et une raie de la vapeur d'eau et ne permet pas l'identification positive du cyanure de méthyle.

Samenvatting

Een bovenlimiet van de mengverhouding van de atmosferische methaancyanide van 3.2×10^{-11} wordt afgeleid uit de infrarode atlas van het zonnenspectrum met hoge resolutie van Kitt Peak. Het onderzoek van het spectraal gebied van de sterkste absorpties van CH_3CN toont slechts lijnen van stratosferische ozon en één waterdamplijn en laat geen positieve identificatie toe van de methaancyanide.

Zusammenfassung

Ein Oberlimit des Mischungsverhältnisses des atmosphärischen Methanzyanides von 3.2×10^{-11} wird abgeleitet vom infraroten Atlas des Sonnenspektrums mit höher Resolution von Kitt Peak. Die Forschung des Spektralgebietes der stärksten Absorptionen von CH_3CN zeigt nur Linien von stratosphärischem Ozon und einer Wasserdampflinie und erlaubt keine positive Identifikation des Methanzyanides.

The recent discovery of acetonitrile (CH_3CN) in the earth's stratosphere through positive ion measurements (Arnold *et al.*, 1978, Arijs *et al.*, 1983) has led to modelling attempts and to a concern for possible sources (Brasseur *et al.*, 1983). While acetonitrile is not involved in the stratospheric ozone chemistry, it is a plausible source of amino acids in the early atmosphere and might have been one of the precursors of life. Now, it is thought to originate from biomass burning and industrial processes; moreover, an understanding of the cyanide chemistry is pertinent to the study of the atmosphere of a satellite of Saturn: Titan, which is marked for future space exploration.

The Kitt Peak National Observatory solar atlas (Delbouille *et al.*, 1981) is presently the best compilation of ground based spectra available for solar physics. It is a cooperative venture of KPNO, the Astrophysics Institute of the University of Liège and the Belgian Royal Observatory. The spectrum used for the present determination was obtained on October 25, 1979 for an air-mass of 1.17. The spectral domain covered wavenumbers between 2385 and 3770 cm^{-1} and the achieved spectral resolution was 0.015 cm^{-1} . This spectral interval is characterized at one edge by the strong 2349 cm^{-1} CO_2 ν_1 band and at the other by the water vapor 3652 cm^{-1} ν_1 band; between these two, lies the intense CH_4 ν_3 band at 3020 cm^{-1} . Together with other weaker telluric bands, these leave very few windows through which weak absorbers could be sought. However, between the manifolds of the CH_4 band, some clean spectral regions emerge and, by chance, one of them between 3040 and 3041 cm^{-1} coincides with the most intense CH_3CN absorption feature.

The resolved structure of the CH_3CN spectrum was first measured by Thompson and Williams (1952) and their analysis was later confirmed by Parker *et al.* (1957), leaving studies of isotopes and more elaborate spectroscopic properties to later authors (Duncan *et al.*, 1978, Kondo and Person, 1974 and references therein). As only Thompson and Williams (1952) published intensity data for the ν_5 band, their work will

be used for the present analysis. Their resolution of 0.3 cm^{-1} permits the observation of narrow features; one of the most intense appears at 3040.52 cm^{-1} and seems to be a single line blended with a weaker one at 3041 cm^{-1} . The total strength of the main line can be inferred from the published quantitative data as $2.5 \times 10^{-20} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$.

As the purpose of the present work was to determine an upper limit, the absorption was assumed to be linear although this is very unlikely at the 60 torr pressure and 60% absorption of the line. This value, if used for determinations of CH_3CN , will always lead to higher values which could be overestimated by a factor which will only be determined by a high resolution study of the curve of growth of the line.

The corresponding Kitt Peak spectral interval is shown on figure 1, where many narrow and weak lines appear, the half line width of the 3040.96 cm^{-1} line being 0.01 cm^{-1} ; only the 3040.75 cm^{-1} line seems to be wider and to exhibit a broad shoulder at 3040.72 cm^{-1} . The AFGL line parameter table (Rothman et al., 1983) shows O_3 lines and a single H_2O line at 3040.728 cm^{-1} in the 1980 edition, and at 3040.741 cm^{-1} in the 1982 edition. This feature could be identified with the wide line shoulder. The 1982 edition mentions also a few weak CH_4 line which cannot be identified on the observed spectrum.

The quoted STP line width parameter for all O_3 lines is 0.11 cm^{-1} which, converted to the Kitt-Peak altitude, is 0.09 cm^{-1} . Even on dividing by 2, to take into account a Curtiss-Godson effect, this is much higher than the 0.01 cm^{-1} observed line width corresponding to a 100 mb level, and indicates that the observed absorption occurs at altitudes of 15 km or above, confirming thus the stratospheric origin of the lines. The analysis of the H_2O shoulder using AFGL water vapor line parameters leads to a water vapor mixing ratio of 1×10^{-3} which is fully in agreement with the 8.1 mm of water vapor indicated by Delbouille et al. (1981) for this spectrum.

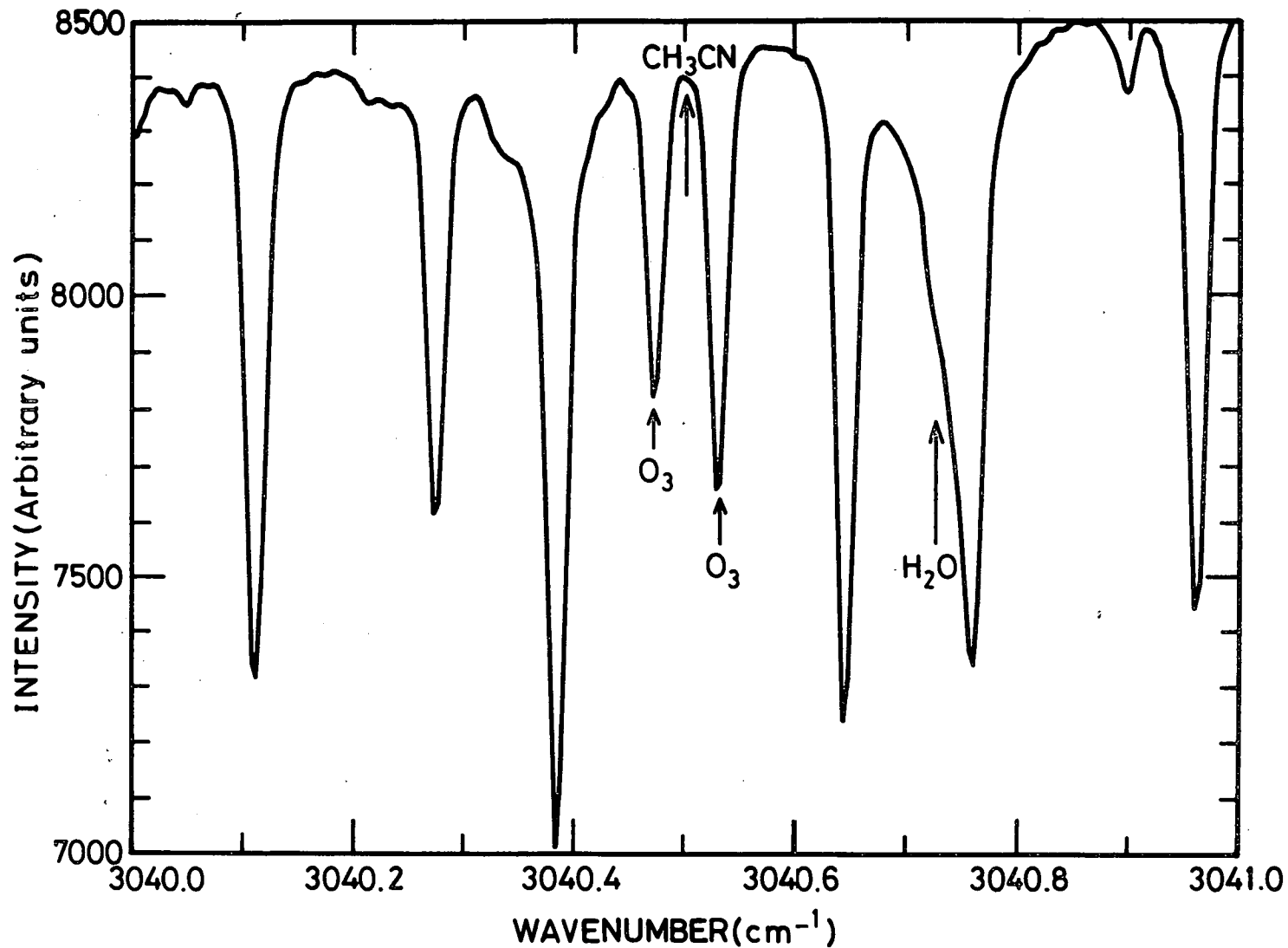


Fig. 1.- Portion of the Delbouille et al. (1981) atlas indicating the region of expected CH₃CN absorption; the width of the lines except for the shoulder marked H₂O permits to identify them as stratospheric ozone lines.

As it is very unlikely that CH_3CN has sources above ground level (Brasseur *et al.*, 1984) it will be assumed to be already mixed in the troposphere, and a line width of 0.05 cm^{-1} will be assigned in agreement with CH_4 . An absorption of 1×10^{-3} at the location indicated by the arrow on figure 1 should lead in this case to a line of 0.02 cm^{-1} half line width. This value leads to an equivalent width of $2.0 \times 10^{-5} \text{ cm}^{-1}$, an optical path of 8×10^{14} molecules of CH_3CN and a corresponding mixing ratio of 3.2×10^{-11} , and it becomes the tentative upper limit of atmospheric CH_3CN .

This value would need to be refined by quantitative ultra high resolution studies of the CH_3CN spectrum; it should be revised to a lower value if the line width should prove narrower than assumed, and to higher if the central absorption were a resolved manifold.

More important, the experimental line strength has been determined by the assumption of linear absorption, which deliberately gives a lower limit. The real value of the line strength could be an order of magnitude higher, but is only accessible to higher resolution studies. This precise determination would be the main factor in significantly lowering the present upper limit.

Attempts have been made to locate the other strong band ν_4 absorption of CH_3CN in the 920 cm^{-1} region but they failed owing to contamination of this region by important tropospheric absorptions of CF_2Cl_2 (Lippens and Muller, 1983).

As an indication of the results of other techniques, the high 7×10^{-9} CH_3CN mixing ratio value reported by Becker and Ionescu (1982) would have led to a 30% absorption on the figure 1 spectrum which would have swamped the O_3 lines. The value of 8.4×10^{-11} , reported is a maximum by Snider and Dawson, would have appeared as a $5 \times 10^{-5} \text{ cm}^{-1}$ integrated absorption and would have been comparable to the weak O_3 line at 3040.04 cm^{-1} .

In conclusion, this work, does not provide any positive identification of CH_3CN , but the October 25, 1979 spectrum leads to a tentative upper limit of 3.2×10^{-11} CH_3CN mixing ratio. As usual with large polyatomic molecules, laboratory studies are necessary to refine the CH_3CN molecular parameters for further quantitative studies.

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