SEARCH FOR EXTRATERRESTRIAL ORIGIN OF ATMOSPHERIC TRACE MOLECULES – RADIO SUB-MM OBSERVATIONS DURING THE LEONIDS

DIDIER DESPOIS, PHILIPPE RICAUD, NICOLAS LAUTIÉ
NICOLA SCHNEIDER and THIERRY JACQ
Observatoire de Bordeaux, B.P. 89, F-33270 Floirac, France
E-mail: despois@observ.u-bordeaux.fr

NICOLAS BIVER
Observatoire de Paris-Meudon, 92195 MEUDON Cedex, France
and IfA, University of Hawaii, 2680 Woodlawn Drive, Honolulu, HI 96822 USA

DARIUSZ C. LIS, RICHARD A. CHAMBERLIN
and THOMAS G. PHILLIPS
California Institute of Technology, Downs Laboratory of Physics,
MS 320-47, Pasadena, CA 91125, USA

MARTIN MILLER
I. Physikalisches Institut, Universität zu Köln,
Zülpicher Str. 77, 50937 Köln, Germany

PETER JENNISKENS
SETI Institute, NASA ARC, MS 239-4, Moffett Field, CA 94035, USA

(Received: 9 August 2000; Accepted 2 September 2000)

Abstract. To identify the effect of meteor showers on the molecular content of the upper atmosphere of the Earth, we have carried out ground-based observations of atmospheric HCN. HCN radio observations at CSO (Hawaii) on Nov 18/19, 1999, the night after the second Leonid shower maximum, show unusually low HCN abundances above 45 km altitude, which are only recovered after sunrise. We also investigated UARS/HALOE satellite data on H_2O and O_3. No correlation appears of year round H_2O and O_3 around 55 km with annual meteor showers, nor with meteor activity at the time of the 1998 Leonid shower.

Keywords: Early Earth, H_2O, HCN, Leonids 1999, lower thermosphere, O_3, mesosphere, meteors, micro-wave, radio

1. Introduction

Earth and planets are not isolated from interplanetary space. Interplanetary Dust Particles (IDPs) enter continuously into the Earth's atmosphere as sporadic meteors or meteor showers up to a total estimated amount of 20–40,000 tons/year (Love and Brownlee, 1993;

Maurette, 1998). These particles were identified as being responsible for the atmospheric neutral atom metal layers (Na, Fe, ...) observed around 90 km altitude (e.g. Höffner *et al.*, 1999; Chu *et al.*, 2000). Recent work has shown that water ice IDPs of cometary origin may explain the presence of H_2O in the upper atmosphere of the giant planets Saturn, Uranus, Neptune (Feuchtgruber *et al.*, 1997). Water ice may survive in the meteoroids while at Saturn's heliocentric distance, but evaporates rapidly at 1 A.U. from the Sun. However, these meteoroids also contain less volatile hydrogen containing organic matter. When hydrogen is released, it can recombine with atmospheric oxygen atoms and ozone, and may thus provide an alternative source for the high altitude atmospheric water ice of noctilucent clouds. The organic matter in meteoroids can also release other compounds, such as HCN or CN radicals when decomposed during ablation.

Looking back in time 4 Gyr ago, at the time of the origin of life, IDPs are believed to be a major source of carbon on the surface of the early Earth, when their input rate was supposed to be a hundred times higher than today (Chyba and Sagan, 1996). It is unclear how much organic carbon may have been delivered through ablation in the atmosphere. The details of the interactions between the entering particles and the atmosphere are still poorly understood, despite years of modelling attempts. In particular, it is not known to what extent molecules, not only atoms and ions, can be injected or produced by meteors in the atmosphere, a key issue in determining the prebiotic chemistry of the early Earth (Jenniskens *et al.*, 2000a).

In order to study qualitatively and quantitatively the impact of meteors on the molecular content of the Earth's upper atmosphere, we started searching for time variations in molecular lines during intense meteor showers, using both existing satellite observations and new ground-based radio sub-mm observations. This provides the most straight forward way to link the presence of a given molecule to the extraterrestrial input. More difficult alternatives are the study of isotopic ratios variations (e.g. D/H), or the precise analysis of the vertical abundance profiles at high altitude.

We present here two such studies: 1) ground-based observations of HCN with special emphasis on the Leonid showers of November 1998 and 1999; and 2) an effort to see meteor related variations in the 1991-1999 O_3 and H_2O contents of the upper atmosphere as retrieved from the Halogen Occultation Experiment (HALOE) on board the Upper Atmosphere Research Satellite (UARS).

2. Search for HCN variations

2.1. Introduction

HCN is a minor constituent of the Earth atmosphere, with a typical volume mixing ratio around 10^{-10} HCN per air molecule. At present, the main source of HCN in the lower atmosphere is expected to be biomass burning (Crutzen and Andreae, 1990). The atmospheric HCN has been observed since 1981, first in the infrared, then at microwave radio frequencies (Coffey *et al.*, 1981; Carli *et al.*, 1982). Figure 1 gathers most of the available measurements of HCN in the atmosphere. These measurements come from a variety of techniques listed in the figure caption.

Globally, above 30 km, HCN measurements are in excess of model predictions based on standard photochemistry and biomass burning as the only HCN source (solid lines in Figure 1). This excess has been explained by 1) ion-catalyzed reactions in the entire stratosphere, involving CH_3CN as a precursor (Schneider et al., 1997) and/or 2) a high altitude source as a result of chemical production from the methyl radical CH_3 (Kopp, 1990), or from injection or production by meteors (Despois *et al.*, 1999). HCN is a minor constituent of cometary ices. HCN polymers or copolymers have been suggested as constituents of cometary refractory organic matter (Matthews, 1997, and refs. therein), and would thus be present in the incoming meteoroids, if these polymers survived their stay in interplanetary space after ejection. HCN may also be created from the CN radical decomposition product of organic carbon, after reaction with hydrogen-bearing molecules.

To test the hypothesis of HCN input by meteoroids or the formation in the upper atmosphere from meteoric ablation products, we decided to monitor the HCN submillimeter lines around a major shower: the Leonids.

2.2. Observations

In 1998, observations of the HCN radio lines were attempted at various radiotelescopes: IRAM 30m (Spain), Bordeaux 2.5m, Caltech Submillimeter Observatory CSO 10m and the JCMT 15m (Hawaii). Unfortunately, instrument problems (IRAM, Bordeaux) and bad weather (Hawaii) prevented obtaining a usefull sensitive limit.

In 1999, time was granted on two telescopes: the CSO 10m and KOSMA 2.5m (Switzerland) telescopes. Weather did not allow any useful observations at KOSMA. Observations at the Caltech Submillimeter Observatory took place from Nov. 16 to Nov 25, 1999, with unfortunately bad observing conditions at the time of the peak on November

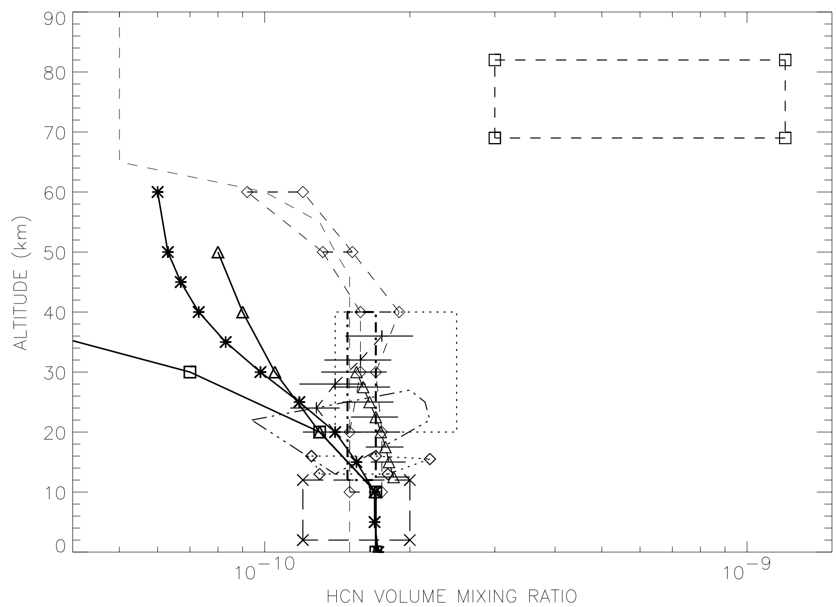

Figure 1. HCN in the atmosphere: models (thick black lines) and observations (others). Observations cover southern mid-latitudes (triangle; Zander *et al.*, 1988) to northern high latitudes (-...-; Spreng and Arnold, 1994), using mass spectrometry (- - - with square; Kopp, 1990), infra-red (+-+; Abbas *et al.*, 1987), and millimeter-wave techniques (- - - with diamond; Jaramillo *et al.*, 1988), with ground-,aircraft-based, balloon-,rocket-, and space-borne sensors. Photochemical models (thick black lines) are from Brasseur *et al.* (1985, with triangle for a photodissociation rate J_{HCN}=0, and with square for J_{HCN}=J_{HCL}) and Cicerone and Zellner (1983, with asterisk). A deficit in modeled HCN appears in the middle atmosphere, although tropospheric amounts agree reasonably well. Note the discrepancy between the photochemical models and the Kopp data around 75 km (dashed rectangle in the upper right corner of the plot). The other data are from Coffey *et al.* (-.-; 1981), Carli *et al.* (...; 1982), Rinsland *et al.* (x-x; 1982), and Schneider *et al.* (... with diamond; 1997). The dashed line without symbol represents the *a priori* HCN profile used in radiative transfer calculations.

18. Here, we report on the observations of the J = 3–2 rotational line of HCN at 265.88 GHz, which was observed in frequency switch mode on Nov. 19, from 15 UT until 21 UT.

In addition, atmospheric HCN observations in Hawaii were obtained serendipitously at JCMT from cometary observations at other periods of the year and can be used for reference. The frequency of the HCN lines observed are: HCN(4–3) = 354.51 GHz at JCMT, and HCN(3–2) = 265.88 GHz at CSO.

2.3. RESULTS

A typical example for a non-Leonid night observation at JCMT is shown in Figure 2. The HCN line is well separated from other emission lines. The other line we see on the spectrum is a CO line that comes from the image band (JCMT measurements are double-side band) and, due to that and to the reduction process of frequency-switched spectra, the line appears as a negative signal.

The CO line is narrower than the HCN line because CO (created in Earth's upper atmosphere from the UV photon dissociation of CO_2) is more abundant in the mesosphere than in the stratosphere, whereas HCN is more abundant at stratospheric altitudes (Figure 1). At lower altitudes, the spectral lines are pressure broadened, increasingly so for lower altitudes. Hence, the HCN line is more pressure-broadened than the CO line, except for the small feature on top of the profile that is from high altitude (> 60 km) HCN. The measurement technique (frequency-switch) removes most of the broad low-altitude wings of the HCN line, so that by choosing the right frequency switch, we end up with a line profile that gives information only above mid-stratosphere (above 35 km).

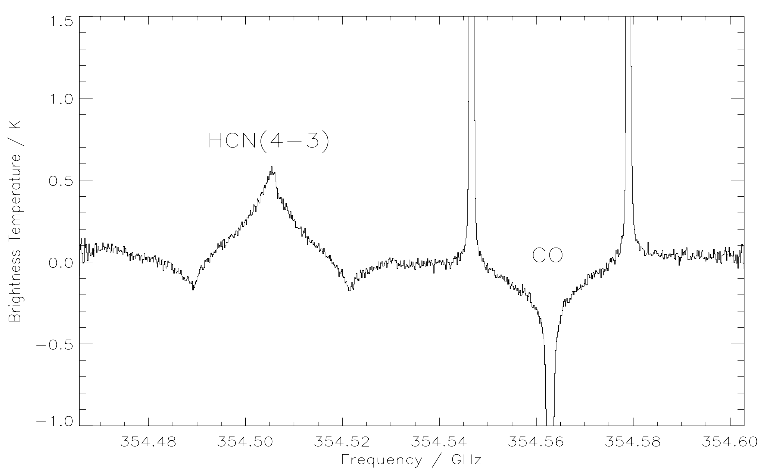

Figure 2. The HCN(4–3) line at 354.51 GHz (left part of the spectrum) observed at JCMT on a day without strong meteor shower activity (25th March, 1998). The frequency switch throw was 16.2 MHz and the integration time 1.5 h. The CO line on the right side of the spectrum comes from the image band of the radiometer and is therefore negative. The mesospheric CO line illustrates the expected width for high (> 70 km) altitude molecules.

The CSO measurements on November 19, 1999, were averaged over 1 hour intervals (2 hours for last scan), and shown in Figure 3. Sunrise in Hilo was at 16:31 UT that day.

We were expecting a small increase in the HCN content at high altitude from the direct release of molecules from ablated meteoroids. Instead, we saw a quite different behavior: in the night after the Leonid shower, the HCN concentration was much less than on other days, only recovering to previous line strength after sunrise (Figure 3). Such a night-to-day variation was not observed on the previous days leading up to the peak of the Leonid shower. Unfortunately, observing conditions prevented the acquisition of good data on the night of the peak itself.

2.4. Comparison with modeled spectra

The line profiles are directly related to the height dependence of the volume mixing ratio (abundance), because the atmospheric pressure broadening quickly decreases with altitude. Above 70 km altitude, Doppler broadening is the dominant broadening mechanism, and thus the line no longer contains specific information about the vertical abundance profile at high altitudes.

We applied the forward model part of the software called Microwave Odin Line Estimation REtrieval (MOLIERE) to simulate the measurements that were made at CSO and JCMT. MOLIERE was developed in the framework of the Swedish Space Corporation (SSC) Odin satellite mission to analyse the microwave measurements of the Sub-Millimeter Radiometer (SMR) onboard Odin (Baron, 1999; Baron *et al.*, 2000). The forward model provides the atmospheric emission measured by radiometers, after taking into account the radiative transfer along the line of sight in a non-scattering atmosphere, the refraction of the signal through the atmosphere, and the satellite and radiometers characteristics. Temperature, pressure and molecular species concentration profiles are given by models or satellite data. Spectroscopic parameters are taken from the Jet Propulson Laboratory, Geisa, and HITRAN catalogues; hyperfine HCN line intensities and frequencies at 265.88 GHz are from Biver (1997). This code has been adapted for ground-based measurements and to the frequency-switch observing technique. It also contains an inversion procedure based on the Optimal Estimation Method (Rodgers, 1976), which was used in the next step of analysis to retrieve the vertical abundance profile of HCN from the spectra.

Figure 4 shows the HCN volume mixing ratio profile and the resulting line shape. The chosen HCN volume mixing ratio vertical profile uses the *a priori* MOLIERE profile from Figure 1. The result is char-

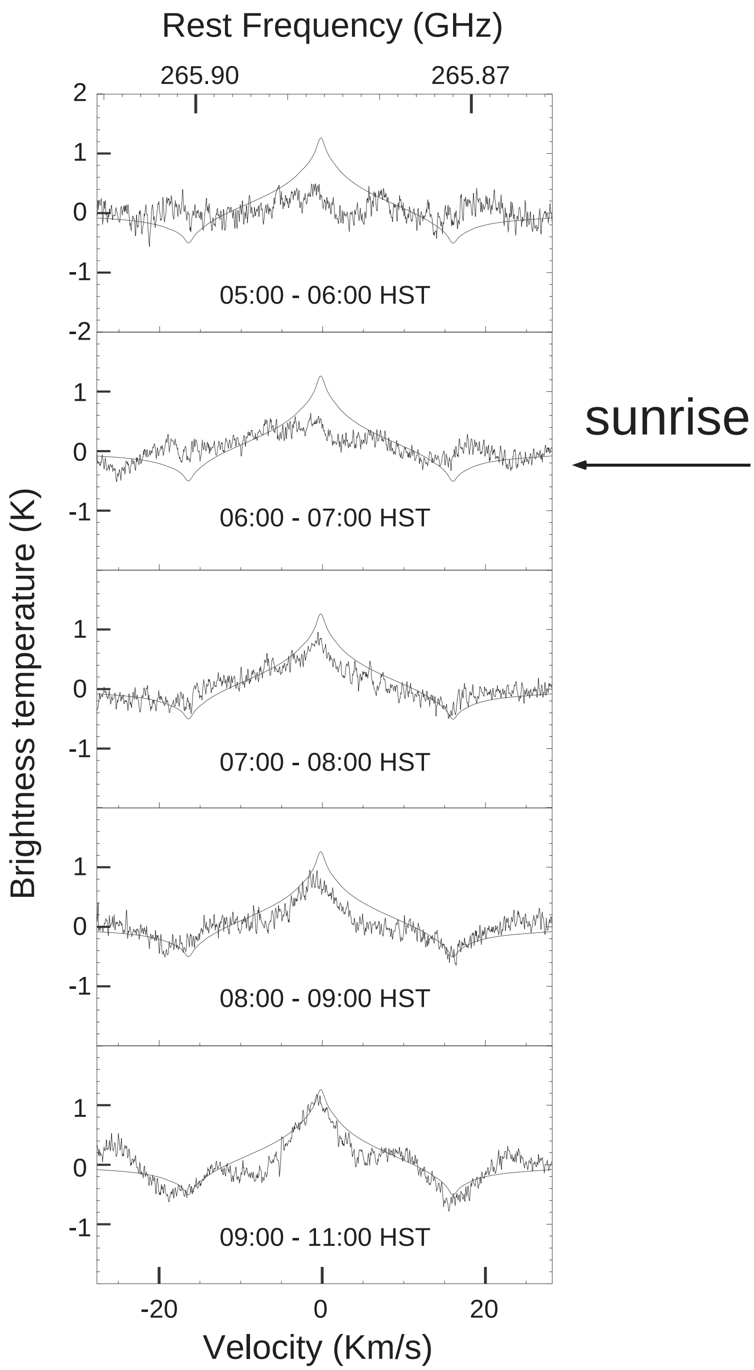

Figure 3. Diurnal variation of HCN on Nov. 19, 1999 measured with the Caltech Submillimeter Observatory (CSO) . The J=3–2 rotational line of HCN at 265.88 GHz has been observed in frequency switch from 15 to 21 UT (05 to 11 HST Hawaiian Standard Time). Sunrise was at about 16:30 UT. The solid line shows a model spectrum of the HCN line computed with the MOLIERE code.

acteristic of our CSO observations on Nov. 19 during day time (Figure 3). It is also characteristic of HCN profiles measured at JCMT at other times in the year (Figure 2).

Figure 5 shows a modeled spectrum calculated for a volume mixing ratio that falls off rapidly above 45 km. This model spectrum reproduced the observed intensity. We conclude that during the night of Nov. 19, the mid altitude HCN concentration was significantly diminished.

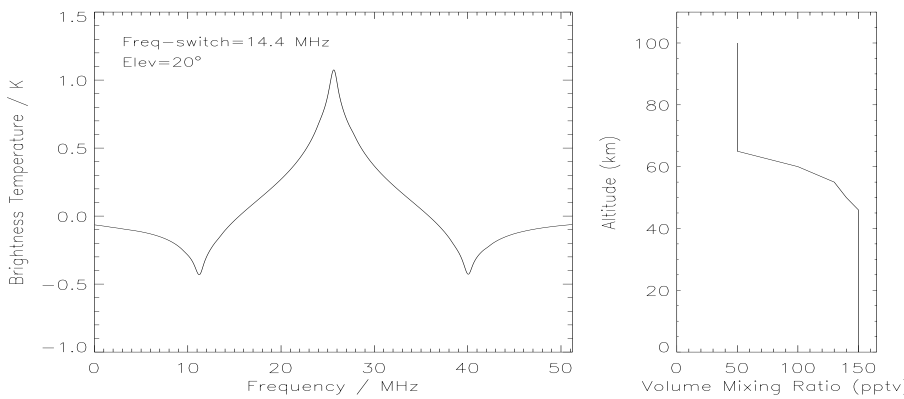

Figure 4. Simulation with MOLIERE of a CSO spectrum and the associated reference HCN volume mixing ratio profile (1pptv = 10^{-12}) used for the computation (here the same profile than the "MOLIERE: A priori" HCN profile plotted in Figure 1).

3. Discussion.

The present observations show no evidence for a direct input of HCN at mid and high altitudes, but it is possible that the meteoric ablation products affected the atmospheric chemistry in the mesosphere and lower thermosphere. Our HCN measurements were done at solar longitude 236.85-90 (J2000), in the night after the secondary maximum in the Leonid activity profile, which peaked over Hawaii at solar longitude 235.9 (Jenniskens *et al.*, 2000b). Any ablation products would have had time to disperse horizontally. However, it is not easy to understand how meteors can affect HCN concentration at such altitudes. HCN may have been chemically attacked by a reactive species such as ozone, atomic oxygen or electrons, known to be produced by the trails of the more massive meteoroids, which are ablated at these altitudes, or produced by lighter ones and transported from higher altitude. Alternatively, a coincidence with a purely atmospheric phenomenon is also

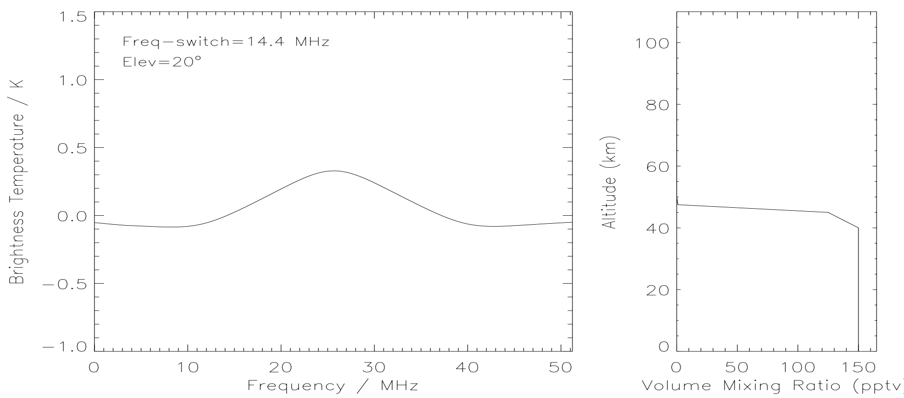

Figure 5. Simulation with MOLIERE of a CSO spectrum using a "truncated" HCN volume mixing ratio profile shown on the right of the picture. With this profile, which indicates no HCN above 45 km, we obtain a spectrum close (in intensity) to the one measured on Nov. 19, 1999 from 05:00 to 06:00 at CSO (see Figure 3).

not excluded, as nothing is known yet about the short-term behavior of this molecule due to gravity waves and tides. In order to establish the link with meteor shower activity, future observations will need to be combined with a characterization of the background airglow.

3.1. H_2O AND O_3 AT 55 KM

To investigate the possibility of ozone concentration variations, we investigated satellite data on this trace gas to search for any correlation with meteor activity. We also looked for H_2O as an indicator of hydrogen release.

Systematic measurements of O_3 and H_2O in the mesosphere have been performed with the HALogen Occultation Experiment (HALOE instrument) onboard the Upper Atmosphere Research Satellite (UARS, launched in September 1991). The HALOE instrument measures the absorption of solar radiation at sunrise and sunset by a variety of trace gases (Russell *et al.*, 1993), sweeping from 80° South to 80° North in latitude approximately every month.

The data covers the years 1991 to 1999, with an altitude coverage up to 80 km. We created averages over various latitude bands and present in Figure 6 the results for the latitude band going from 30° South to 30° North across the equator, for an altitude characterized by a pressure of 0.46 hPa, which corresponds to 55 km according to the standard atmosphere. This altitude is reached by bright and slow meteors, hence a direct influence could be expected from annual shower activity. It is also possible that the ozone and water may be affected by meteoric input at higher altitudes. Ozone and water vapor data at higher altitudes (between 60 and 80 km, by approximately 3 km step) have also been observed by HALOE, which is more relevant for this study, but the signal to noise ratio in the data is much less.

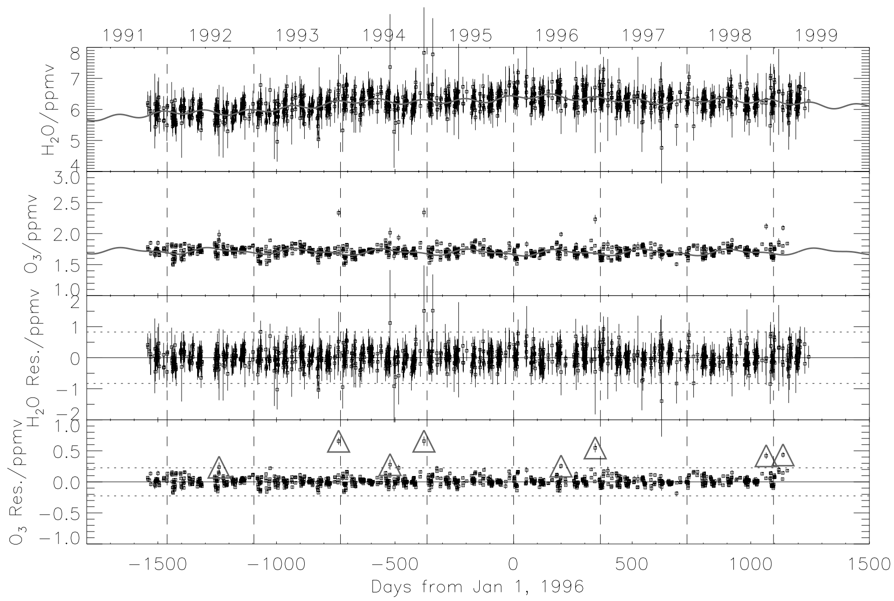

Figure 6. O_3 and H_2O atmospheric abundances (volume mixing ratio in ppmv; 1ppmv $= 10^{-6}$) at 55 km (1991-1999) from UARS/HALOE satellite measurements between 30° South and 30° North. Upper two curves show the rough data for H_2O and O_3 respectively, with the regression model (sinusoidal curve) superimposed. The lower two curves display the residuals (measurements minus model) after having removed the expected long term variations. Dotted lines indicate the 3σ level. Data points above this level are shown by triangles.

In the analysis of the data, we took into account semi-annual, annual, quasi-biennal, solar cycle oscillations (amplitudes and phases), and linear trend over the 9-year period. Using a linear regression model, we removed these oscillations in order to search for a correlation of any residual variation with a meteor shower.

At some periods, the O_3 abundance is more than 3σ above the regression model values (triangles in Fig. 6). However, no correlation has been found at present with annual meteor showers.

3.2. Future work

With an eye on the 2001 and 2002 encounters, we note that radio sub-millimeter observations are very suitable for airborne application in a future Leonid Multi-Instrument Aircraft Campaign, in combination with existing airglow measurements. A good control of sensitivity and baseline irregularities can improve the quality of the observations. Other atmospheric minor constituents can be observed in a similar manner: for example, H_2CO and CH_3CN. In addition, satellite data are expected from the Microwave Limb Sounder instrument (MLS) onboard the UARS satellite (measurements of CH_3CN) and from the soon to be launched (December 2000) Odin Astronomy/Aeronomy satellite.

Acknowledgements

We thank referees Steve Charnley and Frans Rietmeijer for helpfull comments. This work was supported by grants from CNRS/INSU (G.D.R Exobiologie and Action Spécifique "Grands Télescopes Etrangers") and CNES, which also provided financial support to Nicolas Lautié. Didier Despois and Philippe Ricaud thank the CSO for providing excellent working conditions, very valuable technical help, and free accomodation at the telescope. CSO is supported by the National Science Foundation grant AST-9980846. *Editorial handling:* M. Fonda.

References

Abbas, M. M., Guo, J., Carli, B., Mencaraglia, F., Carlotti, M., and Nolt, I. G.: 1987, *Geophys. Res. Lett.* **14**, 531–534.

Baron, Ph.: 1999, *Développement et validation du code MOLIERE: Chaîne de traitement des mesures micro-ondes du Satellite Odin*, PhD thesis, Université de Bordeaux, France.

Baron, Ph., Ricaud, Ph., de La Noë, J., Eriksson, J. E. P., Merino, F., Ridal, M., and Murtagh, D.: 2000, *Can. Journ. of Phys.*, in press.

Biver, N.: 1997, *Molécules mères cometaires: observation et modelisation*, Ph.D. Thesis, Université de Paris VII, France.

Brasseur, G., Zellner, R., de Rudder, A., and Arijs, E.: 1985, *Geophys. Res. Lett.* **12**, 117–120.

Carli, B., Mencaraglia, F., and Bonetti, A.: 1982, *Int. J. Infrared Millimeter Waves* **3**, 385–394.

Chu, X., Pan, W., Papen, G., Gardner, C.S., Swenson, G., and Jenniskens, P.: 2000, *Geophys. Res. Lett* **27**, 1807–1810.

Chyba, C. F., and Sagan, C.: 1996, in P. J. Thomas, C. F. Chyba, C. P. McKay (eds.), *Comets and the Origin and Evolution of Life*, Springer Verlag, p. 147–174.

Cicerone, R. J., and Zellner, R.: 1983, *J. Geophys. Res.* **88**, 10689–10696.

Coffey, M. T., Mankin, W. G., and Cicerone, R. J.: 1981, *Science* **214**, 333–335.

Crutzen, P.J. and Andreae, M.O.: 1990, *Science* **250**, 1669–1678.

Despois, D., Biver, N., Ricaud, Ph., Dobrijevic, M., Baron, Ph., Kieken, J., Selsis, F., Jacq, T., Billebaud, F., Lis, D., Crovisier, J., Paubert, G., Schneider, N., and Matthews,H.: 1999, Poster Abstract at *Asteroids, Comets and Meteors 1999*, Ithaca, USA, July 1999.

Feuchtgruber, H., Lellouch, E., de Graauw, T., Bézard, B., Encrenaz, T., and Griffin, M.: 1997, *Nature* **389**, 159–162.

Höffner, J., von Zahn, U., McNeil, W. J., and Murad, E.: 1999, *J. Geophys. Res.* **104**, 2633–2643.

Jaramillo, M., de Zafra, R. L., Barrett, J. W., Parrish, A., and Solomon, P. M.: 1988, *Geophys. Res. Lett.* **3**, 265–268.

Jenniskens, P., Packan, D., Laux, C., Wilson, M., Boyd, I.D., Popova, O., Krueger, C.H., and Fonda, M.: 2000a, *Earth, Moon and Planets*, **82**–**83**, 57–70.

Jenniskens, P., Crawford, C., Butow, S.J., Nugent, D., Koop, M., Holman, D., Houston, D., Jobse, K., Kronk, G., and Beatty, K.: 2000b, *Earth, Moon and Planets* **82**–**83**, 191–208.

Kopp, E.: 1990, *J. Geophys. Res.* **95**, 5613–5630.

Love, S.G. and Brownlee, D.E.: 1993, *Science* **262**, 550–553.

Matthews, C. N., Pesce-Rodriguez, R. A., and Liebman, S. A.: 1997, in C. B. Cosmovici, S. Bowyer, and D.Werthimer (eds.), *Astronomical and Biochemical Origins and the Search for Life in the Universe*, IAU Coll. 161, Editrice Compositori, p. 179–187.

Maurette,M.: 1998, in André Brack (ed.), *The Molecular Origins of Life: assembling pieces of the puzzle*, Cambridge Univ. Press, p. 147–186.

Rinsland, C. P., Smith, M. A. H., Rinsland, P. L., Goldman, A., Brault, J. W., and Stokes, G. M.: 1982, *J. Geophys. Res.* **87**, 11119–11125.

Rodgers, C. D.: 1976, *Rev. Geophys. Space Phys.* **14**, 609–624.

Russell, J. M., III, Gordley, L. L., Park, J. H., Drayson,S. R., Hesketh, W. D., Cicerone, R. J., Tuck, A. F., Frederick, J. E., Harries, J. E., and Crutzen, P. J.: 1993, *J. Geophys. Res.* **98**, 10777–10797.

Schneider, J., Bürger, V., and Arnold, F.: 1997, *J. Geophys. Res.* **102**, 25501–25506.

Spreng, S. and Arnold, F.: 1994, *Geophys. Res. Lett.* **21**, 1251–1254.

Zander, R., Rinsland, C. P., Farmer, C. B., Namkung, J., Norton, R. H., and Russell, J. M.: 1988, *J. Geophys. Res.* **93**,1669–1678.