

Stratospheric CH₃CN from the UARS Microwave Limb Sounder

Nathaniel J. Livesey¹, Joe W. Waters¹, Rashid Khosravi², Guy P. Brasseur³,
Geoffrey S. Tyndall² and William G. Read¹

Abstract. CH₃CN in the stratosphere has been measured by the Microwave Limb Sounder (MLS) on the Upper Atmosphere Research Satellite (UARS), providing the first global CH₃CN dataset. The MLS observations are in broad agreement with past high and midlatitude observations of CH₃CN, although concentrations are a little larger than previously observed. In the tropics, where CH₃CN has not up to now been measured, a persistent 'peak' in the profiles is seen around 22 hPa, which may be evidence of a tropical stratospheric CH₃CN source. Comparisons are made with the NCAR SOCRATES model, including runs having an artificial tropical stratospheric CH₃CN source.

1. Introduction

Methyl cyanide (CH₃CN, also known as acetonitrile) is a comparatively long-lived trace constituent of the Earth's atmosphere. The principal source is biomass burning [Arijs and Brasseur, 1986; Hamm and Warneck, 1990], which contributes an estimated 0.5–1.0 Tg/year of CH₃CN to the troposphere [Holzinger *et al.*, 1999]. CH₃CN plays an important role in the chemistry of stratospheric ions; it displaces water in ion clusters H⁺(H₂O)_n, leading to clusters H⁺(CH₃CN)_m(H₂O)_{n-m}. Detection of these clusters led to the presence of CH₃CN in the stratosphere being deduced and initially quantified [Böhlinger and Arnold [1981] and references therein]. Initial results indicated less than 10 pptv (parts per trillion by volume) of CH₃CN in the stratosphere. Early studies [Murad *et al.*, 1984] suggested that HCN might be a source of stratospheric CH₃CN, but modeling studies [Brasseur *et al.*, 1985] indicated that this is unlikely.

Early observations of tropospheric CH₃CN were somewhat contradictory. Initial gas chromatography measurements indicated a surface mixing ratio of 7 000 pptv. Concentrations as high as 35 000 pptv were observed following

a fire in a rural area [Becker and Ionescu, 1982]. More recent chromatography measurements at the surface [Snider and Dawson, 1984] indicate much lower abundances (56 pptv on average), with observations [Hamm and Warneck, 1990] ranging from ~50 pptv in the middle of the Atlantic to an average of ~150 pptv in urban areas. Biomass burning can produce 10⁶ pptv CH₃CN [Holzinger *et al.*, 1999].

The main chemical loss mechanism for CH₃CN is thought to be reaction with OH [Arijs and Brasseur, 1986]. The CH₃CN lifetime from this reaction varies from 1 year at the surface to 20 years at 20 km, decreasing to 1 month at 40 km. Reactions with O(¹D), O(³P) and Cl are thought to be less important, although O(³P) is significant in the mesosphere. Measurements of Schneider *et al.* [1997] show a decrease in CH₃CN in the lowest 4 km of the stratosphere, indicating a lifetime of ~1 year; the authors suggest ion-catalyzed destruction as a possible mechanism. The primary sink for tropospheric CH₃CN is thought to be uptake in liquid water (by rain and oceans). A lifetime as short as 15 days due to ocean uptake is possible [Hamm *et al.*, 1984].

2. MLS Measurements of CH₃CN

MLS is one of ten instruments on UARS, launched in September 1991 [Waters *et al.*, 1999]. MLS observes thermal microwave limb emission. The observations of interest are from bands 2 and 3, where previously identified spectral contributors are ClO, SO₂ and HNO₃. Figure 1 shows spectra for a time and region where the ClO, HNO₃ and SO₂ signals are very weak. These are dominated by a feature near 0.9 GHz intermediate frequency that can be explained by emission from rotational lines of CH₃CN near 202.3 GHz. The lines are relatively strong on a per molecule basis due to the large (3.9 D) CH₃CN dipole moment.

CH₃CN abundance is retrieved in the MLS version 5 processing on pressure surfaces from 100 to 0.14 hPa at six surfaces per decade change in pressure. CH₃CN data at 100 hPa are unreliable, as its spectral signature is somewhat contaminated by H₂¹⁸O, and are also not reliable above 1 hPa. The typical precision on a single profile is 40–60 pptv from 68–6.8 hPa. Averaging is needed to produce results useful for scientific studies. For example, the precision of a monthly zonal mean 10° latitude bin is ~1 pptv at 10 hPa. The absolute accuracy of the CH₃CN data is estimated at 10 pptv+20%. This is based on a 10% uncertainty in the CH₃CN pressure-broadened line width, and analysis similar to that for MLS ClO observations [Waters *et al.*, 1996]. Averaging kernels indicate a vertical resolution of ~4 km from 68–10 hPa, broadening to 8 km at 1 hPa.

¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

²Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado.

³Max Planck Institute for Meteorology, Hamburg, Germany.

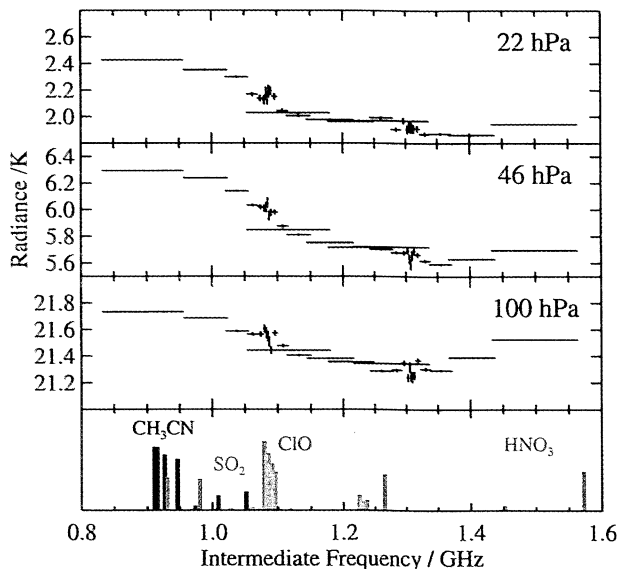


Figure 1. Spectra from MLS bands 2 and 3: zonal mean radiance 10°S–10°N on 8 June 1994. For this region and time the spectra are dominated by CH₃CN emission. Radiances are in units of brightness temperature and averaged over 1/6 of a decade in pressure (~2.5 km). Intermediate frequency is the difference (both positive and negative) from the 203.267 GHz local oscillator frequency. Emission from H₂¹⁸O can explain the increase in 100 hPa radiance near 1.5 GHz. The bottom panel shows positions of spectral lines.

3. Results

Figure 2 compares MLS CH₃CN results with previous observations. The high latitude MLS data are in reasonable agreement with previous observations in the lower stratosphere, but show higher abundances in the upper stratosphere. MLS shows CH₃CN to be more abundant in the tropical stratosphere than at higher latitudes. The tropical profiles show a persistent ‘peak’ in CH₃CN at ~30–10 hPa (~25–30 km) that is possible evidence for a tropical stratospheric source of CH₃CN.

Output from the NCAR 2-D model SOCRATES (Simulation of Chemistry, Radiation, and Transport of Environmentally important Species), has been compared with the MLS data. The updated version of the *Brasseur et al.* [1990] model was used, extending from pole to pole and the surface to 120 km altitude. The horizontal and vertical resolutions are 5° and 1 km, respectively. The model includes 55 species and 144 gas phase, 5 heterogeneous, and 47 photolysis reactions, with all the CH₃CN loss reactions mentioned earlier. The reaction rate coefficients and absorption cross sections are from the JPL 1997 compilation [DeMore et al., 1997]. Surface boundary conditions are specified as mixing ratios which, based on prior observations, decrease from 100 pptv at the equator to 20 pptv at the poles for CH₃CN. The dynamical equations are expressed in the transformed Eulerian mean framework. Zonal mean momentum forcing is provided by dissipation of wavenumber 1 and 2 planetary waves, by gravity waves and tides, and in the troposphere by mesoscale systems (climatology). A simple pa-

rameterization of convection in the tropics and in frontal systems [Langner et al., 1990] accounts for vertical transport in the troposphere. A semi-Lagrangian scheme [Smolarkiewicz and Rasch, 1991] describes large scale advective transport.

Figure 2 includes model CH₃CN results for the latitudes and months of the MLS profiles shown. These agree with MLS near 25 and 40 km at the equator, but do not reproduce the observed peak. An artificial stratospheric CH₃CN source was added in a separate model run to determine the source strength needed to reproduce the MLS observations. Production of ~0.9–1.7 CH₃CN molecules cm⁻³ s⁻¹ between 25 and 32 km, and ±5° latitude, with boundary conditions unchanged, yields a closer match to the MLS equatorial observations between 25 and 40 km. Both model datasets show more equatorial CH₃CN than MLS below ~25 km, due to the tropospheric boundary conditions assumed. Above 40 km at the equator, MLS data show greater CH₃CN abundances than either model run.

At 70°N the MLS and model profiles are very different. Both sets of model data show a much faster vertical decrease in mid to upper stratosphere CH₃CN abundances than the MLS data. In both January and July, MLS shows less CH₃CN than either model run below ~35 km, with higher abundances than the model data above that altitude.

Validity of the MLS detection of a tropical stratospheric peak depends on the accuracy of the smaller mixing ratios seen below the peak. A detailed study has shown that the possible biases in MLS CH₃CN in this region (mainly due

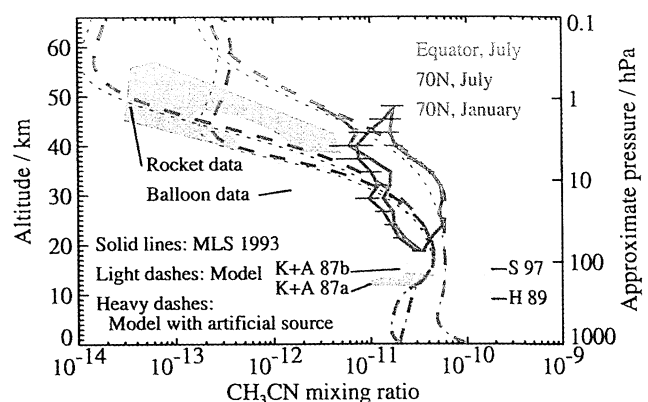


Figure 2. Comparison of MLS CH₃CN observations with previous observations and output from the SOCRATES model. The MLS profiles shown have been generated from the raw MLS data using a Kalman smoother (see the discussion in Figure 4 caption). Error bars (omitted on the 70°N July profile for clarity) indicate the precision of the smoothed estimate (note that for the tropical profile, below ~30 km, the precision is comparable to the width of the red line). Narrow dashed lines denote output from the standard model run. Heavy dashed lines show the run with an artificial tropical source of stratospheric CH₃CN. Previous observations are reproduced from *Schneider et al.* [1997] (=S 97). Other references are: *Hamm et al.* [1989] (=H 89), and *Knop and Arnold* [1987a/b] (=K+A 87a/b). Balloon observations were made in central Europe in the late 1970s and early 1980s. Rocket observations were made at 69°N in May/June 1975 and February 1976 [Arnold et al., 1977].

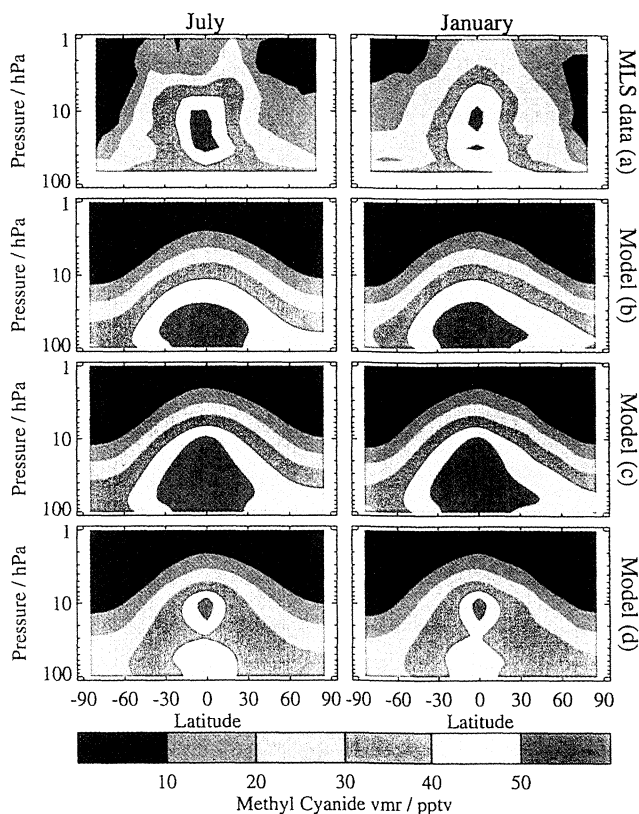


Figure 3. MLS CH₃CN zonal mean (a) compared with model results. Model data shown are (b) first model run, (c) run with artificial stratospheric CH₃CN source, (d) run with decreased CH₃CN surface abundance and increased artificial source. Model fields are for 1 July year 5 and 1 January year 6 of the runs. The corresponding MLS fields are means of June and July 1993, and December 1992 and January 1993, chosen as they have good data coverage.

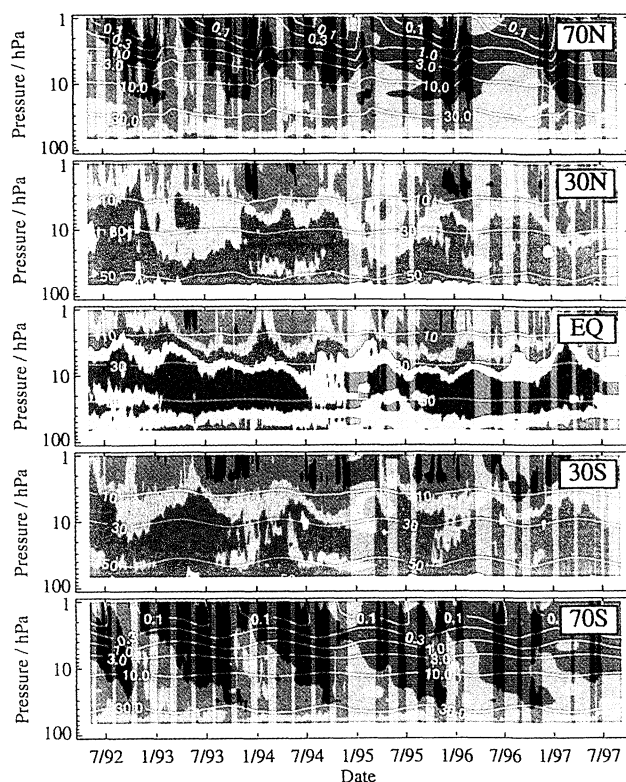
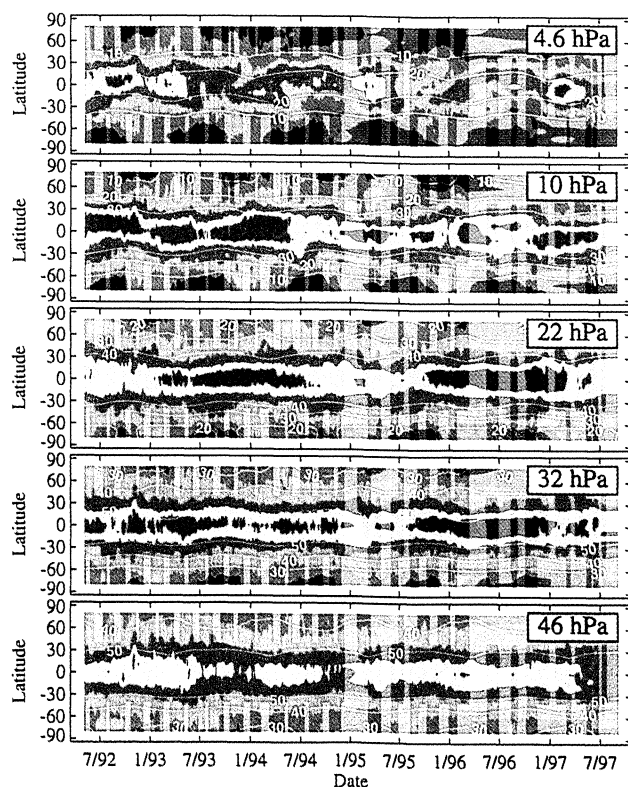


Figure 5. Height/time cross sections of MLS zonal mean CH₃CN, with overlaid white model contours as in Figure 4. Color levels are as in Figure 3. Model contours are logarithmic in the 70°N and 70°S panels and linear elsewhere.

to uncertainty in N₂O concentration) are much lower than the ~20 pptv that would be needed to falsely give a peak.

Figure 3 compares zonal mean CH₃CN for Dec/Jan and Jun/Jul from MLS and the two model runs discussed. Both MLS and the model show more stratospheric CH₃CN in the tropics than at higher latitudes, as expected for a tropospheric source gas entering the stratosphere through the tropical tropopause. The tropical stratospheric peak is clearly seen in MLS data for both periods. The artificial source in the second model run does not produce a peak in the tropics as there is more CH₃CN in the model below ~25 km (~25 hPa) than in the MLS data; the source has little effect on model results outside the tropics. To further investigate what might be required to fit the MLS observations a third model run was performed. In this run, surface bound-

Figure 4. Latitude/time cross sections of MLS zonal mean CH₃CN for June 1992 to December 1997. The data have been binned into daily zonal means with 10° wide latitude bins centered on the multiples of 10°. This dataset has then been interpolated using a Kalman smoother with a decorrelation rate of 1 pptv/day (a smoothing comparable to a ~5 day running average). There is no interpolation or propagation of information in either the height or latitude dimensions. Paler colors denote regions where, because of data gaps, the estimated precision of the interpolated field is worse than 10 pptv. The color levels are as in Figure 3. Overlaid are white contours from the final year of output from the first model run (without the artificial CH₃CN source, see text).

ary conditions were lowered by 25% (near the lower limit of abundances previously observed). The source was increased to 1.4–5.8 CH₃CN molecules cm⁻³ s⁻¹, and confined to the equator. Results of this run are shown in Figure 3; it produces a CH₃CN peak from ~20 to ~10 hPa compared to the somewhat broader observed peak from ~32 to ~10 hPa.

MLS observes notably less CH₃CN between ~50 and ~5 hPa at high latitudes in winter than summer; this is not reproduced by the models, which show greater CH₃CN concentrations in the northern hemisphere than the southern in both January and July, especially below ~30 hPa.

Figures 4 and 5 show vertical and horizontal cross sections of MLS and model CH₃CN. MLS data prior to June 1992 have been omitted because of spectral contamination by SO₂ from the Mt. Pinatubo eruption. The temporal behavior of the tropical peak is interesting. From July to November 1994 CH₃CN abundances in the peak region are depressed, then they steadily increase, reaching a maximum around July 1996. The data show no evidence that this increase is fed from the troposphere. Somewhat similar behavior is seen from July 1992 to January 1994.

The high latitude panels in Figure 5 show annual cycles. These appear more robust in the southern hemisphere than the northern. Qualitatively similar cycles are seen in the model output. At 70°S and 2.2 hPa, for example, the MLS annual cycle range is ~4–12 pptv (~±50%) and the model range is ~0.07–0.19 pptv (also ~±50%). The height variation of the annual cycles in both MLS and model seems to indicate descent at high latitudes. It is unclear whether the difference in absolute values between MLS and the model is a manifestation of a source of CH₃CN at lower latitudes.

4. Issues for future study

The MLS observations provide evidence for a previously unknown tropical stratospheric source of CH₃CN at ~30–10 hPa (~25–30 km). Ground-based far-infrared measurements at 30°N [Abbas *et al.*, 1987] and microwave observations at 19°N [Jaramillo *et al.*, 1988] have indicated an increase in HCN with altitude between ~25 and ~40 km. HCN also has no known stratospheric source. Since there are no identified mechanisms to convert HCN to CH₃CN in the atmosphere, it is speculative to try to link the two phenomena. However, we note that the increase in HCN with altitude in the tropics could be related to that of CH₃CN. Independent observations of both species as a function of altitude in the tropics would be useful. Furthermore, a better understanding of the tropospheric distribution of CH₃CN would better constrain future models, improving their ability to evaluate possible sources in the atmosphere.

Also, a localized CH₃CN enhancement of ~1000 pptv at 100–68 hPa was seen off the southeast U.S. coast on 25 August 1992, (near the northernmost latitude MLS observed that month), which over several days moved westward and dissipated; the cause of this event is under investigation.

Acknowledgments. The authors thank M.L. Santee for useful comments. The research in this paper done at the Jet Propulsion Laboratory, California Institute of Technology, was under con-

tract with NASA. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

References

- Abbas, M., *et al.*, Stratospheric distribution of HCN from far infrared observations, *Geophys. Res. Lett.*, **14**, 531–534, 1987.
- Arijs, E., and G. Brasseur, Acetonitrile in the stratosphere and implications for positive ion composition, *J. Geophys. Res.*, **91**, 4,003–4,016, 1986.
- Arnold, F., D. Krankowsky, and K. Marien, First mass spectrometric measurements of major stratospheric positive ions, *Nature*, **267**, 30–32, 1977.
- Becker, K., and A. Ionescu, Acetonitrile in the lower troposphere, *Geophys. Res. Lett.*, **9**, 1,349–1,351, 1982.
- Böhringer, H., and F. Arnold, Acetonitrile in the stratosphere – implications from laboratory studies, *Nature*, **290**, 321–322, 1981.
- Brasseur, G., M. H. Hitchman, S. Walters, M. Dymek, E. Falis, and M. Pirre, An interactive chemical dynamical radiative two-dimensional model of the middle atmosphere, *J. Geophys. Res.*, **95**, 5,639–5,655, 1990.
- Brasseur, G., *et al.*, Is hydrogen cyanide (HCN) a progenitor of acetonitrile (CH₃CN) in the atmosphere?, *Geophys. Res. Lett.*, **12**, 117–120, 1985.
- DeMore, W., *et al.*, Chemical kinetics and photochemical data for use in stratospheric modeling, *Tech. rep.*, Jet Propulsion Laboratory, 1997.
- Hamm, S., and P. Warneck, The interhemispheric distribution and the budget of acetonitrile in the troposphere, *J. Geophys. Res.*, **95**, 20,593–20,606, 1990.
- Hamm, S., J. Hahn, G. Helas, and P. Warneck, Acetonitrile in the troposphere: Residence time due to rainout and uptake by the ocean, *Geophys. Res. Lett.*, **11**, 1,207–1,210, 1984.
- Hamm, S., G. Helas, and P. Warneck, Acetonitrile in the air over Europe, *Geophys. Res. Lett.*, **16**, 483–486, 1989.
- Holzinger, R., *et al.*, Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile and hydrogen cyanide, *Geophys. Res. Lett.*, **26**, 1,161–1,164, 1999.
- Jaramillo, M., R. deZafra, J. Barrett, A. Parrish, and P. Solomon, mm-wave observations of stratospheric HCN at tropical latitudes, *Geophys. Res. Lett.*, **15**, 265–268, 1988.
- Knop, G., and F. Arnold, Stratospheric trace gas detection using new balloon-borne ACIMS method: Acetonitrile, acetone, and nitric acid, *Geophys. Res. Lett.*, **14**, 1,262–1,265, 1987a.
- Knop, G., and F. Arnold, Atmospheric acetonitrile measurements in the tropopause region using aircraft-borne active chemical ionization mass spectrometry, *Planet. Space Sci.*, **35**, 259–266, 1987b.
- Langner, J., H. Rodhe, and M. Olofsson, Parameterization of sub-grid scale vertical tracer transport in a global two-dimensional model of the troposphere, *J. Geophys. Res.*, **95**, 13,691–13,706, 1990.
- Murad, E., W. Swider, R. Moss, and S. Toby, Stratospheric sources of CH₃CN and CH₃OH, *Geophys. Res. Lett.*, **11**, 147–150, 1984.
- Schneider, J., V. Bürger, and F. Arnold, Methyl cyanide and hydrogen cyanide measurements in the lower stratosphere: Implications for methyl cyanide sources and sinks, *J. Geophys. Res.*, **102**, 25,501–25,506, 1997.
- Smolarkiewicz, P., and P. J. Rasch, Monotone advection on the sphere: An Eulerian versus semi-Lagrangian approach, *J. Atmos. Sci.*, **48**, 1991.
- Snider, J., and G. Dawson, Surface acetonitrile near Tucson Arizona, *Geophys. Res. Lett.*, **11**, 241–242, 1984.
- Waters, J., *et al.*, Validation of UARS Microwave Limb Sounder ClO measurements, *J. Geophys. Res.*, **101**, 10,091–10,127, 1996.
- Waters, J., *et al.*, The UARS and EOS Microwave Limb Sounder (MLS) experiments, *J. Atmos. Sci.*, **56**, 194–217, 1999.

(Received July 13, 2000; revised November 10, 2000; accepted November 20, 2000.)