

EVIDENCE FOR THE PRESENCE OF THE 802.7-CM⁻¹ BAND Q BRANCH OF HO₂NO₂ IN HIGH RESOLUTION SOLAR ABSORPTION SPECTRA OF THE STRATOSPHEREC. P. Rinsland,¹ R. Zander,² C. B. Farmer,³ R. H. Norton,³
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Abstract. Stratospheric solar absorption spectra recorded at ~0.01 cm⁻¹ resolution by the ATMOS (Atmospheric Trace Molecule Spectroscopy) Fourier transform spectrometer during the Spacelab 3 Shuttle mission (4/30-5/6/85) show a weak absorption feature covering ~802.5-803.3 cm⁻¹. We identify this feature as the unresolved Q branch of the 802.7-cm⁻¹ band of HO₂NO₂ and report profiles for 31°N and 47°S.

Peroxyntic acid (HO₂NO₂) is predicted by photochemical models to be an important reservoir gas in the lower stratosphere where it is believed to be formed in a 3-body reaction of HO₂ with NO₂ and is destroyed by photolysis and by reaction with OH [cf. Sze and Ko, 1981].

Infrared laboratory spectra of HO₂NO₂ show moderately strong bands with Q branches at 802.7, 1304.2, 1396.9, 1728.3, and 3540.1 cm⁻¹ [Niki et al., 1977; Graham et al., 1977, 1978; Molina and Molina, 1981]. The Q branch at 802.7 cm⁻¹ is relatively free of strong atmospheric interferences and is the most suitable for atmospheric measurement. A 0.04-cm⁻¹ resolution laboratory spectrum of this band has also been published [Murcray et al., 1984]. Murcray and co-workers found no evidence for this Q branch in stratospheric emission spectra, and, from this work, an upper limit of 0.4 ppbv was reported [NASA, 1979]. In this Letter, we report the identification of the 802.7-cm⁻¹ Q branch in ~0.01 cm⁻¹ resolution stratospheric solar absorption spectra recorded by the ATMOS (Atmospheric Trace Molecule Spectroscopy) Fourier transform spectrometer during the Spacelab 3 Shuttle mission [Farmer and Raper, 1986].

Table 1 summarizes experimental parameters for the ATMOS spectra used in this analysis. These spectra were recorded during 1 sunrise (47°S lat., 50°W long. on 5/1/85) and 3 sunsets (33°N lat., 115°E long. on 4/30/85; 31°N lat., 0°E long. on 4/30/85; 30°N lat., 115°W long. on 5/1/85).

Four ATMOS spectra at 803 cm⁻¹ are shown in Figure 1. The top 3 spectra are plotted on the same vertical scale, but offset from one another. The top spectrum, with a signal-to-rms noise of 1900, was obtained by coadding 66 high sun spectra from a sunset occultation. It shows OH pure rotation solar lines of the v = 1, N'' = 25 quartet [Sauval et al., 1984]. The other 3 spectra (33.5, 25.5, and 19.5 km) are the result of coadding

nearly equal tangent altitude scans from 3 sunset occultations to produce zonal average low sun scans (signal-to-rms noise 400). The tick marks correspond to the measured positions and identifications given in Table 2. The positions have been calibrated using standards for the 00011-10001 band of ¹²C¹⁶O₂ [Petersen et al., 1983]. For unblended, strong (>20% depth) lines, the positions are estimated to be accurate to ~4 × 10⁻⁵ cm⁻¹; the accuracies are reduced for weak and blended lines. One digit beyond the estimated accuracy of each position has been retained. The identifications are based on comparisons between the ATMOS spectra and simulations with the line parameters discussed below and on the agreement between the measured and reference line positions. Atmospheric O₃, H₂O, and CO₂ and solar OH lines were readily identified; the identifications in most cases are the same as those reported by Goldman et al. [1985]. In addition, the bottom plot, on an expanded scale, shows a weak, broad absorption feature around 802.7 cm⁻¹ (shaded area). This feature is not reproduced in the synthetic spectrum, which was calculated without HO₂NO₂ parameters. Based on the agreement between the position and shape of this feature and the HO₂NO₂ laboratory spectrum of Murcray et al. [1984], we identify this absorption in the ATMOS spectra as the unresolved Q branch of the 802.7-cm⁻¹ band of HO₂NO₂.

An onion-peeling nonlinear least squares spectral fitting procedure was used to analyze the ATMOS spectra. Correlative pressure-temperature profiles derived from National Meteorological Center global satellite and radiosonde measurements have been assumed (R. Nagatani, private communication, 1985).

Line parameters for the analysis were taken mostly from the 1982 Air Force Geophysics Laboratory (AFGL) compilation [Rothman et al., 1983a,b]. For CO₂ these parameters were supplemented by results of a preliminary analysis by one of us (L. Brown) of laboratory spectra recorded with the McMath interferometer on Kitt Peak. For the 11101-10002 band of ¹⁶O¹²C¹⁸O, which has a weak line near the strongest part of the HO₂NO₂ Q branch, the AFGL line intensities were divided by 2.6 and the AFGL line positions were increased by 0.001 cm⁻¹. For the 11101-10002 band of ¹²C¹⁶O₂, the AFGL line intensities were divided by 1.4. For O₃, we adopted improved positions and intensities from a preliminary analysis of millimeter, submillimeter, and infrared spectra (H. Pickett, private communication, 1985). Solar OH lines have been simulated assuming a Doppler line shape.

Unfortunately, line parameters have not been reported for the 802.7-cm⁻¹ band of HO₂NO₂. Therefore, an empirical model was used to reproduce the Q-branch absorption. The values for the parameters were determined from a nonlinear least squares fit to the 802.0-804.0-cm⁻¹ region of a

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Table 1. Parameters for ATMOS Spectra Covering the HO₂NO₂ 802.7-cm⁻¹ Q Branch

Parameter	Value
Orbital altitude	~360 km
Scan time	2.2 sec
Maximum path difference	47 cm
Field of view	2 mrad
Spectral coverage	600-1200 cm ⁻¹
Spacing in tangent height of successive spectra	~4 km

digitized copy of the Murcray et al. [1984] laboratory data. Lines with a spacing of 0.004 cm⁻¹ and a linear decrease in intensity about the absorption peak were used to model the Q-branch envelope. Additional lines with the same spacing and a Gaussian distribution of intensities were used to model the narrow, prominent features near 802.57 cm⁻¹ and 802.78 cm⁻¹. For all lines, lower state energies of 300 cm⁻¹ and halfwidths of 0.1 cm⁻¹ atm⁻¹ at 296 K were assumed. The absorption cross section of 5.6×10^{-19} cm² measured for 810-814 cm⁻¹ [Graham et al., 1978; Molina and Molina, 1981] was assumed to estimate the HO₂NO₂ partial pressure, which was needed to scale the relative intensities to absolute values from the Murcray et al. [1984] measurements. The derived partial pressure, 0.121 Torr, was calculated from the assumed cross section and a measurement of the absorption depth at 812 cm⁻¹ in the compressed plot of Fig. 250A in the Murcray et al. [1984] atlas. The 100% transmission level was defined by drawing a straight line between the data near 770 cm⁻¹ and 840 cm⁻¹. The intensity sum of the 341 "lines" between 802.48 cm⁻¹ and 803.65 cm⁻¹ is 9.16×10^{-19} cm molecule⁻¹. The line list is available from the authors.

Figure 2 presents fitting results for two 31°N

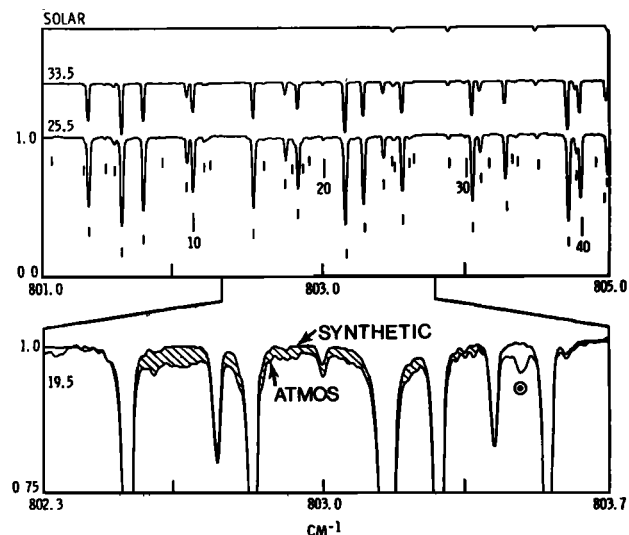


Fig. 1. ATMOS spectra in the region of the 802.7 cm⁻¹ Q branch of HO₂NO₂ at 19.5, 25.5 and 33.5 km tangent heights along with a high sun scan (see text for details). Tick marks correspond to the positions and identifications given in Table 2.

Table 2. Identification of Atmospheric and Solar Features between 801.0-805.0 cm⁻¹

Line No.	Position cm ⁻¹	Molec. ID	Line No.	Position cm ⁻¹	Molec. ID
1	801.087	?	23	803.4099	O ₃
2	801.3258	O ₃	24	803.455	C ₂ O ₂ NO ₂
3	801.35477	O ₃	25	803.4823	Solar OH
4	801.4685	O ₃	26	803.5409	O ₃ ,H ₂ O
5	801.5342	O ₃	27	803.5905	O ₃
6	801.58659	CO ₂	28	803.6133	O ₃
7	801.73971	O ₃	29	803.8670	Solar OH
8	801.8770	O ₃ ?	30	803.9795	O ₃
9	802.04465	O ₃	31	804.0312	O ₃
10	802.08698	O ₃	32	804.0857	O ₃ ,CO ₂ ?
11	802.1619	O ₃	33	804.1442	?
12	802.1853	O ₃	34	804.2601	O ₃
13	802.50732	O ₃	35	804.3120	O ₃
14	802.5767	CO ₂ ?,HO ₂ NO ₂	36	804.3366	O ₃
15	802.7297	O ₃	37	804.4823	Solar OH
16	802.7877	O ₃ ,HO ₂ NO ₂	38	804.70165	CO ₂
17	802.81552	O ₃	39	804.75723	O ₃
18	802.8425	O ₃	40	804.78760	O ₃
19	802.9012	O ₃	41	804.8848	O ₃
20	802.99054	H ₂ O	42	804.97634	O ₃
21	803.14441	CO ₂	43	804.9957	Solar OH
22	803.27129	O ₃			

The 802.5-803.3 cm⁻¹ interval contains a weak, broad absorption feature identified as the Q branch of the 802.7-cm⁻¹ band of HO₂NO₂.

zonal scans. Above both spectra, the residuals without HO₂NO₂ (denoted WO) and with HO₂NO₂ (denoted W) lines are plotted on an expanded vertical scale; the standard deviation is given in the upper right of each residual plot. The region of HO₂NO₂ Q-branch absorption has been indicated above the upper residual plot. For the 33.5-km tangent altitude spectrum, the quality of both fits is about the same. The next 2 spectra (not plotted) were recorded at tangent altitudes of 29.4 and 25.5 km, and the resulting "WO" residuals show evidence for weak, broad absorption in the HO₂NO₂ Q-branch region. This absorption is stronger and more evident in lower sun spectra. The fit for the 22.3-km tangent altitude spectrum shown in Figure 2 is much improved with the HO₂NO₂ lines included; the broad feature (~2% peak absorption) is nearly absent in the "W" residual plot, the standard deviation of this fit is reduced by ~50%, and there is an improved match between the measured and fitted 100% transmission levels. Still, minor inadequacies remain in the fitting results, indicating a need for additional improvements in the line parameters.

Figure 3 presents for the 19.5-km zonal spectrum a comparison of the residuals without HO₂NO₂ lines in the analysis (upper plot) and the transmittance of HO₂NO₂ calculated from the retrieved profile (lower plot). Despite the difference in the temperature of the Murcray et al. [1984] laboratory spectrum (-5°C) and that of the lower stratosphere (typically -40°C) and imperfections in fitting the interfering lines in the ATMOS data, there is fairly good agreement in both the position and shape of the broad feature in the residual plot and the calculated HO₂NO₂ absorption, especially near the low wavenumber edge of

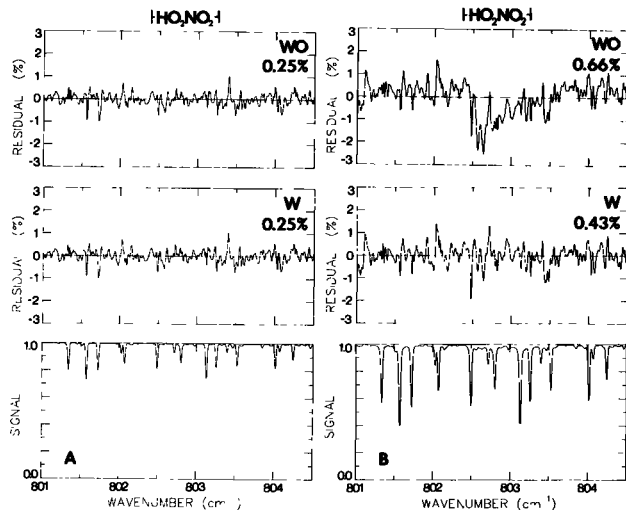


Fig. 2. Fitting results for zonal spectra ($\sim 31^\circ\text{N}$) with mean tangent heights of 33.5 km (A) and 22.3 km (B). Residuals (observed-calculated) and corresponding standard deviations with (W) and without (WO) HO₂NO₂ lines in the fit are shown at top.

the feature. However, absorption by the atmospheric feature decreases more rapidly to higher wavenumbers than calculated for HO₂NO₂. This difference is likely to be caused by the temperature dependence of the Q-branch absorption which, unfortunately, cannot be modeled from the published laboratory measurements. Also, unpublished 0.015-cm⁻¹ resolution laboratory spectra of HO₂NO₂ (L. Molina, private communication, 1985) show fine structure within the Q branch, and this structure has not been included in our model.

An asterisk in Figure 3 indicates a very weak absorption feature broader than the width of isolated lines. This absorption, which also appears in the residual plot of the 22.3-km tangent altitude scan (see Figure 2), has a position, 803.455 \pm 0.010 cm⁻¹, in agreement with that of a weak feature in the ClONO₂ laboratory spectra of Murcray et al. [1984]. Based on this evidence and the unambiguous identification of several stronger ClONO₂ features in the ATMOS spectra [Zander et al., 1986], we have assigned the 803.455-cm⁻¹ feature to ClONO₂.

Measurements on L. Molina's unpublished laboratory spectrum of HO₂NO₂ indicate that absorption peaks within the Q branch occur at 802.575 \pm 0.005 cm⁻¹ and 802.785 \pm 0.005 cm⁻¹. The higher wavenumber peak is overlapped by a weak O₃ line. The ATMOS spectra show a weak feature at 802.5767 \pm 0.0004 cm⁻¹, in agreement with the position of the lower wavenumber HO₂NO₂ peak. However, calculations with the parameters discussed above produce weak absorption by the R16 line of the 11101-10002 band of ¹⁶O¹²C¹⁸O at 802.5842 cm⁻¹, only \sim 0.007 cm⁻¹ above the position of the observed feature. A search in the same region for additional lines of this CO₂ band was inconclusive and, therefore, HO₂NO₂ may cause at least part of the 802.5767-cm⁻¹ absorption.

The HO₂NO₂ laboratory spectra of Murcray et al. [1984] show that the 802.7-cm⁻¹ band extends over the 770-830-cm⁻¹ region and has absorption peaks near 794 cm⁻¹ and 810 cm⁻¹ that are about one-

third as strong as the peak absorption in the Q branch. To search for this broad absorption, ATMOS transmittance spectra were calculated by ratioing the intensities in low sun spectra to the corresponding values from coadded high sun scans. The resulting spectra show a depression in the background envelope between 770 and 820 cm⁻¹ (\sim 2% maximum absorption for a tangent height of 22 km) which, according to simulations, cannot be explained by lines of H₂O, O₃, and CO₂. This absorption is probably caused in part by HO₂NO₂, but other trace gases with broad envelopes in the same region, such as ClONO₂ and CCl₄ [Murcray et al., 1984], may contribute.

Figure 4 presents HO₂NO₂ profiles deduced from fits to the Q-branch region in the 31°N zonal spectra and in the 47°S spectra. The error bars indicate the estimated total uncertainty (1 sigma). The error sources and the estimated uncertainty in the HO₂NO₂ mixing ratio resulting from each are (i) uncertainty due to instrument effects (noise, 0% transmission level shifts,...) (25-100%), (ii) uncertainty in the tangent height (\pm 10-20%), (iii) uncertainty in the assumed HO₂NO₂ line parameters (\pm 20%), (iv) uncertainty in the assumed pressure-temperature profile (\pm 10%), and (v) uncertainty in the simulation of interfering lines (\pm 20%). The error bars are largest above 25 km primarily because of the weakness of the observed absorption.

The measured profiles have similar vertical distributions with maximum HO₂NO₂ mixing ratios near 26 km of \sim 0.35 ppbv for 31°N and \sim 0.24 ppbv for 47°S and total vertical columns above 20 km

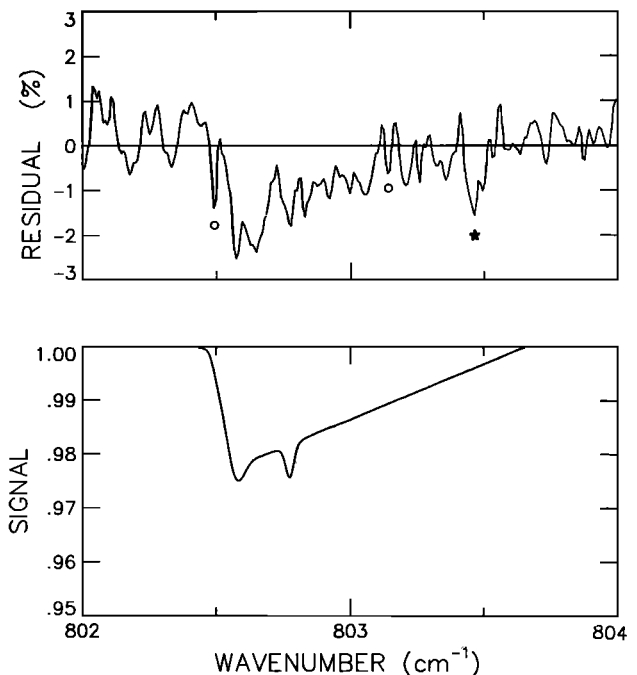


Fig. 3. Comparison for the 19.5-km zonal spectrum of residuals (observed-calculated) obtained without HO₂NO₂ lines in the fit (upper plot) and HO₂NO₂ absorption calculated from the retrieved profile (lower plot). Open circles indicate residual features resulting from imperfect fitting of strong lines; an asterisk marks a weak absorption assigned to ClONO₂.

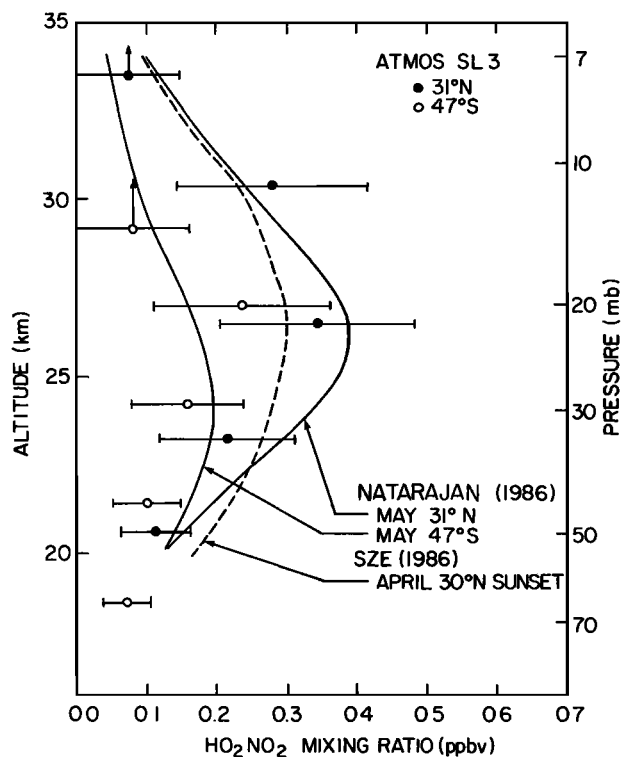


Fig. 4. Comparison of retrieved profiles and calculated HO₂NO₂ profiles.

that differ by a factor of 1.6 (2.0×10^{14} as compared to 1.2×10^{14} molecules cm^{-2}). These differences are reproduced by the model calculations of M. Natarajan (private communication, 1986) in Figure 4, which indicate they are produced by latitudinal rather than seasonal variations; diurnal changes are predicted to be small below 30 km [Ko and Sze, 1984]. These model mixing ratios are ~ 0.6 times the values calculated with the same model and input profiles [Callis et al., 1986], because of recent revisions in reaction rates involving HO₂NO₂ [JPL Publication 85-37, 1985]. The model values of N. D. Sze (private communication, 1986), calculated for 30°N at sunset and shown by a dashed line in Figure 4, are also in close agreement with the retrieved values.

The 1304.2-, 1728.3-, and 3540.1- cm^{-1} HO₂NO₂ Q branches fall in regions of strong stratospheric absorption and are unobservable. The 1396.9- cm^{-1} Q branch occurs in a region of relatively weak interfering absorption, but its intensity is three times weaker than the 802.7- cm^{-1} Q branch [Graham et al., 1978]. Lower stratospheric ATMOS spectra do not show any obvious absorption assignable to the 1396.9- cm^{-1} Q branch. In the future, spectra from additional ATMOS missions will be coadded to the Spacelab 3 spectra in an effort to improve the signal-to-noise sufficiently to detect the 1396.9- cm^{-1} Q branch, thus providing further verification and quantification of stratospheric HO₂NO₂.

References

Callis, L.B., et al., Stratospheric photochemical studies using Nimbus 7 data 2. Development of inferred trace specie distributions, *J. Geophys. Res.*, **91**, 1167-1197, 1986.

- Farmer, C.B., and O.F. Raper, High resolution infrared spectroscopy from space: A preliminary report on the results of the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment on Spacelab 3, NASA Conference Proceedings, "Spacelab 3 Mission Review", CP-2429, May, 1986.
- Goldman, A., et al., New atlas of stratospheric IR absorption spectra, Vol. 1, Line positions and identifications; Vol. 2, The spectra, report, Dept. Phys., Univ. Denver, Denver, Colo., 1985.
- Graham, R.A., A.M. Winer, and J.N. Pitts, Jr., Temperature dependence of the unimolecular decomposition of pernitric acid and its atmospheric implications, *Chem. Phys. Lett.*, **51**, 215-220, 1977.
- Graham, R.A., A.M. Winer, and J.N. Pitts, Jr., Ultraviolet and infrared absorption cross sections of gas phase HO₂NO₂, *Geophys. Res. Lett.*, **5**, 909-911, 1978.
- JPL Publication 85-37, Chemical kinetics and photochemical data for use in stratospheric modeling - Evaluation No. 7, July 1, 1985.
- Ko, M.K.W., and N.D. Sze, Diurnal variations of ClO: Implications for stratospheric chemistries of ClONO₂, HOCl, and HCl, *J. Geophys. Res.*, **89**, 11,619-11,632, 1984.
- Molina, L.T., and M.J. Molina, UV absorption cross sections of HO₂NO₂ vapor, *J. Photochem.*, **15**, 97-108, 1981.
- Murcray, D.G., et al., High resolution IR laboratory spectra, *Appl. Opt.*, **23**, 3502, 1984.
- NASA, The stratosphere: Present and future, NASA Ref. Pub. 1049, ed. R.H. Hudson and E.I. Reed, 1979.
- Niki, H. et al., Fourier transform IR spectroscopic observation of pernitric acid formed via HOO + NO₂ → HOONO₂, *Chem. Phys. Lett.*, **45**, 564-566, 1977.
- Petersen, F.R., E.C. Beaty, and C.R. Pollock, Improved rovibrational constants and frequency tables for the normal laser bands of ¹²C¹⁶O₂, *J. Mol. Spectrosc.*, **102**, 112-122, 1983.
- Rothman, L.S., et al., AFGL atmospheric absorption line parameters compilation: 1982 edition, *Appl. Opt.*, **22**, 2247-2256, 1983a.
- Rothman, L.S., et al., AFGL trace gas compilation: 1982 version, *Appl. Opt.*, **22**, 1616-1627, 1983b.
- Sauval, A.J., et al., The pure rotation spectrum of OH and the solar oxygen abundance, *Astrophys. J.*, **282**, 330-338, 1984.
- Sze, N.D., and M.K.W. Ko, The effects of the rate for OH + HNO₃ and HO₂NO₂ photolysis on stratospheric chemistry, *Atmos. Environ.*, **15**, 1301-1307, 1981.
- Zander, R., et al., Observation of several chlorine nitrate (ClONO₂) bands in stratospheric infrared spectra, *Geophys. Res. Lett.*, this issue, 1986.

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