Vertical Profiles of Molecular H_2 and CH_4 in the Stratosphere

D. H. Ehhalt* and L. E. Heidt†
National Center for Atmospheric Research, Boulder, Colo.

Stratospheric profiles of H_2 and CH_4 up to 35 km altitude have been derived from balloon flights over Mississippi on March 21, 1973 and are compared with profiles obtained previously over eastern Texas. The older profiles indicate an increase of the H_2 concentration in the lower stratosphere from about 0.5 ppm per volume at the tropopause to about 0.8 ppm at around 27 km altitude. Above that altitude the H_2 concentration decreases again. In the recent profile the H_2 increase extends to higher altitudes. An air sample collected in 1968 between 44 and 62 km by a rocket-borne cryogenic sampler had an H_2 concentration of 0.4 ppm. The CH_4 profiles showed a decrease in CH_4 concentration with altitude generally with a steeper gradient directly above the tropopause and a weaker gradient at higher altitudes, reaching an average of 0.9 ppm at 30 km altitude. The CH_4 concentration in the rocket sample was 0.25 ppm, in good agreement with the weak gradient obtained from the balloon samples.

Introduction

THE presence of hydrogen compounds is quite important to the chemistry of the stratosphere. They give rise to radicals such as OH and HO_2 which interact rapidly with NO_x and O_3. Until a few years ago water vapor was the only stable hydrogen compound considered. But since the flux of water vapor from the troposphere to the stratosphere is limited by the low temperatures at the tropopause, other hydrogen-containing trace gases with concentrations in the ppm range contribute significantly to the hydrogen budget of the stratosphere. Of particular importance are CH_4 and H_2. All of the CH_4 and much of the H_2 are released at the Earth's surface and both gases reside in the troposphere with lifetimes on the order of a few years and with mean concentrations of 1.4 and 0.5 ppm, respectively. Thus a fraction of these gases should be transported into the stratosphere. The CH_4 flux into the stratosphere is 1×10^{14} g CH_4/yr, and as this study shows, CH_4 and H_2 contribute nearly one-half of the hydrogen compounds in the middle stratosphere. Eventually the CH_4 is oxidized to H_2O and CO_2 but as recently proposed,[1,2] the oxidizing reactions also produce radicals like HO_2, and, as intermediate products, H_2 and CO.

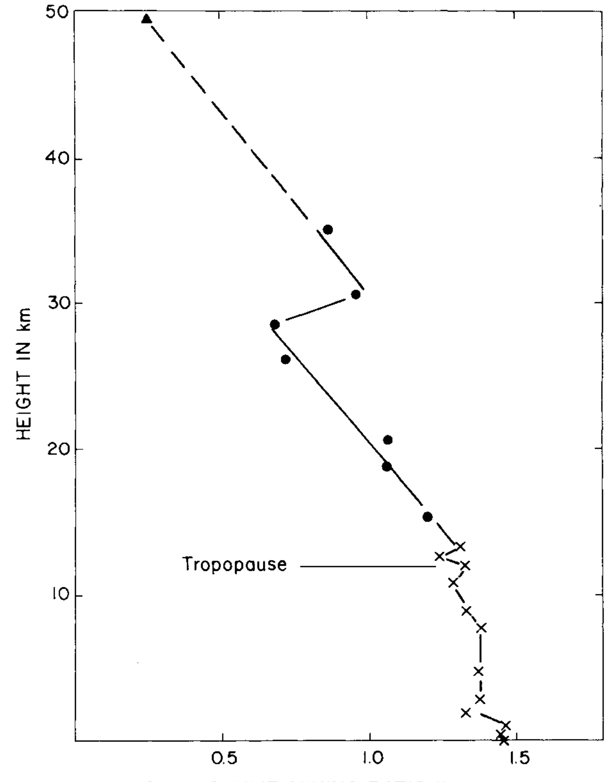

Fig. 1 Stratospheric profile of CH_4 from March 21, 1973. The triangle represents the measurement of a previous rocket flight.[5]

Assessment of the role of CH_4 in the stratosphere requires information on its vertical distribution, supplementary information is provided by the vertical distribution of H_2. We have, therefore, measured a number of vertical profiles of CH_4 and H_2 in the stratosphere, and this paper describes our latest results. The profiles were obtained from grab samples of ambient air collected aboard a balloon at eight different altitudes. The balloon flown from Palestine, Texas (32°N) on March 21, 1973 drifted 500 km to the east so that the actual sampling was done over Mississippi. The air samples were analyzed for their H_2, CH_4 and Ne content by gas chromatography. Details of the sampling and analysis technique as well as the problems of contamination have been discussed previously.[3,4]

Results

The flight reached 35 km maximum altitude and penetrated more deeply into the stratosphere than any in our past flight series. Results are shown in Figs. 1 and 2. The CH_4 profile (Fig. 1) shows a rapid decrease above the tropopause and is, in fact, the steepest stratospheric decrease we have observed so far. An interesting feature of the general decrease is its interruption by an inversion between 28 and 30 km. Aircraft samples which were obtained simultaneously to cover the altitudes below 13 km are indicated by crosses.

The profile has been extended to 50 km altitude with data from a rocket flight over White Sands, N. Mex. (32°N), on Sept. 4, 1968. The cryogenic rocket sampler collected an integrated sample between 44 and 62 km altitude, the mean weighted altitude being 50 km. The CH_4 concentration in that sample was 0.25 ± 0.02 ppm.[5]

Presented as Paper 73-518 at the AIAA/AMS International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere, Denver, Colo., June 11–13, 1973; submitted June 11, 1973; revision received January 11, 1974. The National Center for Atmospheric Research is sponsored by the National Science Foundation. A portion of this work was supported by the Department of Transportation's Climatic Impact Assessment Program.

Index category: Atmospheric, Space, and Oceanographic Services.

* Scientist.

† B.S. Scientist.

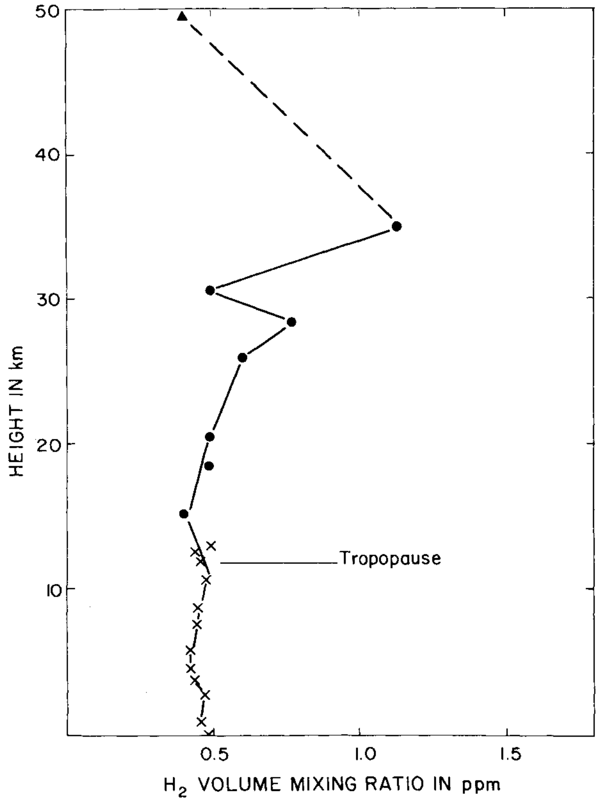

Fig. 2 Stratospheric profile of H_2 from March 21, 1973. The triangle represents the measurement of a previous rocket flight.[6]

The corresponding H_2 concentrations are shown in Fig. 2. At the time of writing, the calibration for the balloon samples is preliminary. The final profile might differ by as much as 10%, but the relative concentrations are correct. The stratospheric H_2 profile shows an increase from 0.43 ppm at 15 km to 0.83 ppm at 28.4 km, a decrease from 0.83 ppm at 28 to 0.53 ppm at 30 km and then another steep increase to 1.22 ppm at 35 km. The last value was measured during floating of the balloon when the danger of contamination is highest. We will therefore await confirmation of this high concentration before stressing it too heavily. The rocket sample showed an H_2 concentration of 0.4 ppm at 50 km altitude. Thus the H_2 concentration exhibits a broad maximum in the stratosphere whose upper, decreasing part is not yet well defined.

It is interesting to compare the present profiles with results from previous balloon flights from Palestine, Texas. The data are summarized in Fig. 3.[4] The CH_4 data are shown in the upper row. The balloon data (solid dots) collected below the tropopause show a constant CH_4 concentration with altitude and agree with the concentration obtained from aircraft flights (crosses) in the upper troposphere.[7] The stratospheric part of the balloon profiles, however, shows a decrease in the CH_4 concentration starting right at the tropopause. But we also notice that in most profiles the decrease is much weaker than in the March 21 profile. Examining the dates, we see that the March 1965 profile has a similarly steep decrease, and that the profiles collected in June or July show the weaker decrease. In addition, it appears that the average gradient of the CH_4 concentration is somewhat steeper directly above the tropopause and becomes weaker above 20 km. This steeper decrease directly above the tropopause could be real. The stratospheric branch of the Hadley circulation extends to 32°N and it is possible that the gradient in the lower stratosphere is steepened by mean downward motion. Since the Hadley circulation is more pronounced during March, it would also offer an explanation for the steeper gradient observed during that month. Finally, also, these CH_4 profiles indicate an occasional increase of the CH_4 concentration at around 30 km altitude.

The corresponding H_2 profiles are plotted in the lower row. The two earlier profiles required quite large corrections for contamination; these corrections are indicated by the dashed line between the bars and triangles which represent the corrected concentrations. The corrections for both the June 6, 1972 flight and the present flight are much smaller: 0.16 ppm at 30 km altitude and even smaller below. Again the balloon samples collected below the tropopause agree well with aircraft profiles over eastern Texas and with our average profile obtained over Scottsbluff, Neb. in 1966 which gave an average H_2 mixing ratio of 0.49 ppm. Similarly to the profile shown in Fig. 2, the H_2 concentration in all profiles increases in the lower stratosphere. It reaches a maximum at 25–27 km and decreases to 30 km, the maximum altitude reached on these earlier flights.

Since the H_2 measurement from the rocket sample gave a low concentration at 50 km, we assumed tentatively that the H_2 concentration decreased more or less monotonically above 27 km.

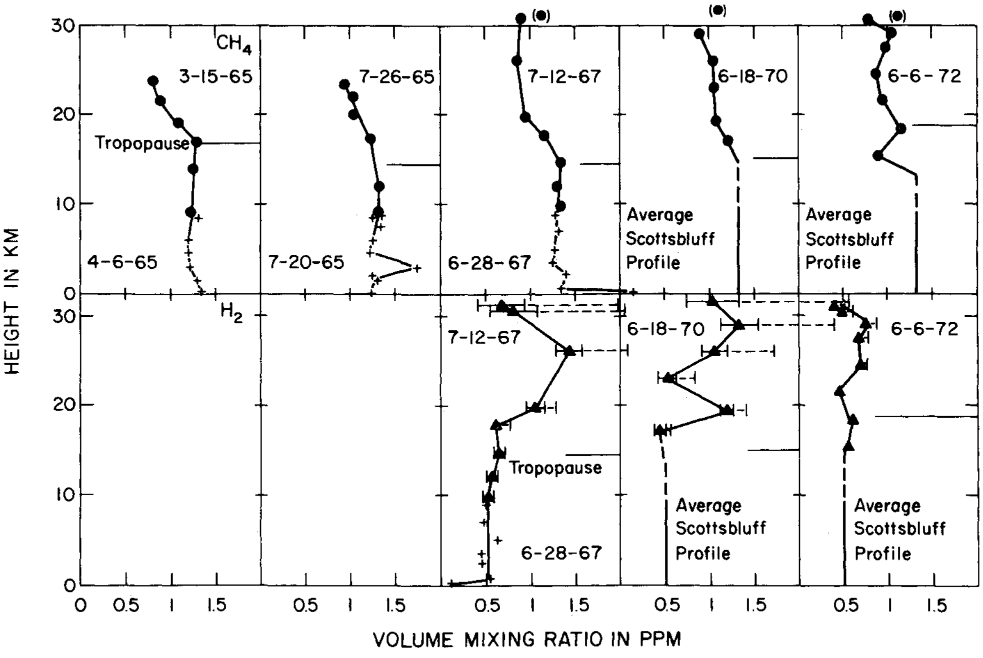

Fig. 3 Tropospheric and stratospheric profiles of molecular H_2 and CH_4 over eastern Texas, 32°N. Crosses represent samples from aircraft flights collected on the lower dates; dots samples from balloon flights collected on the upper dates. (The standard error of the CH_4 measurements is ±5%.) Triangles represent the H_2 mixing ratio corrected for contamination; dashed lines connect them to the measured values. Bars give the errors for H_2 (no bars indicate an error of 5% or less). The two earliest CH_4 profiles are the ones measured by Bainbridge and Heidt.[8]

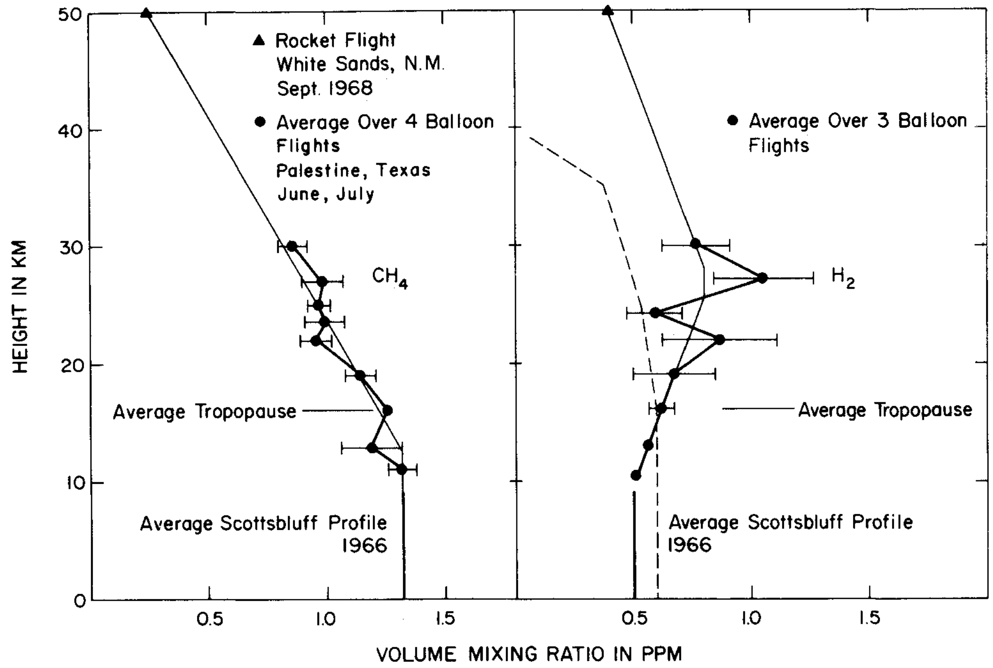

Fig. 4 Stratospheric H_2 and CH_4 profiles averaged over the individual profiles in Fig. 1. Bars indicate mean standard deviation due to scatter in individual profiles. Dashed H_2 profile is from a model calculation by Hesstvedt.[9] Heavy lines connect measured values. Thin lines represent curves adopted as average.

We were, therefore, rather surprised to find a large increase of the H_2 concentration between 30.5 and 35 km in the recent profile, especially since below 30.5 km the recent profile agrees rather closely with the previous ones.

To show the common features more clearly, the H_2 and CH_4 profiles obtained during June and July are combined in averages (Fig. 4). Altitudes are shown with respect to the tropopause. In view of the large standard deviations (5–10%) and for the sake of simplicity, we fitted a straight line to the stratospheric CH_4 data, neglecting a possibly steeper decrease immediately above the tropopause. For H_2 we adopted a mean profile with an increase to a maximum of about 0.8 ppm at 27 km and with a decrease at higher altitudes, obtained by connecting the data points between 30 and 50 km by a straight line. Obviously our most recent results in March 1973 are not included in the averaging; in fact, if confirmed, they would put the maximum H_2 concentration at or above 35 km. Also included in Fig. 4 is a theoretical H_2 profile (thin dashed line) which has been calculated from a chemical model assuming upward diffusion of H_2 from the troposphere and oxidation in the stratosphere.[9] Comparison with the theoretical profile shows that a net production of H_2 in the stratosphere is required to explain the H_2 increase in the experimental profile.

It seems that inclusion of the CH_4 chemistry would provide such an H_2 source. Recently Levy[1] and McConnell et al.[2] have suggested a destruction mechanism of CH_4 in the troposphere. The first reaction is the attack of CH_4 by the OH radical

$$CH_4+OH \rightarrow H_2O+CH_3$$

Judging from the OH profile given by McConnell et al.[2] this reaction will also be primarily responsible for the destruction of CH_4 in the lower stratosphere. CH_3 then is proposed to react further to H_2CO, which can react in three ways:

$$h\nu \rightarrow H_2+CO \qquad (1)$$

$$H_2CO+h\nu \rightarrow H+HCO \qquad (2)$$

$$OH \rightarrow H_2O+HCO \qquad (3)$$

Reaction (1) suggests that molecular H_2 is produced in the photolysis of H_2CO. In the presence of sunlight the photolytic decomposition of formaldehyde (reactions 1 and 2) is much faster than the reaction with OH, whose concentration should, furthermore, also decrease during night. The quantum yields

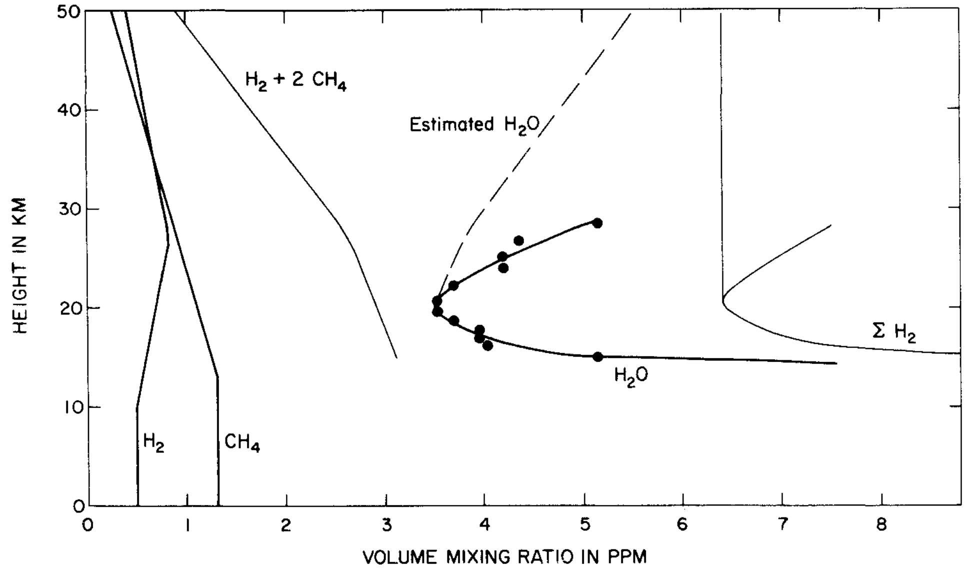

Fig. 5 Average profiles of H_2 and CH_4 (from Fig. 4) and H_2O.[12] Thin curves represent sum of H_2+2CH_4 and sum of all H_2 compounds. Thin dashed line is H_2O profile based on the assumption that the combined mixing ratio of all H_2 compounds is constant with altitude above 20 km.

derived by McQuigg and Calvert[10] show that reaction (1) leading to H_2 is more important at wavelengths greater than 3100 Å. Thus H_2 will be produced from CH_4 below the O_3 layer and we might expect that one CH_4 molecule yields between one-half and one H_2 molecule. In addition, H_2 reacts with OH more slowly than does CH_4, so that the H_2 concentration can build up to a measurable increase. Accordingly, the lower stratosphere should represent a source region of H_2.[11]

When we compare the average CH_4 decrease with the average H_2 increase between the tropopause and 28 km (Fig. 4), we find that the CH_4 concentration decreases by 0.4 ppm and the H_2 concentration increases by 0.3 ppm. Thus destruction of CH_4 could supply the increase of stratospheric H_2. This could also be tentatively interpreted as confirmation that a reaction scheme leading from CH_4 to CH_2O is operative in the stratosphere.

To obtain a complete budget of the stratospheric hydrogen compounds we must compare the average H_2 and CH_4 profiles to the profile of water vapor, the only other major hydrogen compound in the stratosphere (Fig. 5). The water vapor profile shown is the annual average of the median of the H_2O volume mixing ratio over Washington, D.C. (39°N) and Trinidad, W.I. (11°N) during 1964 and 1965.[12] Also included in Fig. 5 is the sum of H_2 and CH_4 (counted twice to account for four H atoms). The sum decreases through the stratosphere, at first slowly, due only to the oxidation of CH_4, but more rapidly above 28 km where both H_2 and CH_4 are destroyed. At 20 km H_2 and CH_4 contribute nearly as much to the H_2 compounds as H_2O itself. Since the final reaction product of CH_4 and H_2 oxidation is H_2O, we expect the H_2O mixing ratio to increase with altitude. This is indeed the case. But comparison of the gradients shows that the decrease of the sum of H_2 and CH_4 cannot explain the rapid increase of the H_2O mixing ratio above 20 km as observed by Mastenbrook.[12] Some additional source of H_2O is required. As Mastenbrook[12] himself has pointed out, the problem of H_2O contamination is very serious especially at the highest altitudes. Thus, part of the measured H_2O increase might be due to contamination. If so, contamination at 20 km should be at least three times smaller than at 28 km, because of the increase in density at the lower altitude and should amount to less than 0.5 ppm at 20 km. The H_2O mixing ratio at 20 km should therefore be rather reliable. If we assume that the H_2O mixing ratio at 20 km is correct and further that the sum of the hydrogen compounds remains constant with altitude, we predict the H_2O increase with altitude which is indicated by the dashed line in Fig. 5. This increase is due to the oxidation of H_2 and CH_4 alone. This H_2O profile reaches a H_2O concentration of 5.5 ppm at 50 km. The fact that the H_2O mixing ratio shown has a minimum at about 20 km altitude causes a convergence of the vertical eddy diffusion flux of H_2O. This makes it obvious that the chemistry and budget of hydrogen compounds cannot be treated by a one-dimensional transport model, and the calculated increase in H_2O represents a limiting case only.

Finally, the present H_2 profiles are important not only for the general chemistry and the water budget of the stratosphere but also for the tropospheric H_2 cycle. The stratosphere clearly represents a sink for tropospheric CH_4 as has been known for quite some time. However, the same is not true for H_2; the stratosphere seems to act rather as a source for tropospheric H_2, which is in contrast to presently held views.

References

[1] Levy, H., "Normal Atmosphere: Large Radical and Formaldehyde Concentrations Predicted," *Science*, Vol. 173, 1971, pp. 141–143.

[2] McConnell, J. C., McElroy, M. B., and Wofsy, S. C., "Natural Sources of Atmospheric CO," *Nature*, Vol. 223, 1971, pp. 187–188.

[3] Heidt, L. E. and Ehhalt, D. H., "Gas Chromatographic Measurement of Hydrogen, Methane and Neon in Air," *Journal of Chromatography*, Vol. 69, 1972, pp. 103–113.

[4] Ehhalt, D. H. and Heidt, L. E., "The Concentration of Molecular H_2 and CH_4 in the Stratosphere," *Pure and Applied Geophysics*, Vol. 106–108, 1973, pp. 1352–1360.

[5] Ehhalt, D. H., Heidt, L. E., and Martell, E. A., "The Concentration of Atmospheric Methane between 44 and 62 Kilometers Altitude," *Journal of Geophysical Research*, Vol. 77, 1972, pp. 2193–2196.

[6] Scholz, T. G., Ehhalt, D. H., Heidt, L. E., and Martell, E. A., "Water Vapor, Molecular Hydrogen, Methane and Tritium Concentrations near the Stratopause," *Journal of Geophysical Research*, Vol. 75, 1970, pp. 3049–3054.

[7] Ehhalt, D. H. and Heidt, L. E., "Vertical Profiles of CH_4 in the Troposphere and Stratosphere," *Proceedings of the Symposium on Sources, Sinks and Concentrations of Carbon Monoxide and Methane in the Earth's Environment*, St. Petersburg Beach, Fla., p. 11.1–11.11.

[8] Bainbridge, A. E. and Heidt, L. E., "Measurements of Methane in the Troposphere and Lower Stratosphere," *Tellus*, Vol. 18, 1966, pp. 221–225.

[9] Hesstvedt, E., "On the Photochemistry of Ozone in the Ozone Layer," *Geophysical Publications of Norway*, Vol. 27, 1968, pp. 1–16.

[10] McQuigg, R. D. and Calvert, J. G., "The Photodecomposition of CH_2O, CD_2O, CHDO and CH_2-CD_2O Mixtures of Xenon Flash Lamp Intensities," *Journal of American Chemical Society*, Vol. 91, 1969, pp. 1590–1599.

[11] Crutzen, P., "Gas Phase Nitrogen and Methane Chemistry in the Atmosphere," Rept. AP-10, 1972, Institute of Meteorology, University of Stockholm, Stockholm, Sweden.

[12] Mastenbrook, H. J., "Water Vapor Distribution in the Stratosphere and High Troposphere," *Journal of Atmospheric Sciences*, Vol. 25, 1968, pp. 299–311.