Adv. Space Res. Vol.12, No.11, pp.(11)11–(11)18, 1992
Printed in Great Britain. All rights reserved.

0273-1177/92 $15.00
Copyright © 1992 COSPAR

HYDROCARBONS AND EDDY MIXING IN NEPTUNE'S ATMOSPHERE

S. K. Atreya

Department of Atmospheric, Oceanic and Space Sciences, The University of Michigan,
2455 Hayward Avenue, Ann Arbor, MI 48109-2143, U.S.A.

ABSTRACT

The most recent analysis of the Voyager ultraviolet solar occultation observations at Neptune indicates a methane mixing ratio 1-10 times above saturation in the lower stratosphere, unlike the value of 500-1000 times saturation which was suggested just before the encounter of Voyager with Neptune. The acetylene mixing ratio in the 0.1 mb region is found to be (6 - 8) x 10^{-8}, which is approximately a factor of 3 lower than the value reported in our Voyager/Science paper. The eddy diffusion coefficient at the homopause, (1 - 3) x 10^7 cm^2 s^{-1}, is found to be more like that on Saturn than Uranus. The new results on CH_4, C_2H_2 and K have strong implications for the stratospheric temperatures, now warmer, and the source of heating. Furthermore, the pre-Voyager models of the hydrocarbon hazes need to be revised in view of the new model atmosphere.

Hydrocarbons were detected in Neptune's atmosphere by the Ultraviolet Spectrometer, UVS /1/, and the Infrared Spectrometer, IRIS /2/, on Voyager 2. The UVS measurements rely on precise monitoring of the solar flux in the 500-1700Å region as the sun 'sets' and 'rises' in Neptune's atmosphere -- the occultation experiment. Because of the long line of sight, these measurements yield hydrocarbon distributions high in the atmosphere -- at pressures less than about 0.1 millibar on Neptune. Also, by careful analysis of the ultraviolet albedo measurements in the 1500-1700Å region, it is possible to derive the acetylene abundance deeper in the stratosphere, i.e., at 10-20 mb level. The IRIS measurement of a strong emission feature at 13.7 microns yield the C_2H_2 mixing ratio in the 0.03-2.5 millibar region. In addition, the Voyager radio science, RSS /3/, and the imaging, ISS /4/, results are consistent with the existence of an optically thin cloud of methane at around the 1500 mb level, which implies a deep tropospheric CH_4 volume mixing ratio of ~2%. Another cloud deeper in the atmosphere is implied by these as well as ground-based observations. It is suggested that a cloud of perhaps H_2S-ice or NH_3-ice is present at ~3 bar pressure level. Radio observations with the VLA along with their interpretation using thermochemical cloud models, however, cast doubt on the existence of an optically thick cloud at this level -- either the Voyager results correspond to a local phenomena, e.g., of updraft, or they refer to pressures greater than 5 bars /5/. This paper, however, deals with the question of the hydrocarbon distributions and the inference of the eddy diffusion coefficient therefrom.

A cartoon, shown in Figure 1, illustrates the regions of gas-phase photochemistry, hazes, and the formation of methane and other possible clouds in Neptune's atmosphere. Although the condensation of methane into an ice cloud occurs at ~1500 mb level, its saturated vapor pressure, (3-8) x 10^{-3} mb, at the tropopause cold-trap temperature of 50-52 K is large enough to produce an optical depth of 17,000-45,000 at the Lyman-alpha wavelength! This also means that for a uniformly mixed atmosphere, the unit optical depth in methane would occur nearly 10 scale heights (~500 km) above the tropopause on Neptune. Hence, despite its condensation, methane gas must undergo photolysis to quite high altitudes in Neptune's atmosphere. Other photochemically active species, such as NH_3 and H_2S on Jupiter and Saturn, however, have exceedingly low vapor pressures in the Neptune atmosphere (above the 1500 mb level), therefore they do not participate in photochemistry.

JASR 12:11-B

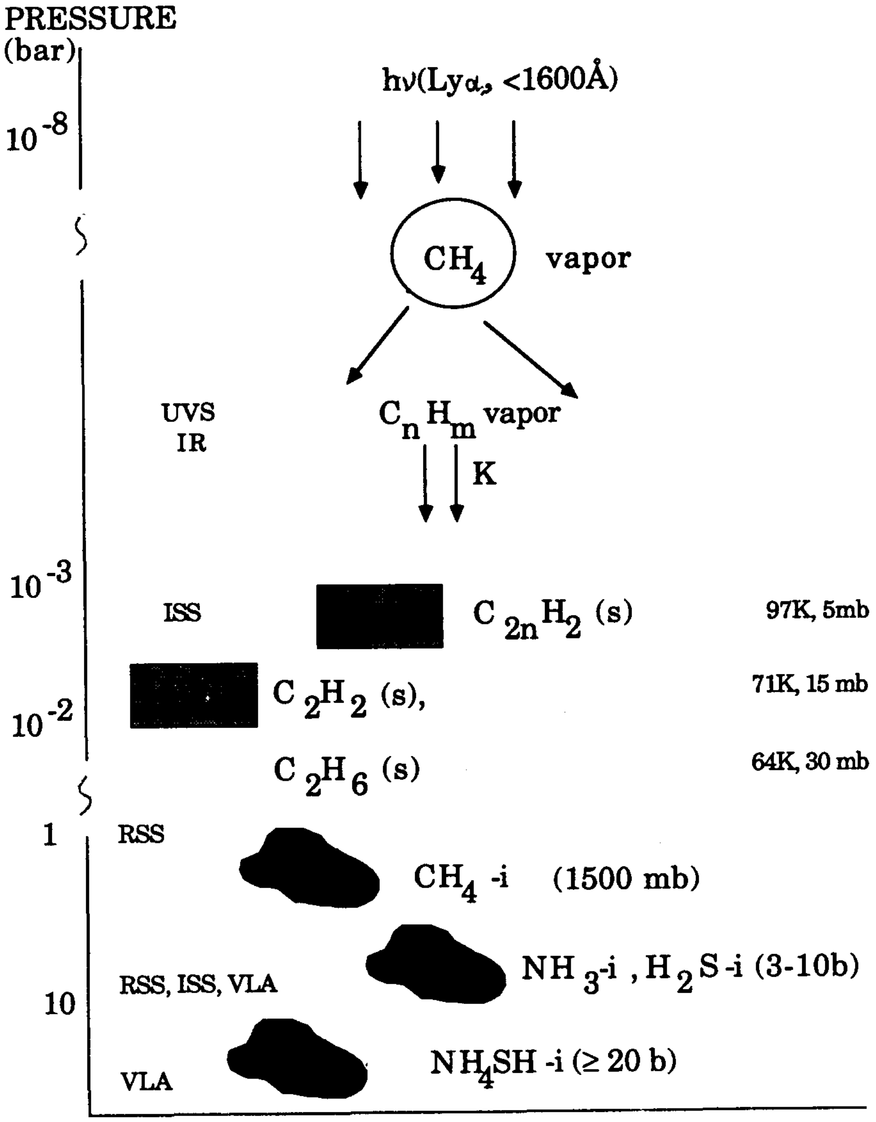

Fig. 1. A cartoon showing the regions of CH_4 photochemistry, hydrocarbon ice-hazes ($C_{2n}H_2$(s), C_2H_2(s), C_2H_6(s)); CH_4-ice and other possible clouds on Neptune. The acronyms on the left (UVS, IR, etc.) refer to the various instruments, mostly on Voyager, which have produced the critical data on these species.

The photolysis of methane proceeds following the absorption of solar photons with wavelengths below 1600Å. Because of the preponderance of the solar flux at 1216Å, however, 92% of the CH_4 dissociation occurs at the Lyman-alpha wavelength. The photodissociation of CH_4 results primarily in the formation of radicals CH_2; CH radicals have a much lower quantum yield (<10%) whereas direct production of the methyl radicals is kinetically forbidden. Subsequent reactions of the CH_4 photo-products with H_2, however, produce CH_3, whose self-reaction in turn produces ethane (C_2H_6). Reactions of CH with CH_4, of CH_2 with CH_3, and photolysis of C_2H_6 produce small amounts of ethylene (C_2H_4). Photolysis of C_2H_6 and C_2H_4 are also the major sources of acetylene (C_2H_2). A complete photochemical scheme for CH_4 in Neptune's atmosphere is shown in Figure 2a. Photolysis of C_2H_2 at wavelengths below ~2000Å

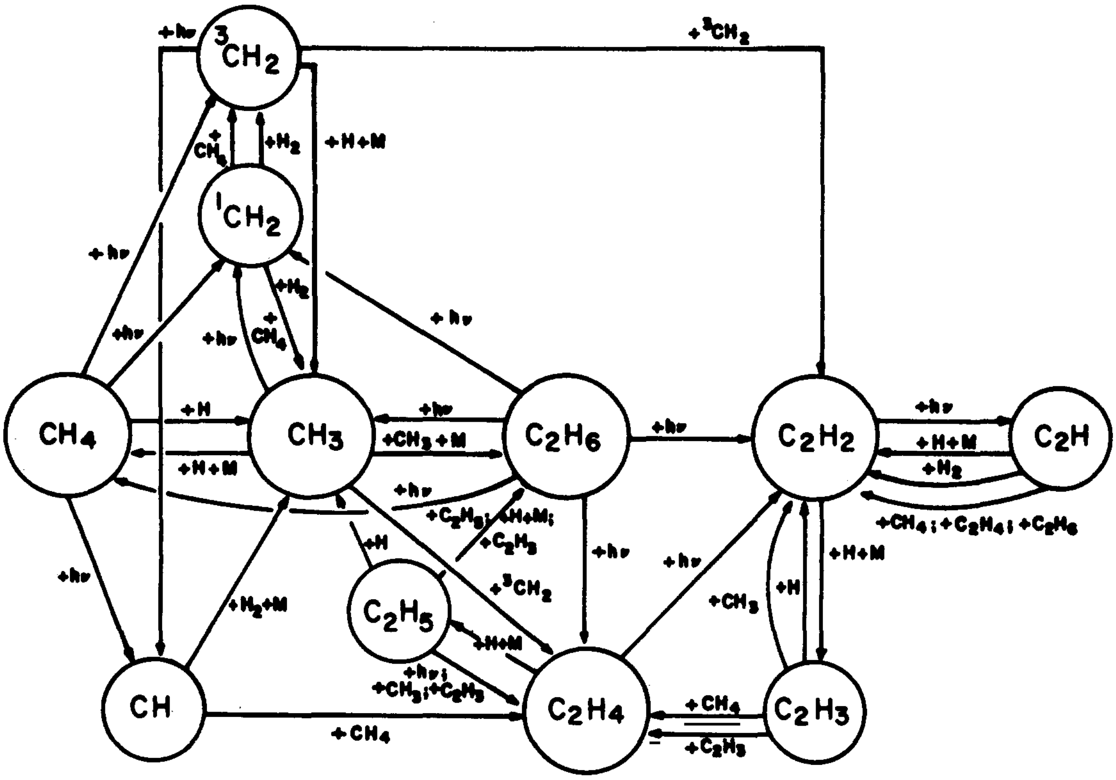

Fig. 2a. CH_4 photochemistry (from /6/, p. 99).

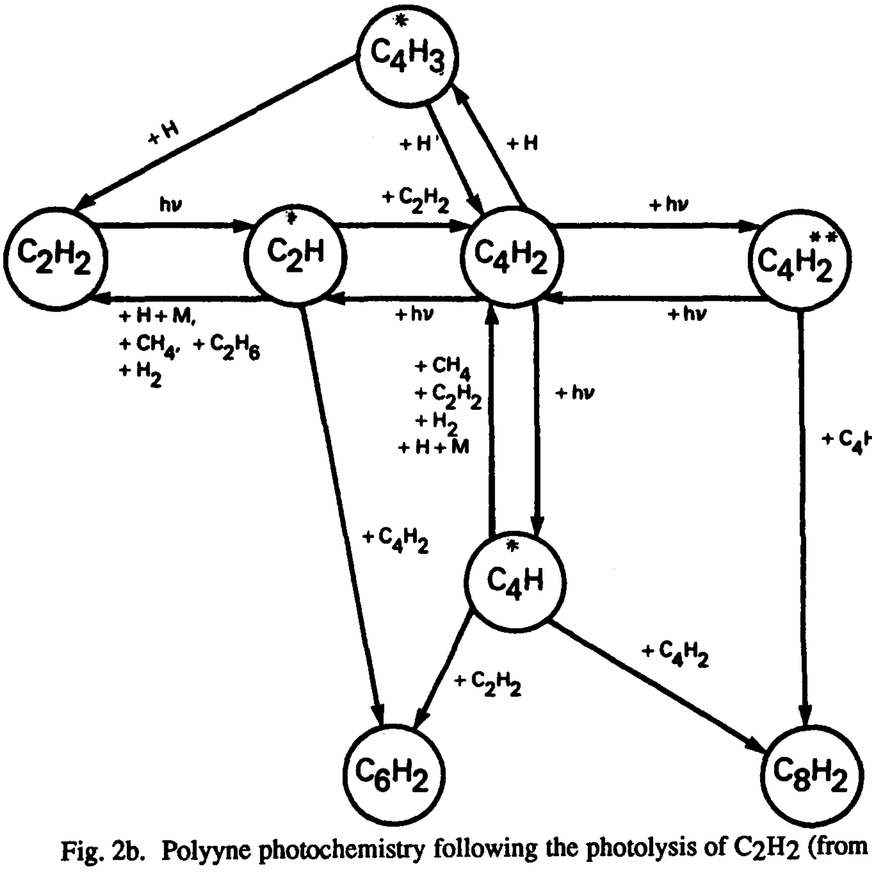

Fig. 2b. Polyyne photochemistry following the photolysis of C_2H_2 (from /7/).

results in the formation of C_2H radical. The reaction between C_2H and C_2H_2 can form diacetylene (C_4H_2). Subsequent chemistry is highly speculative as the absorption cross sections and the vapor pressures of C_4H_2, and chemical kinetics of reactions following C_4H_2 photodissociation are very uncertain. Nevertheless, it is suspected that there is a good likelihood of the formation of higher order polyynes ($C_{2n}H_2$, where n = 3, 4, ...). Such a possibility is illustrated in the chemical scheme shown in Figure 2b.

Once produced in the gas phase, the hydrocarbon products are removed by downward mixing, condensation, and charged particle induced polymerization (with subsequent condensation). In the cold stratosphere of Neptune where the temperature ranges from 50-52K at the tropopause (100 mb) to ~150K (0.1 microbar), most of the products of methane photochemistry are expected to freeze to their respective ices at various levels in the atmosphere. The hazes will be removed from their region of formation following coalescence, coagulation and mixing. In the deep troposphere, they may be polymerized by action of charged particles, such as cosmic rays, undergo further cloud microphysical processes, and will be eventually re-evaporated or pyrolyzed. The re-formation of methane, followed by its convection to the upper atmosphere maintains this important trace constituent at a stable level in Neptune's atmosphere. The gas phase distribution of the hydrocarbons is controlled not just by photochemical processes but by the strength of vertical mixing. By comparing photochemical models with actual observations one can determine the value of eddy diffusion coefficient. (The reader is referred to Chapters 4 and 5 of Atreya /6/ for addition discussion on vertical mixing and the photochemistry.)

The Voyager ultraviolet solar occultations at Neptune occurred at 61^oN, 259^oW (entrance) and 49^oS, 160^oW (exit). The northern latitude occultation point corresponds to arctic winter, while the southern one was close to the summer solstice at the time of Voyager 2 observations at Neptune. So far only the entrance occultation data have been analyzed since the exit data are statistically poor. The small range of the spacecraft to the planet resulted in excellent height resolution (5 km at entrance, 15 km at exit) which is far better than the scale height (30-50 km) in Neptune's stratosphere. An example of the 1474Å and 1548Å transmission curves is shown in Figure 3. The much lower scale height and the faster decrease in the transmission at 1474Å is indicative of the dropoff in the density of the heavier constituent, C_2H_2, near and above the homopause. Because of photochemistry, the level of dropoff is usually lower than the homopause.

Figure 4 shows the model calculations which best fit the data on CH_4 and C_2H_2. In order to simulate the conditions of entrance solar occultation (61^oN), a solar zenith angle of 87^o was assumed. The best fit for this case is obtained with a combination of $K_h = 5 \times 10^6$ cm^2 s^{-1} (at the homopause) and a CH_4 mixing ratio of 6×10^{-3} at the tropopause. (In the numerical models discussed here, CH_4 mixing ratio is fixed at the lower boundary, which is assumed to be the tropopause. It should be emphasized, however, that the model calculation results do not change by fixing the same mixing ratio for methane in the *lower stratosphere* rather than the tropopause.) The Voyager UVS observations, however, revealed that the Local Interstellar Medium (LISM) Lyman-alpha intensity at Neptune is equal to the solar Lyman-alpha. It is a particularly important factor for the entrance occultation point which was in the arctic winter, thus receiving virtually no sunlight. The LISM essentially causes even this occultation point to experience midlatitude summer conditions. The solid line curves in Figure 4 are an attempt at simulating the effect of LISM. The best fit to the data are obtained with a combination of $K_h = 3 \times 10^7$ cm^2 s^{-1} and CH_4 mixing ratio of 2×10^{-4} at the tropopause. The models incorporating the effect of LISM properly are being calculated at this time -- early indications are that K_h between 10^7 and 10^8 cm^2 s^{-1} provide reasonable fits to the data, whereas the most acceptable methane mixing ratios at the tropopause are in the range of $(1\text{-}3) \times 10^{-4}$. The homopause characteristics for the abovementioned K are listed in Table 1a. Additional details will be provided in our paper /8/.

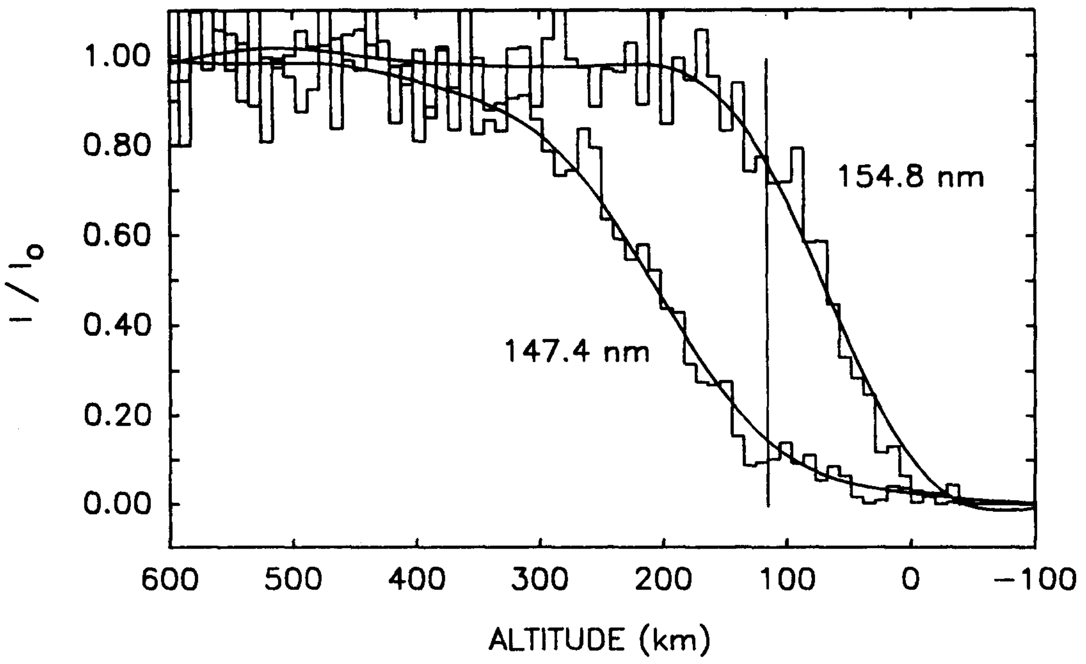

Fig. 3. Transmission curves for the 147.4 nm (C_2H_2) and the 154.8 nm (H_2 Rayleigh scattering) channels. Altitudes are above the tropopause (100 mb level) which is located approximately 60 km above the 1-bar level. The radius of Neptune at the 1-bar level and 61°N latitude is assumed to be 24,600 km.

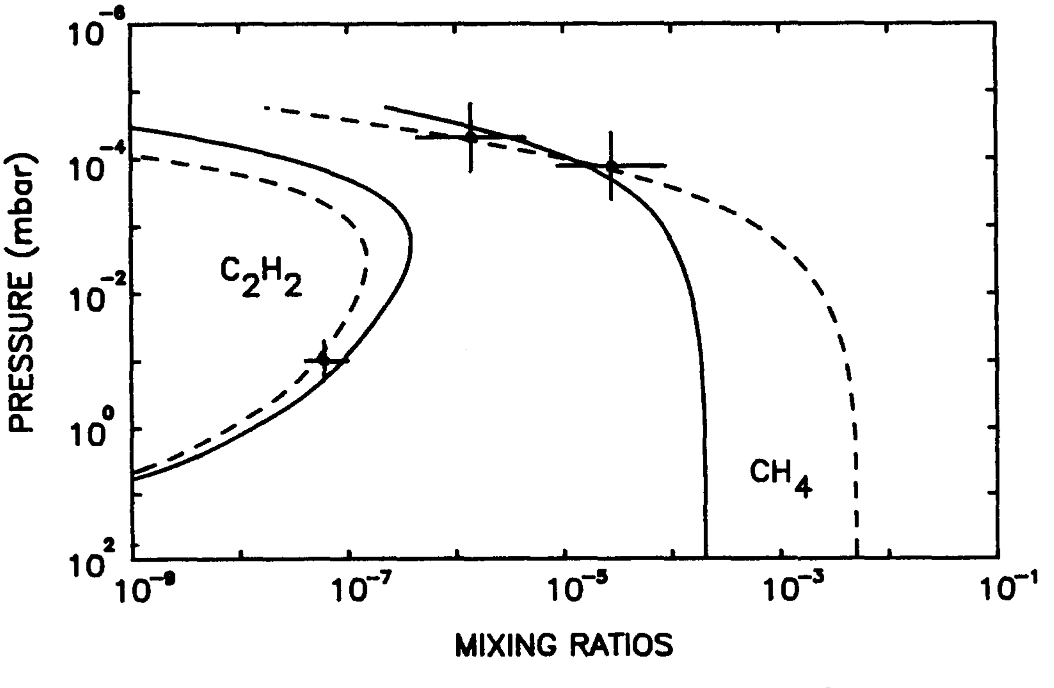

Fig. 4. Photochemical models for C_2H_2 and CH_4 which best fit the 61°N occultation results. Broken line curves correspond to a solar zenith angle of 87° (which is used to simulate the 61°N conditions) and $K_h = 5 \times 10^6$ cm^2 s^{-1}, and CH_4 mixing ratio of 6×10^{-3} at the tropopause. The solid line curves correspond to a solar zenith angle of 50°, $K_h = 3 \times 10^7$ cm^2 s^{-1} and CH_4 mixing ratio of 2×10^{-4} at the tropopause.

TABLE 1a Neptune Eddy Diffusion Coefficient

K_h ($cm^2\ s^{-1}$)	P_h (nanobar)	$n(H_2)$ (cm^{-3})
10^7	50	1.4×10^{12}
3×10^7	20	5.3×10^{11}
10^8	7	1.8×10^{11}

A comparison between the eddy diffusion coefficient at Neptune with that on the other planets (Table 1b) indicates that vertical mixing in the atmosphere of this planet is similar to that on Saturn, but not Uranus, which is sometimes referred to as Neptune's twin. This difference in the strength of vertical mixing appears to be correlated with the strength of internal heat source. Uranus, which has virtually no internal heat, has sluggish vertical mixing in its atmosphere, whereas Neptune whose internal energy is at least equal to the absorbed solar energy, displays a vigorous atmospheric vertical mixing.

Table 1b. Eddy Diffusion Coefficients

	$K_h(cm^2\ s^{-1})$	P_h(bar)
NEPTUNE	3×10^7	2×10^{-8}
URANUS	10^4	2×10^{-5}
SATURN	8.0×10^7 -- 1.7×10^8	4×10^{-9}
JUPITER	1.4×10^6	10^{-6}
TITAN	1.0×10^8	6×10^{-10}
EARTH	$(0.3 - 1) \times 10^6$	3×10^{-7}
VENUS	10^7	2×10^{-8}
MARS	$(1.3 - 4.4) \times 10^8$	2×10^{-10}

This brings up the question of stratospheric heating. Prior to the Voyager UVS observations, it was suggested on the basis of ground-based IR observations that the CH_4 mixing ratio in the lower stratosphere of Neptune is 2% /9/, /10/, which is a little over 500 times the saturated mixing ratio of 3×10^{-5} at the 50K cold-trap tropopause. The ground-based IR data yield, however, only a tightly coupled combination of the CH_4 abundance and the stratospheric temperature. In fact Lellouch, et al. /11/ derived a CH_4 mixing ratio of 0.6% (with a factor of 10 uncertainty) at the 0.3 mb level. They arrived at this value by attributing the entire observed 30% decrease in the mean central flash intensity in the August 20, 1985 infrared stellar occultation to methane. Reinterpretation of the same data by Hubbard, et al. /12/, however, assumed no opacity due to methane. Hubbard et al., however, concluded that the truth perhaps lies somewhere in between --- a height variable stratospheric temperature like Orton et al.'s, and a stratospheric methane mixing ratio less than 1%. The abovementioned UVS results on the CH_4 mixing ratios at the tropopause or in the lower stratosphere do not require a high degree of supersaturation. In fact, supersaturation may not be required at all if the tropopause temperature were greater by even a few degrees. B. Conrath /13/ has re-examined the Voyager IRIS data, and he finds tropopause temperatures as high as 57° at some locations on the planet. Until the issue of the tropopause temperatures for the solar occultation region is settled, it would be premature to develop theories to explain the lower stratospheric supersaturation of methane, even if it is by a factor of 2. It is nevertheless clear that for Orton, et al to match the abovementioned UVS results on the lower stratospheric CH_4 mixing ratio, they would have to raise the stratospheric temperature by 8-10 K. This poses a dilemma -- the lower methane abundance would result in a colder stratosphere, thus necessitating the existence of another heat source. It is suggested here that the break-up of upward propagating gravity waves in the stratosphere could result in the additional heating. The strong vertical mixing in Neptune's atmosphere certainly gives a clue to such an activity. Another possible source of heating is the atmospheric aerosols. The pre-Voyager model of Romani and Atreya /7/ yielded a haze production rate of $\sim 4 \times 10^{-15}$ g cm^{-2} s^{-1}, with nearly 75% of it attributable to C_2H_6, 24% to C_2H_2 and less than 1% to C_4H_2. This amount of the haze is far too low for changing the stratospheric temperature appreciably. Now, with the inclusion of LISM, lower (than 2%) stratospheric CH_4 mixing ratio at the tropopause boundary, and the larger value of eddy diffusion coefficient, both the total production rate and the relative allocation of hazes amongst C_2H_6, C_2H_2 and C_4H_2 are expected to change. Early indications from the Voyager imaging data /14/ are for a lower haze production rate. This would further reduce the role of aerosols in Neptune's stratospheric heating.

In conclusion, the need for strong convection of methane crystals to the lower stratosphere is considerably less severe now. Additional theoretical work must be done to account for the inevitably higher stratospheric temperatures as well as for the strong vertical mixing in Neptune's atmosphere.

ACKNOWLEDGMENT

Discussions with James Bishop, Paul Romani, Imke dePater, Bill Sandel, Jim Pollack and Bill Hubbard were helpful. This work was supported by a grant from NASA's Solar System Exploration Division, Planetary Atmospheres Program.

REFERENCES

1. A.L. Broadfoot, et al., Ultraviolet spectrometer observations of Neptune and Triton, *Science*, 246, 1459 (1989).
2. B. Conrath, et al., Infrared observations of the Neptunian system, *Science*, 246, 1454 (1989).
3. G.L. Tyler, et al., Voyager radio science observations of Neptune and Triton, *Science*, 246, 1466 (1989).
4. B.R. Smith, et al., Voyager 2 at Neptune: Imaging science results, *Science*, 246, 1422 (1989).
5. I. dePater, P.N. Romani and S. K. Atreya, Microwave spectra of Uranus and Neptune: new data and new models, submitted to *Icarus* (1990).
6. S.K. Atreya, *Atmospheres and Ionospheres of the Outer Planets and their Satellites*, Springer-Verlag, New York and Heidelberg, 1986.
7. P.N. Romani and S.K. Atreya, Stratospheric aerosols from CH_4 photochemistry on Neptune, *Geophys. Res. Lett.*, 16, 941 (1989).
8. J. Bishop, S.K. Atreya, B.R. Sandel and P.N. Romani, CH_4, C_2H_2 and K from Voyager/UVS solar occultation experiment, to be submitted to *Geophys. Res. Lett.* (1990).

9. G.S. Orton and J. Appleby, Temperature structures and infrared derived properties of Uranus and Neptune, in: *Uranus and Neptune*, ed. J.T. Bergstralh, NASA CP 2330, Washington, D. C. 1984, p. 89.

10. G. S. Orton, et al., Calibration of the 7-14 min brightness spectra of Uranus and Neptune, *Icarus*, in press (1989).

11. E. Lellouch, et al., Occultation determination of Neptune's oblateness and stratospheric methane mixing ratio, *Nature*, 324, 227 (1986).

12. W. B. Hubbard, et al., Oblateness, radius, and mean stratospheric temperature of Neptune from the 1985 August 20 occultation, *Icarus*, 72, 635 (1987).

13. B. Conrath, private communication (1990).

14. J. B. Pollack, private communication (1990).