

FIRST OBSERVATIONS OF CO AND HCN ON NEPTUNE AND URANUS AT MILLIMETER WAVELENGTHS AND THEIR IMPLICATIONS FOR ATMOSPHERIC CHEMISTRY

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ABSTRACT

We report the discovery of carbon monoxide and hydrogen cyanide in the atmosphere of Neptune through detection of their rotational emission lines in the planet's millimeter spectrum. The (3–2) line of CO at 345.8 GHz was detected with the JCMT radiotelescope, on Mauna Kea, HI. The CO(2–1) line at 230.5 GHz was subsequently observed at the CSO also located on Mauna Kea as was the (4–3) transition of HCN at 354.5 GHz. The discovery of HCN was confirmed with the JCMT. Hydrogen cyanide is confined to Neptune's stratosphere and its mean mole fraction in the 0.003–30 mbar pressure level range is 1.0×10^{-9} . Carbon monoxide is present in both the stratosphere and in the troposphere and observations are consistent with a uniformly mixed mole fraction of 1.2×10^{-6} . Both abundances are inferred with an accuracy of 30%. Uranus was also observed at the same frequencies with the JCMT and upper limits of 1.0×10^{-10} and 3.0×10^{-8} mole fractions were derived for HCN and CO, respectively. The origin of these species in the atmosphere of Neptune and their nondetection in that of Uranus are extensively discussed. The source of CO and HCN in Neptune may be internal or external. In view of difficulties presented by the second assumption, we conclude that the most plausible scenario invokes upward convection of CO and N₂ from Neptune's deep interior. While the amount of N₂ required to make HCN is consistent with current thermochemical models, the observed amount of CO is several orders of magnitude higher than predicted by models and the Prändtl mixing-length theory. That suggests a failure of chemical equilibrium at deep atmospheric levels, allowing excess CO (and presumably N₂) to reach the upper atmosphere. The nondetection of CO and HCN in Uranus may be explained by the lack of a significant internal heat source in the planet and the consequent suppression of vertical convection, at least in a part of the deep atmosphere. On the other hand, both planets exhibit strong depletion of ammonia relative to the solar value of C/N. The assumption that nitrogen is mainly in the form of N₂ in the deep tropospheres provides a simple explanation for the surprisingly low ammonia mixing ratio required to fit the microwave spectra of both Uranus and Neptune. Finally, we discuss the consequences of our results for the origin of the atmospheres of these objects.

Subject heading: planets and satellites: individual (Neptune, Uranus)

1. INTRODUCTION

Atmospheric models of the giant planets developed under the assumption of chemical equilibrium predict that carbon should exist mainly in the form of CH₄ and that nitrogen is essentially locked up in NH₃ in the upper atmospheres of these objects. CO and N₂ should be present only in the deeper atmospheric layers at nonobservable levels. CH₄ has been detected and evaluated spectroscopically in the atmospheres of all four planets, while NH₃ has only been observed on Jupiter and Saturn. The upper tropospheres of Uranus and Neptune are too cold to permit the existence of remotely detectable lines of gaseous ammonia, but the interpretation of the microwave spectra of both planets is consistent with the presence of small amounts of this species in their deep, warmer atmospheres (De Pater, Romani, & Atreya 1991). Whereas the methane mixing ratio on both Uranus and Neptune is at least 30 times the value expected from the solar abundance of carbon (Lutz, Owen, & Cess 1976; Baines & Smith 1990), the amount of

ammonia indicated by the microwave observations is even less than that predicted by solar N/H (De Pater, Romani, & Atreya 1989, 1991).

The existence of nonequilibrium atmospheric constituents resulting from vertical convection from the deep atmosphere into the upper tropospheres of Jupiter and Saturn has been demonstrated by the detection of trace molecules (PH₃, GeH₄, AsH₃) in abundances considerably in excess of those predicted by equilibrium models (Bézar et al. 1989; Noll & Larson 1990). This is also the case for CO in Jupiter's troposphere (Noll et al. 1988) while it is uncertain if the Saturnian CO observed comes from the deep troposphere or is produced in the stratosphere from infalling material originating in Saturn's ring system (Noll & Larson 1990).

The strong atmospheric activity of Neptune revealed by *Voyager* and the relative strength of its internal heat source suggest that nonequilibrium processes should also be significant in this planet. Surprisingly, the question of a disequilibrium chemistry has only been discussed for Uranus, which exhibits a small or zero source of internal heat, but not for Neptune. For Uranus, Stevenson (1984) has suggested that convective upwelling might produce up to 1% of N₂ and 10⁻⁵ of CO in the troposphere. However, Fegley et al. (1991), as the result of a detailed study, concluded that much smaller abundances are to be expected.

Heterodyne techniques and large radio telescopes now oper-

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TABLE 1
NEPTUNE OBSERVATIONS

Transition	Frequency (GHz)	Telescope	Date (1991)
CO(3-2)	345.80	JCMT	May 24, 30
CO(2-1)	230.54	CSO	Jun 19
HCN(4-3)	354.51	CSO	Aug 2
HCN(4-3)	354.51	JCMT	Sep 9

ational in the millimeter and submillimeter range permit the detection of narrow spectral lines and thus the determination of quite small abundances of selected molecular species. Emission lines of CO and HCN have been detected on Titan, using the 30 m radiotelescope of IRAM, at Pico-Veleta, Spain (Marten et al. 1988; Tanguy et al. 1990). In this context, we have undertaken a program of observations of Uranus and Neptune at millimeter wavelengths, using the 15 m James Clerk Maxwell Telescope (JCMT)⁶ and the 10.4 m Caltech Submillimeter Observatory (CSO),⁷ both located on Mauna Kea (Hawaii). The (3-2) and (2-1) lines of CO, centered at 345.79 and 230.54 GHz, respectively, were clearly observed for the first time in emission on the disk of Neptune in 1991 May and June with the two radio telescopes. The (4-3) line of HCN was discovered subsequently on the same planet, in August and September (Marten et al. 1991a, b, 1992). No lines of either molecule were found on Uranus. Additional continuum observations were made with the JCMT, in order to assess broadband spectral features at the CO(3-2) frequency.

In this report of our work, we first present the observations (§ 2). The method for deriving the vertical distributions of CO and HCN in the atmosphere of Neptune is given in § 3, and the results are given in § 4. Section 5 is devoted to discussion and § 6 to the implications of our measurements for the chemistry of the Uranus and Neptune atmospheres. Conclusions are given in § 7.

2. OBSERVATIONS AND RESULTS

The spectral line observations obtained with the JCMT and the CSO radiotelescopes are summarized in Table 1. The main characteristics of both the JCMT and CSO telescopes and receivers are given in Table 2 (see also Matthews 1991; Ellison

⁶ The telescope is managed by the Royal Observatory Edinburgh and funded jointly by the Science and Engineering Research Council (United Kingdom), the National Research Council (Canada), and the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (The Netherlands).

⁷ The CSO is operated by the California Institute of Technology under funding from the National Science Foundation, contract AST-9015775.

et al. 1989), together with the integration times on Neptune. At the epochs of observations, the angular diameters of Uranus and Neptune (3'8 and 2'3, respectively) were considerably smaller than the half-power beamwidth of either the JCMT or the CSO.

At the JCMT the telescope pointing and focus adjustment were maintained by frequent observations of Neptune and Uranus themselves, using the secondary mirror chopped at a frequency of 7.8 Hz with a throw of 60" in azimuth to eliminate atmospheric background variations to first order. By feeding the intermediate frequency output (the "total power" signal—about 1 GHz wide at 3.94 GHz) of the heterodyne receiver into a phase-sensitive lock-in amplifier which takes as its reference input the driving waveform of the chopping secondary mirror, sensitive narrow-band continuum observations of the planets were routinely obtained. Throughout the observations the rms pointing error was less than $\sim 2''$.

For the spectral line observations at the JCMT we also made use of the chopping secondary mirror to remove most of the adverse effects of the atmosphere. These observations were made by chopping 60" in azimuth at a rate of 1 Hz in the standard mode. Two-position chopping was used, in which the source was alternately placed in the signal and reference beams, each for 30 s. Typically, this cycle was repeated 10 times to form a 10 minute "beamswitched" integration. The signals were processed using an acousto-optical spectrometer (AOS) having a total bandwidth of 500 MHz, and an effective spectral resolution of 330 kHz (Matthews 1991). The temperature scale of the spectra was determined by observing the relative power levels when loads at ambient and liquid nitrogen temperature were switched into the beam path of the receiver.

During our first observations with the JCMT on 1991 May 24, we were surprised by the appearance of a clear CO(3-2) line toward Neptune after an integration time of only 10 minutes' duration, while no CO line could be observed toward Uranus. Because the result was so unexpected we carried out a number of checks to confirm its origin and nature. First, since both planets were near the Galactic plane, we observed the sky at two points offset by 1' either side of Neptune. No line was observed, indicating that the observed line was unlikely to arise from a background object. Second, we noted that the CO line had the correct Doppler shift for it to arise in the atmosphere of the planet. Third, in the further observations of Neptune made on May 30, the frequency shift corresponded once again to the velocity expected for Neptune, including the slight additional shift expected due to the intervening time. Subsequent observations continue to confirm this result. The fact that the relative frequency shifts are in the correct sense

TABLE 2
MILLIMETER OBSERVATIONS OF NEPTUNE: SUMMARY

Frequency (GHz)	Main Beam Efficiency B_{eff}	Beam Width B_w	T_{sys} Measured (K)	Receiver Used for Observations	Integration Time (mn)
JCMT 15 Meter Telescope					
345.80.....	0.55	14"4	2150	0.8 mm Schottky	45
354.51.....	0.54	14.1	2550	0.8 mm Schottky	30
CSO 10.4 Meter Telescope					
230.54.....	0.72	31	700	1.3 mm SIS	48
354.51.....	0.60	20	1400	0.8 mm SIS	60

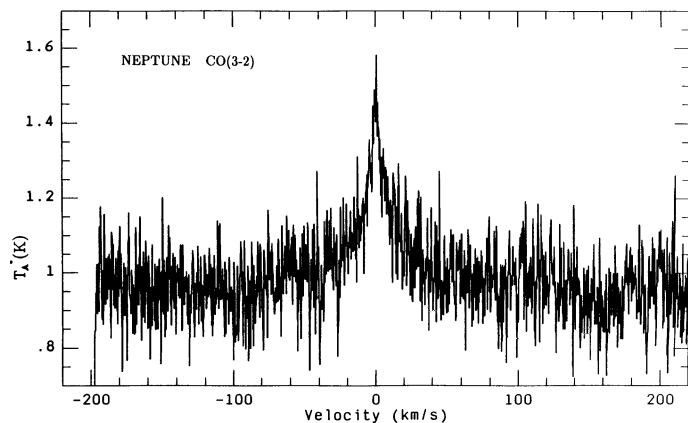


FIG. 1.—Raw data of the average antenna temperature spectrum of the (3–2) line of CO on Neptune centered at 345.80 GHz, recorded with the JCMT on 1991 May 24 and 30. The effective spectral resolution is 0.35 MHz. The integration time on Neptune is 45 minutes. The average system temperature is 2150 K.

showed that the observed line was in the expected sideband of the receiver and remove any remaining doubt that the observed feature was in fact CO(3–2). The average of the spectra recorded on May 24 and 30, corresponding to a total integration time of 90 minutes, and after correction of the Doppler shift for the 2 days, is shown in Figure 1.

This, and other spectra obtained at the JCMT and CSO, have been placed on a common temperature scale (T_a^*), corrected for atmospheric and telescope losses. The calibration is estimated to be accurate to $\sim 15\%$. In all cases a linear baseline has been removed from the raw data, and the zero level of the temperature scale is unknown. The latter, however, is difficult to measure reliably with an AOS, and we resorted to another approach to obtain this information. We discuss this below.

On June 19, additional confirmation of the detection of CO on Neptune was obtained with the observations of the $J = 2-1$ line at 230 GHz using the CSO. The spectrum acquired after an integration time of 48 minutes on the planet and at a resolution of 0.5 MHz is shown in T_a^* units in Figure 6b. A linear baseline has been removed, and we do not know the zero level of the temperature scale.

Our success in detecting CO led us to search for the $J = 4-3$ line of HCN at 354 GHz. This transition was readily detected at the CSO on August 2 (Figs. 2 and 5a), and verified with the JCMT on September 9 (Fig. 5b). On the latter occasion, Uranus was observed for a total of 70 minutes, but no line was detected. The CSO facility 1.3 and 0.8 mm SIS receivers were used in conjunction with a 500 MHz AOS, giving a total bandwidth of 650 km s^{-1} at 230 GHz and 415 km s^{-1} at 354 GHz at an effective spectral resolution of 490 KHz (Machilvich & Schinckel 1990). All observations were made with the telescope switched on and off the source. The temperature scale was calibrated with a standard chopper wheel technique and is estimated to be accurate to $\sim 30\%$.

In addition to spectral line measurements, observations of the continuum emission from Saturn, Uranus, and Neptune within a frequency range defined by the band of the spectral line receiver were performed with the JCMT. These measurements made use of the same instrumental setup (i.e., with the chopping secondary mirror, and phase-sensitive detector system) as for the pointing and focus determinations. Having

first pointed on each object, we then integrated on source for either 1 (for Saturn) or 2 minutes (Uranus and Neptune).

Using this approach, we obtained a signal from each object in millivolts. In order to relate this to either flux density or brightness temperature, we next used the standard heterodyne chopper wheel calibration method to measure the sky temperature both on and off source. Only Saturn was bright enough to allow an accurate determination of this equivalence. The off-source sky brightness allowed us to determine the atmospheric transmission. Then, using the ratio between the strength of the chopped signal, and the temperature difference on and off source, together with the atmospheric transmission and a knowledge of the telescope losses, allowed us to derive the measured antenna temperature (T_a^*) for each object.

In order to obtain the true brightness temperature (T_B) of a planetary disk of apparent angular size θ we then use the relationship:

$$T_B = T_a^* \frac{1}{B_{\text{eff}}} \frac{1}{1 - 2^{-(\theta/B_w)^2}},$$

where B_{eff} is the beam efficiency and B_w is the half-power beam width. The third term of the right-side of the equation represents the coupling factor between the beam (assumed to be Gaussian) and the planetary disk. Their values for each radio-telescope are given in Table 2.

From our observations we then obtain brightness temperatures of Uranus and Neptune of 85.8 and 69.0 K, respectively, after applying the Planck correction ($\sim 8 \text{ K}$ at 350 GHz). For Saturn itself, we obtain $\sim 135 \text{ K}$, consistent with previous estimates if we take into account the small contribution of the rings of Saturn (Muhleman & Berge 1991). The expected errors on these data are dominated by systematic errors in our knowledge of the telescope parameters (beamwidth, beam efficiency, and telescope losses particularly) rather than measurement errors (the internal errors on each data set do not exceed 2%), but are unlikely to be greater than $\pm 10\%$.

Although these results are in good general agreement with previous broad-band observations in the same spectral range (see § 4 and Figs. 7 and 8), it is worth noting that the result for

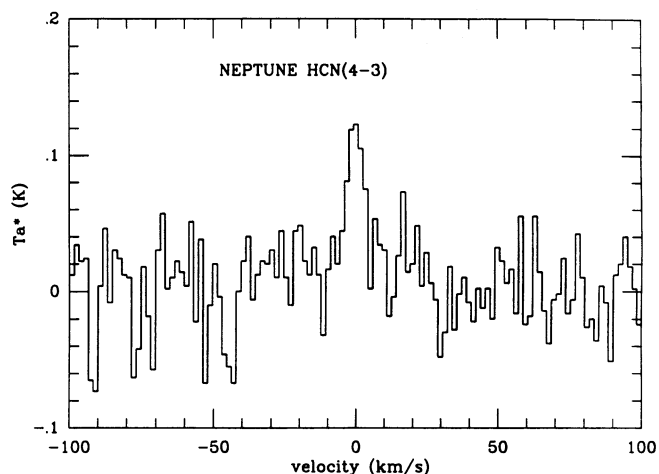


FIG. 2.—Raw data of the average antenna temperature spectrum of the (4–3) line of HCN on Neptune, centered at 354.51 GHz, recorded at the CSO on 1991 August 2. The effective spectral resolution is 2 MHz. The integration time on Neptune is 60 minutes. The average system temperature is 1400 K.

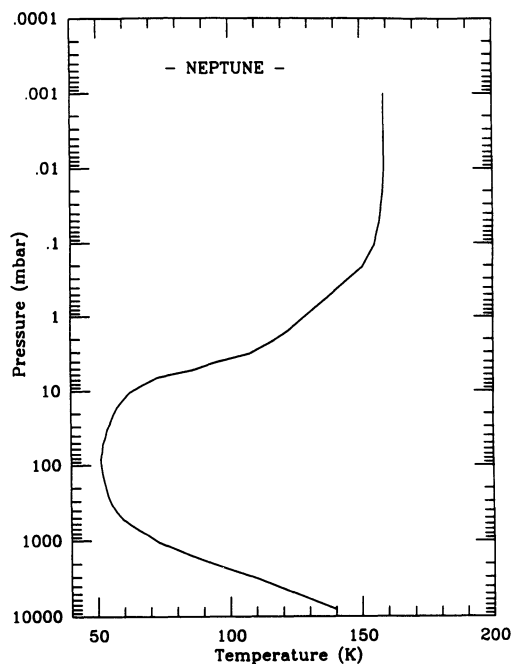


FIG. 3.—Temperature vs. pressure profile on Neptune, derived from *Voyager* radio occultation and ground based star occultations by Bézard et al. (1991). The H_2/He ratio is taken equal to 81/19, as in Conrath et al. (1991). See text for explanation.

Neptune is significantly lower (by ~ 12 K) than would be indicated by Orton et al. (1986). However, as discussed below, it is this particular observation, together with previous broad-band measurements made by other authors in the 80–440 GHz spectral range, that permit us to conclude that CO absorption lines are formed in the troposphere of Neptune (see Fig. 7).

3. RADIATIVE TRANSFER AND OPACITIES

Synthetic spectra of *Neptune* were modeled from a thermal profile (Fig. 3) derived by Bézard et al. (1991) from the *Voyager* radio occultation experiment (Lindal et al. 1990) and from ground-based stellar occultation measurements (Hubbard et al. 1987). The radio-occultation profile temperature versus pressure depends upon the mean molecular weight m and the mean coefficient of refractivity. The He/H_2 ratio is taken equal to 19/81 according to Conrath et al. (1991a). (Note that this value may be different; see § 7.1). Then m is equal to 2.39 in the upper troposphere where the CH_4 vapor pressure is quite low and is somewhat higher in the atmospheric regions where the abundance of methane is large. For the upper stratosphere, Bézard et al. (1991) rescaled the radio and stellar occultation profiles to $m = 2.41$, assuming a 0.1% CH_4 mole fraction. In the deep atmosphere, the abundance of methane was taken equal to 2%. Methane was assumed to follow the saturation law above the condensation level located near 1.3 bar. The thermal lapse rate is assumed to be adiabatic below this level.

For calculations of the *Uranus* spectrum, we used the thermal profile of Lindal et al. (1987). Methane was considered to be negligible in the stratosphere and similar in abundance to the values on Neptune in the deep atmosphere. The H_2/He ratio was taken equal to 85/15, as in Conrath et al. (1987).

Continuum opacities on both planets result mainly from pressure-induced absorptions due to collisions between $H_2 - H_2$, $H_2 - He$, and $H_2 - CH_4$. The absorption coefficients

used for $H_2 - H_2$ are based on the work of Dore, Nencini, & Birnbaum (1983) while those for $H_2 - He$ take into account the work of Bacht (1986). $H_2 - CH_4$ coefficients are from A. Borysov (private communication). The $H_2 - He$ ortho-para ratio was assumed to be the equilibrium value, as in Conrath et al. (1991a). The far-wing contribution of NH_3 microwave lines was calculated as in De Pater & Massie (1985) and the wings of submillimeter lines were modeled as in Marten et al. (1980).

Spectroscopic parameters for CO, HCN, and NH_3 lines were taken from the JPL catalog (Poynter & Pickett 1982) and the GEISA catalog (Husson et al. 1986). We used a Voigt line shape with H_2 -broadened half-widths of 0.075 and 0.14 $cm^{-1} atm^{-1}$ for CO and HCN, respectively (Draeger & Williams 1968; Derozier 1987).

HCN must condense at temperatures occurring in the lower stratosphere and the upper troposphere of Neptune. A two-parameter saturation law was used, following data given in the Handbook of Chemistry and Physics (1987). For the considered abundances of HCN, this gas condenses around the 110 K atmospheric level. CO does not condense at Neptunian temperatures and is a very stable molecule. In principle, its vertical distribution depends upon the value of the eddy diffusion coefficient (Landry, Allen, & Yung 1991). However, considering the high level of convective activity observed on Neptune (see below), it is reasonable to assume that CO is uniformly mixed in a large part of the observable atmosphere, whatever its origin. The vertical distributions of CO and HCN resulting from these calculations are shown in Fig. 4.

4. RESULTS AND ANALYSIS

The antenna-temperature spectra of the (4–3) line of HCN recorded on Neptune by CSO and JCMT are shown in Figure 5a and 5b. Both spectra are well fitted by synthetic spectra calculated from the vertical HCN distribution shown in Figure

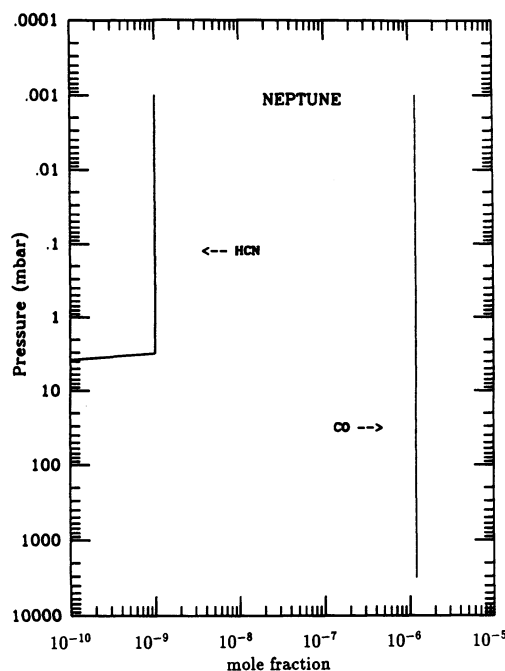


FIG. 4.—Vertical distributions of CO and HCN in the atmosphere of Neptune which lead to the best fit of observations. HCN is constrained to follow the saturation law and then condenses in the lower stratosphere.

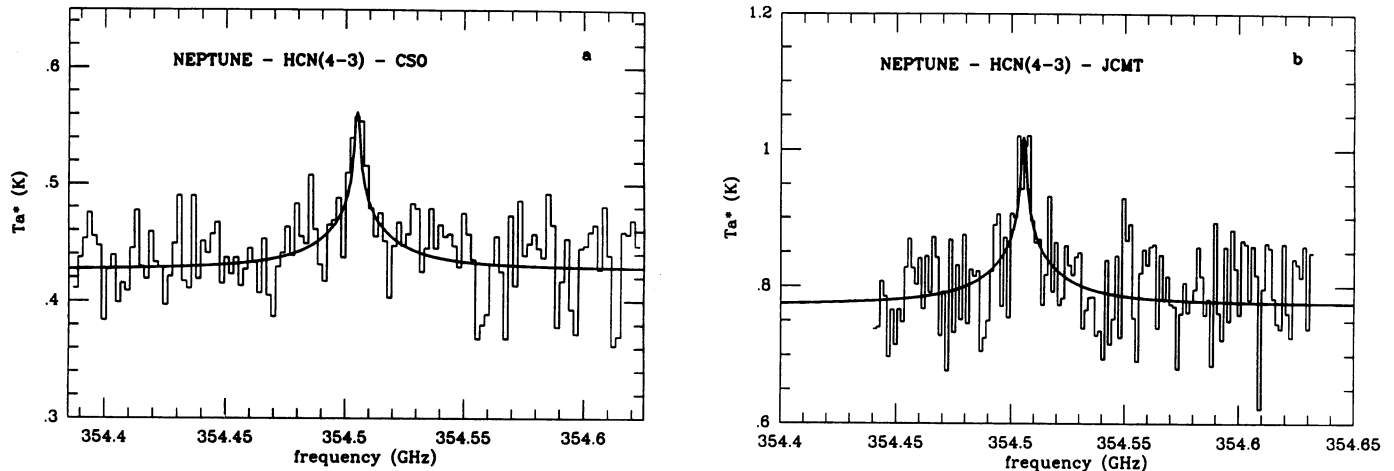


FIG. 5.—(a) Comparison of the antenna temperature spectrum of the (4–3) line of HCN on Neptune observed at the CSO with the synthetic spectrum calculated from the HCN vertical distribution shown in Fig. 4. The spectral resolution is 2 MHz. (b) Comparison of the antenna temperature spectrum of the (4–3) line of HCN on Neptune observed at the JCMT with the synthetic spectrum calculated from the same vertical HCN distribution. In this case, the spectral resolution is 1.5 MHz.

4. Since the abundance of HCN is substantial only at low pressure levels, the emission line is relatively narrow. Accordingly, the far wings of the line do not contribute to the planetary radiance in the continuum, and no absorption line is expected. Assuming that the thermal profile is precise enough, the synthetic calculation of the continuum is well defined and the observed continuum may be constrained to be in agreement with the theoretical one. In other words, the contrast between the top of the line and the continuum is reasonably well determined.

The spectra of the (3–2) and (2–1) lines of CO are shown in Figures 6a and 6b, respectively, together with the predicted line shapes derived from the CO vertical distribution shown in Figure 4. However, if CO is really present in the troposphere, the CO line is in fact much broader than the 500 MHz bandwidth of the spectrometers used at the JCMT and the CSO, and we detect only the core of the line in emission while in the wings the line would be in absorption.

With this in mind, and for comparison with theoretical predictions, we have calculated the spectrum of Neptune in the range 80–440 GHz from the vertical distributions of CO and

HCN (Fig. 4). Our results are shown in Figure 7. As previously mentioned, the HCN emission lines do not have extended pressure-broadened wings, but the $J = 1-0$, $2-1$, and $3-2$ lines of CO are clearly dominant features of the spectrum, in absorption.

Previous observations of the brightness temperature of Neptune within this range are shown superposed on our synthetic spectrum. Broad-band measurements made by Orton et al. (1986), as revised by Conrath et al. (1991b), with the UKIRT and the IRTF are not really conclusive concerning the presence or absence of CO because of the large bandwidth of the filters used. This is also the case for the recent measurement by Muhleman & Berge (1991) made near the $J = 1-0$ line at ~ 2.66 mm wavelength with the three element interferometer of 10.4 m telescopes at the Owens Valley Radio Observatory.

Our recent narrow-band observations of the continuum that covers part of the region of the CO line is intriguing in this respect and deserves some further discussion.

We have obtained a brightness temperature for Neptune of 69 K, with an error estimated at ~ 5 K. This observation was made with the receiver tuned to the frequency of the CO(3–2)

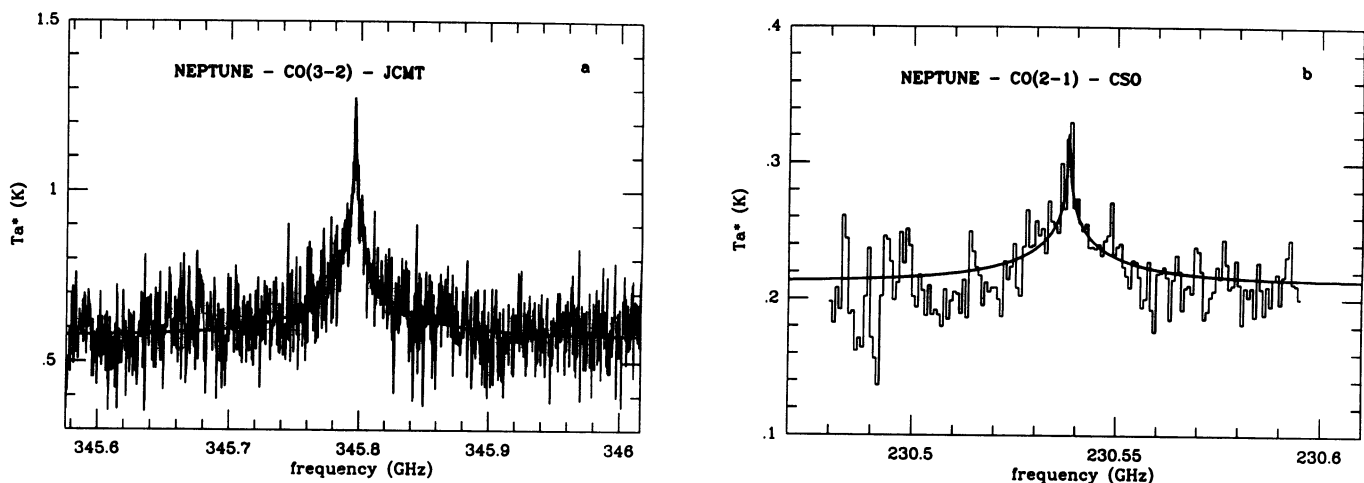


FIG. 6.—(a) Comparison of the antenna temperature spectrum of the (3–2) line of CO observed at the JCMT with the synthetic spectrum calculated from the CO vertical distribution shown in Fig. 4. The spectral resolution is 0.35 MHz. (b) Comparison of the antenna temperature spectrum of the (2–1) line of CO observed at the CSO with the synthetic spectrum calculated from the same CO vertical distribution. In this case, the spectral resolution is 0.5 MHz.

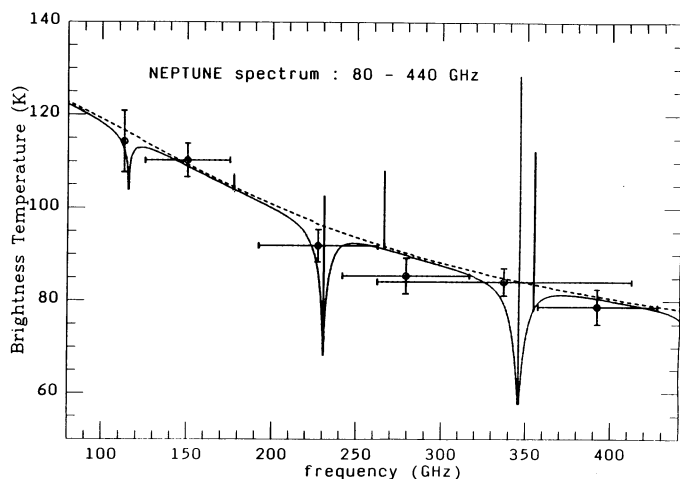


FIG. 7.—Brightness temperature spectrum of Neptune calculated in the 80–440 GHz spectral range from the thermal profile and the vertical distributions displayed in Figs. 3 and 4. The spectrum due to $\text{H}_2 - \text{H}_2$, $\text{H}_2 - \text{He}$, $\text{H}_2 - \text{CH}_4$ collision-induced absorption and to the far wings of the NH_3 lines is shown as a dashed line. The spectrum resulting from adding the opacity due to CO and HCN lines is shown as a continuous line. The cores of these lines appear in emission, as indicated by a vertical line. HCN is only in emission as explained in the text. For comparison, are shown measurements by Orton et al. (1986) (open circles), and the interferometric observation of Muhleman & Berge (1991) at 115 GHz. Horizontal bars indicate the radiation bandwidth of the photometric measurements.

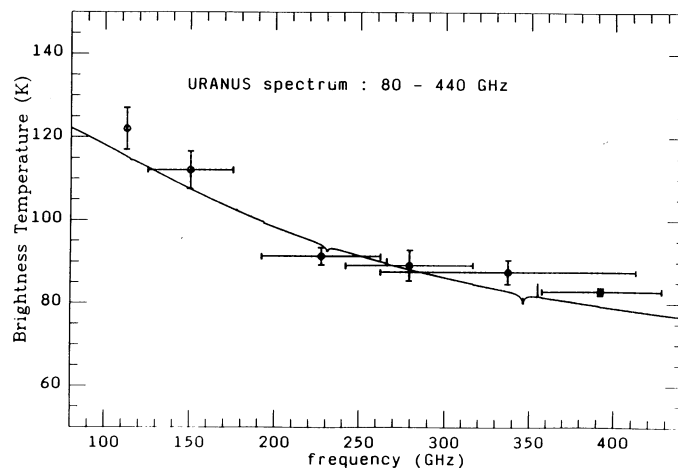


FIG. 8.—Brightness temperature spectrum of Uranus as in Fig. 7. The used thermal profile is from Lindal et al. (1987) and the abundances of CO and HCN are taken equal to the upper limits derived from heterodyne observations. HCN is constrained to follow the saturation law and, accordingly, is negligible in the troposphere. Observations are indicated as in Fig. 7.

these upper limits in the 80–440 GHz range is compared, in Figure 8, with broad-band measurements. This shows that the continuum is indeed consistent with observations.

line (345.8 GHz). However, since the lower sideband of the mixer response was used to observe the line, and no image sideband rejection filter was employed, signals were also received from the upper sideband. In this particular instance, continuum signals were therefore received from two ~ 1 GHz wide bands centered at ~ 345.8 and 353.8 GHz. Since the ratio of the gains of the two sidebands at these frequencies is about unity, the brightness temperature derived is the *average* of these values measured in the two sidebands. Close examination of Fig. 7 shows that we predict considerably more power to be received in the upper sideband at 353.8 GHz, since this is positioned well out in the wing of the CO line [the observed band does not, however, include the HCN(4–3) line at 354.5 GHz]. Our synthetic spectrum predicts a brightness temperature of ~ 78 K around this frequency. Thus, in order to result in an average of 69 K for both sidebands, the lower sideband, at the center of the CO line, would be expected to “see” a brightness temperature of ~ 60 K. This value agrees very well within the estimated errors with the predicted minimum value of the broad CO(3–2) absorption feature and provides good support for the model of the CO distribution in Neptune’s atmosphere.

We may conclude that CO is present in the troposphere of Neptune. The combination of observation and theory in fact requires that strong absorption features are present. The errors preclude a precise determination of the troposphere abundance but the results are consistent with the assumption of a vertical distribution of CO which is constant with height (i.e., well mixed) in both the troposphere and the stratosphere.

Uranus offers a strong contrast to the case of Neptune. From our observations we conclude that the CO and HCN stratospheric mole fractions in Uranus are *not greater* than $\sim 3.0 \times 10^{-8}$ and 1.0×10^{-10} , respectively, assuming vertical distributions similar to those of Neptune. (The upper limit for CO is 30 times lower than that previously derived by De Bergh, Lutz, & Owen 1985). The spectrum calculated from

5. DISCUSSION

5.1. Inferred Distributions

On Neptune, the CO and HCN stratospheric mole fractions appear to be equal to 1.2×10^{-6} and to 1.0×10^{-9} , respectively. The fact that observations made with two different telescopes and in different conditions agree so well must be noted.

The normalized contribution functions corresponding to the (4–3) line of HCN are shown in Figure 9. Even in the core of the line, the flux originating from the troposphere, where the HCN mixing ratio is practically zero, is not negligible. Accordingly, the thermal profile and the opacity in this region of the atmosphere must be precisely known in order to evaluate properly the HCN stratospheric contribution to the whole emission from which the HCN abundance is derived. The tropospheric opacity is mainly due to the H_2 collision-induced absorption which varies as the square of the pressure and thus is practically zero in the stratosphere. That is confirmed by the behavior of the contribution function at 50 MHz from the center of the HCN line, since it is almost entirely confined to the troposphere. We believe that our measurements do not permit the retrieval of firm information on the vertical distribution of the stratospheric HCN. The best least-squares fit to the observations corresponds to a mixing ratio that is constant with altitude.

The contribution functions corresponding to the (3–2) and (2–1) lines of CO are shown in Figures 10 and 11, respectively. Although the two contribution functions peak at similar levels in the stratosphere, the function corresponding to the (2–1) line is considerably broader than the one corresponding to the (3–2) line. In fact, the troposphere contributes substantially to the flux emitted in the (2–1) line while this is not the case for the (3–2) line. As a result, it is likely that, if they existed, substantial vertical variations of the CO abundance would have been detected from comparison of the two lines. That is not the case. We conclude that heterodyne measurements indicate that CO

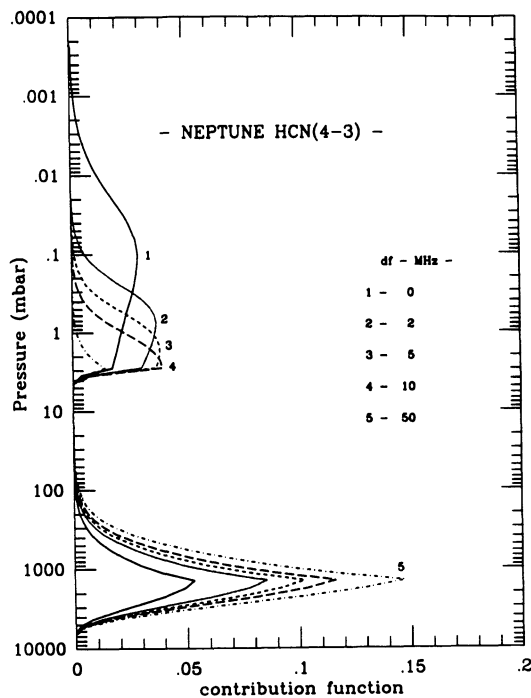


FIG. 9.—Contribution functions calculated at various frequencies around the (4–3) HCN line frequency. df is the frequency shift (in MHz) from the line center. The vertical distribution of HCN displayed in Fig. 4 has been used.

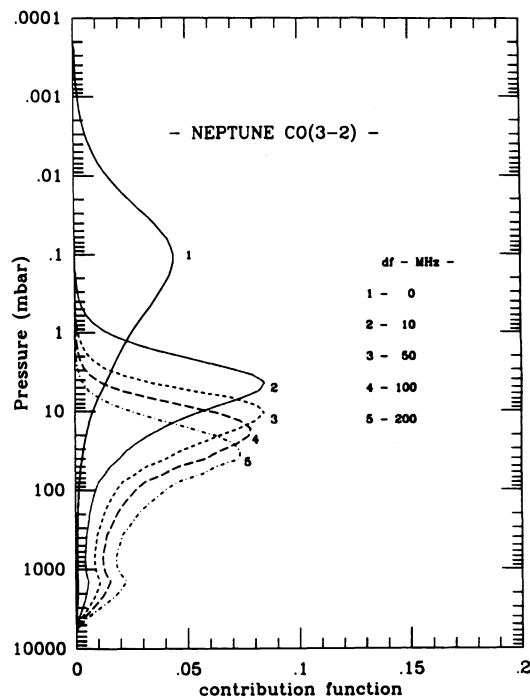


FIG. 10.—Contribution functions calculated at various frequencies around the (3–2) CO line frequency. df is the frequency shift (in MHz) from the line center. The vertical distribution of CO displayed in Fig. 4 has been used.

is present in both the stratosphere and the troposphere and is apparently uniformly mixed at the altitudes probed by these observations, in accord with expectation.

5.2. Error Analysis

The uncertainty due to the noise measurement is negligible compared to systematic errors resulting from uncertainties in the calibration and in the assumed thermal profile.

1. *Influence of calibration uncertainties.*—In § 2, we have estimated the uncertainty in the calibration to be $\sim 15\%$ for JCMT observations and 30% for CSO data.

2. *Influence of the temperature profile.*—The assumed thermal profile is relatively well defined in the troposphere but much less so in the stratosphere. In the troposphere, the thermal profile retrieved from the *Voyager* radio occultation experiment depends in principle on the H_2/He ratio, but Conrath et al. (1991a) have shown that profiles calculated for various helium abundances coalesce in the troposphere. At deeper levels, where the CH_4 mixing ratio is not negligible anymore, the retrieved profile warms up, but that does not affect the millimeter spectrum too much because the additional opacity from $CH_4 - H_2$ tends to decrease the brightness temperature. To some extent, therefore, the two effects compensate for one another. On the contrary, in the stratosphere, the retrieved profile depends upon the mean molecular weight. Hence the uncertainty in the helium abundance determined at the tropopause and the value of the CH_4 mixing ratio which is poorly determined and may vary with altitude become very significant. At the levels probed by the stellar occultation, the uncertainty is still higher since Roques, Sicardy, & Brahic (1993) have shown that the temperature near the $25 \mu\text{bar}$ level varied from 140 to 190 K during the 1983–1990 period.

3. *Total uncertainties.*—From these considerations it is diffi-

cult to evaluate systematic errors very precisely. We conservatively consider that the inferred abundances are determined with an uncertainty of $\sim 30\%$, including all sources of errors and taking into account the whole set of observations.

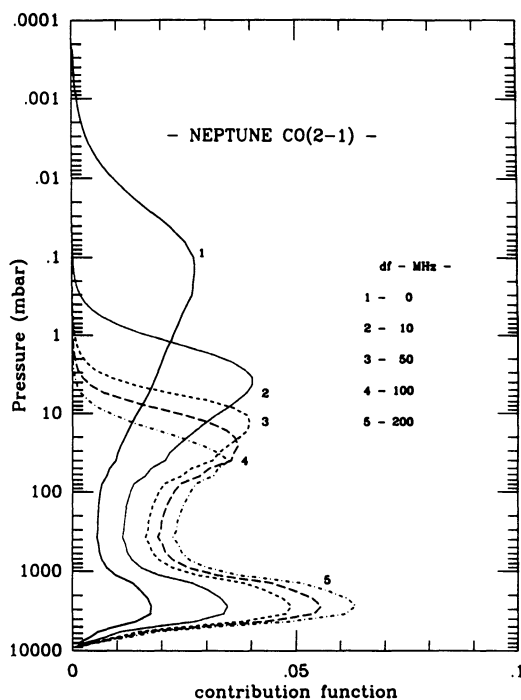


FIG. 11.—Contribution functions calculated at various frequencies around the (2–1) CO line frequency, as in Fig. 10.

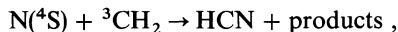
5.3. Comparison with Other Observations

In response to our IAU Circular announcement of the discovery of CO and HCN in the atmosphere of Neptune (Marten et al. 1991a), Rosenqvist et al. (1992) observed the (2–1) line of CO and the (3–2) line of HCN of Neptune on 1991 October at the IRAM 30 m Radiotelescope. The abundances they derived are somewhat lower than ours ($6.5 \pm 3.5 \times 10^{-7}$ for CO and $3 \pm 1.5 \times 10^{-10}$ for HCN). We do not know the reasons for these differences. We note, however, that their values of the continuum brightness temperature (47 K for CO and 79 K for HCN) are in conflict with both the theoretical values and the observations of Orton et al. (1986) (see Fig. 7). We do not know either if their calculations are consistent with the continuum observations.

Finally, our combined observations of the (3–2) line and of the (2–1) line of CO do not reveal the decrease of CO abundance with altitude they suggest from their observation of the (2–1) line by itself.

6. ORIGIN OF CO AND HCN IN THE ATMOSPHERE OF NEPTUNE

We have demonstrated that CO is present in both the troposphere and the stratosphere of Neptune, suggesting that it originates in the deep interior of Neptune. However, it could also result from chemical reactions of incoming extraplanetary material with atmospheric species. It is highly unlikely that the stratospheric HCN could have its origin in Neptune's interior since any upwelling HCN, if present, would be cold-trapped at the tropopause of Neptune where its mixing ratio, limited by saturation, as for NH_3 , would be some 20 orders of magnitude less than its measured stratospheric value. Therefore, we propose that HCN is formed locally in the stratosphere by the following chemical reactions which are similar to those on Titan (Yung, Allen, & Pinto 1984):



$^3\text{CH}_2$ is produced by the ultraviolet photolysis of CH_4 which is present in large quantities in Neptune's upper atmosphere (Atreya, Bishop, & Romani 1991; Bishop et al. 1992); CH_3 results from a reaction between Neptune's H_2 and $^1\text{CH}_2$, which is also a CH_4 photolysis product. The ground-state nitrogen atoms, $\text{N}(^4\text{S})$, may be produced by dissociation of N_2 welling up from Neptune's interior, or they could have an extraplanetary origin, e.g., on Triton. In the next subsections we will weigh the arguments in favor of and against the indigenous and extraplanetary origins of both CO and nitrogen.

In order to evaluate these arguments we first estimate the flux of nitrogen atoms in Neptune's atmosphere required to produce the observed HCN mixing ratio of 1.0×10^{-9} in the stratosphere. We can estimate this flux by calculating the HCN column production rate using the flux equation (see, e.g., Atreya 1986):

$$\Phi_N = q_{\text{HCN}} = K [\text{HCN}]/H_a = K f_{\text{HCN}} n_a/H_a$$

where q_{HCN} , $[\text{HCN}]$, and f_{HCN} are, respectively, the column production rate (in $\text{cm}^{-2} \text{s}^{-1}$), number density (in cm^{-3}) and the mixing ratio of HCN in the stratosphere (taken constant), n_a and H_a are the atmospheric density and the scale height, respectively, and K is the corresponding eddy diffusion coefficient. The production region of HCN is around the 1 mb level, where the atmospheric temperature is ~ 125 K. The principal

loss of HCN is by downward diffusion, followed by condensation below the (approximately) 110 K level in Neptune's atmosphere. The value of K at ~ 1 mb is on the order of $10^5 \text{ cm}^2 \text{ s}^{-1}$ (Bishop et al. 1992), although values somewhat greater cannot be ruled out. With the above information, we estimate the required N atom flux in Neptune's stratosphere to be $1.9 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$. Larger values of K would require a correspondingly greater flux of nitrogen atoms.

6.1. Internal Origin of N_2 and CO

There are no observations that preclude the existence of N_2 in the upper troposphere of Neptune. Analysis of *Voyager* IRIS spectra in the 200–400 cm^{-1} range permits the evaluation of the mean molecular weight, m , in this part of the atmosphere. Conrath et al. (1991a) find $m = 2.39$. Should the atmosphere be composed of only hydrogen and helium, the H_2/He ratio is equal to 81/19. All species not condensable at the relevant temperatures, except for neon and nitrogen, should have a negligible contribution to m (Conrath et al. 1987, 1991a). The vapor pressure of N_2 at these temperatures is great enough to allow a mole fraction as high as 1.7% at the tropopause. In such a case, the $\text{H}_2 - \text{N}_2$ collision induced absorption would modify the shape of the calculated spectrum. This effect allowed Gautier et al. (1992) and Conrath et al. (1992) to set an upper limit of 0.3% N_2 in Neptune's atmosphere without violating the requirement of a satisfactory fit to the *Voyager* spectra. It is noteworthy that for 0.3% of N_2 , the H_2/He ratio is equal to 85/15, the same as on Uranus, which appears to be the protosolar value (Conrath et al. 1987). If the CH_4 mixing ratio is 2%, as we have assumed above, then 0.3% N_2 is also an upper limit on the total nitrogen content of the atmosphere, assuming carbon and nitrogen are released from the core in solar proportions. In other words, if the N_2 mixing ratio is actually 0.3%, then all the nitrogen in the observable atmosphere is in the form of N_2 . This value for the N_2 abundance therefore can be considered as a firm upper limit.

No thermochemical models have yet been published for the atmosphere of Neptune, so it is not possible to compare this result with any predictions. However, models that have been developed for Uranus may actually be more appropriate for Neptune, since these models have all assumed that the transfer of energy in the atmosphere of Uranus is dominated by convection, thereby producing an adiabatic lapse rate (Fegley & Prinn 1986; Fegley et al. 1991). As Wallace (1980) pointed out long ago, this cannot be true because of the low internal heat flux on Uranus (see § 6.3). Fegley et al. (1991) assumed values of K for Uranus ranging from 10^7 to $10^8 \text{ cm}^2 \text{ s}^{-1}$, which is appropriate for convective heat fluxes of 10–100 $\text{ergs cm}^{-2} \text{ s}^{-1}$. In fact the internal energy source of Uranus is indeed within this range, producing $42 \pm 42 \text{ ergs cm}^{-2} \text{ s}^{-1}$ while Neptune generates $433 \pm 46 \text{ ergs cm}^{-2} \text{ s}^{-1}$ (Pearl & Conrath 1991). Since K is proportional to the cube root of the convective flux, the value of K for Neptune should be ~ 1.7 times the value of Uranus. With this slight modification, we may then use the predictions of the Uranus models to interpret the Neptune results.

The case of N_2 is quite straightforward, since Figure 12 of Fegley et al. (1991) indicates that the predicted tropospheric mixing ratio is fairly insensitive to the assumed rate of vertical mixing in the deep troposphere of Uranus, and thus presumably of Neptune, considering the large range of eddy diffusion coefficients used by the authors. As a consequence, the observed N_2 mixing ratio would depend mainly on the

assumed elemental enrichment over the solar composition. From Figure 13 of Fegley et al. (1991), an enrichment factor from 30 to 75, which corresponds to the estimates of the carbon abundance on Neptune (Lutz, Owen, & Cess 1976; Baines & Smith 1990; Lindal et al. 1990), gives an N_2 mixing ratio of $3\text{--}7 \times 10^{-5}$. This is the range of values needed to produce an HCN mole fraction of 1.0×10^{-9} , with the cascading cosmic rays (see below) as the primary dissociating mechanism for N_2 (Atreya et al. 1992).

Molecular nitrogen convected to the upper atmosphere can undergo dissociation to yield ground-state $N(^4S)$ and excited $N(^2D)$ atoms. The production of nitrogen atoms by the solar EUV dissociation of N_2 is inhibited due to the presence of much more copious amounts of H_2 which absorbs the radiation below 1000 Å in its Lyman and Werner bands and its continuum. The other possibility for dissociation of N_2 is by charged particles, which will produce equal amounts of $N(^4S)$ and $N(^2D)$ atoms. The magnetospheric power input implied by the observed auroral intensity at Neptune is between 10^8 and 10^9 W (Broadfoot et al. 1989; Sandel et al. 1990). The precipitation of these particles is confined to the magnetic poles, but even more important, the particles not only have to be very energetic, our initial calculations indicate that their power input is too low to produce the needed N atom flux. Galactic cosmic rays are another potentially important source of charged particles. The secondary electrons produced from the cascading cosmic rays are expected to dissociate N_2 from the stratosphere down to pressures around 10 bars. Only the most energetic cosmic rays with energies in excess of 1 BeV will make it to the deep troposphere. Because of the very low flux of these energetic cosmic rays, however, the nitrogen atom production in the troposphere would be insignificant. In fact, the cross section for the absorption of cosmic rays in the atmosphere of Neptune is 8×10^{-26} cm², which implies that the primary cosmic rays will penetrate to an atmospheric pressure level of only 50–100 mb. Most of the nitrogen atom production from the cascading cosmic rays occurs from the upper stratosphere ($p \geq 0.1$ mb) down to about the tropopause level on Neptune. In the stratosphere, the nitrogen atoms would react with CH_3 and CH_2 to produce HCN, as discussed earlier. It is important to point out that possible reactions of nitrogen with H_2 in the troposphere (or in the stratosphere, for that matter) do not alter this conclusion, as discussed below.

In principle, nitrogen atoms in the ground state, $N(^4S)$ or simply N, can react with H_2 to produce NH_2 radicals at high pressures such as those prevalent in Neptune's troposphere. The latest laboratory measurements indicate that the rate constant for this spin forbidden, termolecular reaction is very small. Only a very low *upper limit* of 1×10^{-36} cm⁶ s⁻¹ at room temperature and relatively high pressure has been obtained (Petrishchev & Sapozhkov 1981). Since, scarcely any nitrogen atoms are produced by cosmic rays in the troposphere, the possibility of their removal by reaction with H_2 there is a mute point. In the stratosphere where the pressures are much lower, and so are the temperatures (~ 100 K), there is even a lower likelihood of the N atoms reacting with H_2 . It is also important to note that the only actual measurements (not upper limit) of the reaction between N and H_2 are at high temperature and pressure, and they too give an extremely small value of the rate constant, as low as $3.94 \times 10^{-15} e^{(-16606/T)} \text{ cm}^3 \text{ s}^{-1}$ (Koshi et al. 1990). Moreover, the product of this reaction is NH. On the other hand, there is some likelihood of the reaction between nitrogen atoms in the excited state, $N(^2D)$, which have an energy level 2.38 eV above

the ground state, and H_2 . It is not known with certainty whether the $N(^2D)$ atoms are simply quenched to ground state by H_2 or they react with it to form NH; the rate constant of the process is 5×10^{-12} cm³ s⁻¹ at room temperature (Donovan & Husain 1970). Similar possibilities exist for the interaction between $N(^2D)$ and CH_4 ; additionally, there is also a possibility of direct HCN formation (Blades & Winkler 1951). Even if the interaction between $N(^2D)$ and H_2 led to the production of NH, it does not imply a catastrophe as $N(^2D)$ account for only half of the total N atom production by cascading cosmic rays; the other half in the ground state are still available for reaction with CH_3 and CH_2 . In summary, we wish to state that although additional laboratory measurements are highly desirable and extremely important to fully understand the fate of nitrogen atoms and to properly model the HCN production rate on Neptune (and in the outer solar system in general), the available data point to the removal of nitrogen atoms in Neptune's atmosphere by the hydrocarbons, with subsequent formation of HCN. Preliminary calculations also indicate that a level of 0.3% of N_2 is more than sufficient for the cascading cosmic rays to produce the nitrogen atom flux in the stratosphere needed to account for the observed 10^{-9} (ppb) level of HCN.

There is also a very slim possibility of the formation of HCN directly in the troposphere by the cosmic-ray-induced chemical reactions between N_2 and CH_4 (most likely their dissociation products). Any such HCN would be cold trapped at the tropopause and would not make it to the stratosphere. Another possibility, proposed previously for Jupiter (Kaye & Strobel 1983), is the UV photolysis of aziridine, C_2H_5N , which may be produced below the NH_3 condensation level on Neptune by reactions between NH_2 and CH_3 , both of which may be dissociation products of NH_3 and CH_4 following the precipitation of the most energetic cosmic rays. Because of the relatively low flux of such cosmic rays, we regard this scenario for the formation of HCN as far-fetched.

The case for CO is less clear since its tropospheric abundance depends in principle on the value of the eddy diffusion coefficient K . Assuming a mole fraction of CH_4 of 2% in the deep atmosphere, the observed CO/ CH_4 ratio appears to be on the order of 6×10^{-5} , which corresponds, according to Fegley et al. (1991), to a quench temperature ~ 1700 K. That is in disagreement with the theoretical predictions of these authors who derived a CO/ CH_4 ratio of $\sim 10^{-9}$ and quench temperatures of 830–880 K for eddy coefficient values $\sim 10^7\text{--}10^8$ cm² s⁻¹. In fact, calculations made by Fegley & Prinn (1986) indicate that a CO tropospheric abundance of 1×10^{-6} requires a value of K higher than 1×10^{14} cm² s⁻¹, while Fegley et al. find $K \sim 2 \times 10^{18}$ cm² s⁻¹ for $T_{\text{quench}} \sim 1700$ K. The latter authors note that this value of K corresponds to physically impossible vertical mixing velocities ($\sim 10^5$ times sound speed in a solar composition gas) and internal heat fluxes ($\sim 10^{32}$ ergs cm⁻² s⁻¹). In other words, our discovery that the CO mixing ratio on Neptune is 1.2×10^{-6} is grossly incompatible with thermochemical models associated with the Prandtl mixing theory. On the other hand, it is intriguing that such models are successful for Jupiter and Saturn, where values of $K \sim 10^8\text{--}10^9$ cm² s⁻¹ seem to account for conditions in the deep atmospheres (Stone 1976; Prinn et al. 1984). In the case of Neptune, the problem may lie in part with a breakdown of the Prandtl mixing-length theory.

Alternatively, the excess CO may reflect a decrease in the efficiency of the $CO \rightarrow CH_4$ reaction caused by poor catalysis, as appears to be the case for $N_2 \rightarrow NH_3$ (see § 6.3). If we reject

this possibility, the Neptunian troposphere appears to be a sink for CO which then should be continuously replenished from the stratosphere. Let us examine the conditions required to permit this alternative scenario for the formation of both HCN and CO.

6.2. External Origin

The presence of nitrogen in the atmosphere of Triton provides a tempting alternative to Neptune's intrinsic source of nitrogen. The nitrogen escaping from Triton could conceivably populate Neptune's magnetosphere and provide an extra-planetary source of nitrogen to Neptune's upper atmosphere. Here we will examine the implications of such a possible scenario. The published aeronautical models of Triton arrive at conflicting conclusions. In one, the escape of nitrogen occurs mainly in the form of neutral N at a rate of $3.4 \times 10^{25} \text{ s}^{-1}$, or $1.4 \times 10^8 \text{ N atoms cm}^{-2} \text{ s}^{-1}$, corresponding to the surface area of Triton (Summers & Strobel 1991). In this model, the N^+ escape rate is $<4\%$ of N, i.e., $1.3 \times 10^{24} \text{ s}^{-1}$ or $5.8 \times 10^6 \text{ N}^+ \text{ ions cm}^{-2} \text{ s}^{-1}$, from Triton. At the other extreme is a model which predicts escape mainly in the form of N^+ ions with a rate of $8 \times 10^{24} \text{ s}^{-1}$, or $3.4 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1} \text{ N}^+ \text{ ions cm}^{-2} \text{ s}^{-1}$, whereas the escape in the form of neutral atoms is smaller, $\sim 2 \times 10^{24} \text{ s}^{-1}$, or $8.6 \times 10^6 \text{ N atoms cm}^{-2} \text{ s}^{-1}$, from Triton (Yung & Lyons 1990). Richardson et al. (1991) argue for a magnetosphere pick-up of nitrogen ions directly from the ionosphere of Triton.

In view of the abovementioned controversies, we will assume here the published values of N and N^+ escape rates as representative of their possible ranges, i.e.,

N atom escape rate from Triton ($R = 1350 \text{ km}$)

$$= (0.2\text{--}3.4) \times 10^{25} \text{ s}^{-1}$$

or $(0.086\text{--}1.4) \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$.

N^+ ion escape rate from Triton ($R = 1350 \text{ km}$)

$$= (1.3\text{--}8) \times 10^{24} \text{ s}^{-1}$$

or $(0.58\text{--}3.4) \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$.

If the escape from Triton were in the form of neutral N atoms, then the maximum flux of N atoms that could be available at Neptune is $\sim(0.1\text{--}2) \times 10^3 \text{ cm}^{-2} \text{ s}^{-1}$, not accounting for the orbital inclination of Triton, which would reduce this value even further. Thus the available flux of nitrogen is at least three orders of magnitude lower than needed to explain the observed HCN mixing ratio of 1.0×10^{-9} as derived above. Even if the nitrogen atoms were ionized in the magnetosphere subsequent to their escape from Triton, the flux at Neptune would still not be adequate because of the numerous losses in the magnetosphere (see below). Furthermore, as mentioned earlier, direct pick-up of N^+ ions from the ionosphere of Triton is the likely scenario as argued by Richardson et al. (1991).

If the escape from Triton were in the form of N^+ ions, and if the entire amount picked up in the magnetosphere were lost to the upper atmosphere of Neptune, then the globally averaged flux of N^+ ions into Neptune would be on the order of $(0.17\text{--}1) \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$. This is still at least a factor of 10 too low. Furthermore, it is virtually inconceivable that all of the magnetospheric N^+ would be lost to Neptune's atmosphere. Many other processes such as loss to the solar wind, Neptune's rings and moons, reaction of N^+ with hydrogen which is present in roughly equal proportions in the magnetosphere, etc., are expected to be equally or even more important. Note

also the N^+ ions would enter the atmosphere in the magnetic regions only, additionally restricting the available flux. Once in the atmosphere of Neptune, rapid chemical reactions of incoming N^+ with H_2 would further impede the production of HCN.

In summary, it appears that an external source of nitrogen, although quite feasible, in principle, is in fact not sufficient for producing the measured abundance of HCN in Neptune's atmosphere (Atreya 1992).

CO in the stratosphere may result from reactions between oxygen or certain oxygen-bearing molecules and the products of methane photochemistry. Moses (1992) has estimated that "meteorites" composed primarily of water ice would ablate at high elevations, i.e., around the microbar level, in Neptune's atmosphere. Water could also be supplied by comets. The OH radicals produced by the UV dissociation of water molecules can, in principle, react with CH_3 , C_2H_2 , C_3H_2 or CH_2 to produce CO. Strobel & Yung (1979) proposed this possibility for Jupiter (it is now known, however, that CO on Jupiter originates from its interior [Noll et al. 1988]). This external source scenario has been suggested for Titan to explain the presence of CO_2 in its upper atmosphere since this gas cannot originate from the surface (Samuelson et al. 1983). Several arguments raise doubts about the validity of this mechanism for producing the observed amount of CO on Neptune, however. First, the same mechanism should operate on Uranus where CO has not been detected. Second, on Jupiter and Saturn, this process should produce several hundred times more CO than observed, unless the flux of incoming meteorites on these planets is substantially lower than on Neptune. Given Saturn's icy satellites and rings, this seems quite unlikely. One could argue that the large amount of CO on Titan supports an external scenario. However, there are strong indications of the primordial origin of this gas in the atmosphere of the satellite (Owen & Gautier 1989).

Rosenqvist et al. (1992) mention the possibility that atomic oxygen could be produced by sputtering and collisions of water ice on the rings and the small satellites of Neptune. CO would then be formed through reactions between O and CH_3 , C_2H_4 , or C_2H_2 . There is, however, no evidence of the presence of water on the surfaces of Neptune's rings and moons (Cruikshank et al. 1991). If the water ice sputtering scenario were valid for Neptune, one would expect a much more efficient and abundant supply of oxygen from Saturn's rings and moons to the atmosphere of Saturn producing much greater CO than has been measured in its atmosphere. The same mechanism should also operate on Uranus, where no CO has been detected. Finally, the low upper limit of CO in the atmosphere of Triton derived by Broadfoot et al. (1989) from *Voyager* UVS observations rules out the possibility of Triton being a source of the Neptunian CO, even though CO is present on this satellite's surface (Cruikshank et al. 1991).

In conclusion, we do not find an external source for CO on Neptune to be an attractive possibility. Therefore, in spite of the difficulties mentioned in § 6.1. concerning the difference between the observed CO abundance and the predictions from available thermochemical models (based on estimates of K), we are inclined to favor the scenario of an internal origin for both N_2 and CO on Neptune.

6.3. Comparison of Uranus and Neptune

The observations reported here show that the abundances of CO and HCN in the stratosphere of Uranus are lower than in Neptune's stratosphere by *at least* factors of 40 and 10, respec-

tively. We examine this difference below in light of the differences in the internal heat sources of the two planets.

The relatively small internal heat of Uranus must affect the transfer of energy in the deep troposphere. Wallace (1980) has shown that the vertical structure of the troposphere in the 0.5–30 bars region should not be homogeneous. It is composed of layers in which the transfer is successively governed by convection and by radiation. The analysis of Wallace made in the gray case has been confirmed in the nongray case by Bézard & Gautier (1986). Since upward movement of matter is strongly inhibited in radiative regions, the assumption of an adiabatic lapse rate with efficient convection in the troposphere is probably not valid for Uranus. But convection will dominate on Neptune whose internal heat source is at least 10 times larger (§ 6.1.) The thermochemical model described in Fegley et al. (1991) would then be applicable to Neptune but not to Uranus. However, as previously mentioned, the predictions of this model are compatible with the detection of HCN but not with the observed abundance of CO. Evidently the disequilibrium processes occurring in the deep atmosphere of Neptune are more effective than these models predict. In any case, stronger than expected convective transport is manifested by the measured abundance of methane in the stratosphere of Neptune. The stratospheric methane abundance is much greater than in the Uranus stratosphere and is greater than the value permitted by the saturation law at the temperature of Neptune's tropopause. For Neptune, the most recent evaluation of the stratospheric CH_4 mole fraction by Bézard et al. (1991) is $(3\text{--}4) \times 10^{-3}$ around the 1 mbar pressure level. For Uranus, the stratospheric value is not higher than 1×10^{-5} (Orton et al. 1987). Presumably some methane shoots past the tropopause cold trap on Neptune, while it does not in Uranus. This overshoot provides another indication that vertical convection is much more efficient on Neptune than on Uranus. *Voyager* imaging observations give similar indications (Smith et al. 1986, 1989).

It is well known that the microwave opacities of both Uranus and Neptune require a subsolar mixing ratio of ammonia in the upper atmospheres of these planets, at least at the 150–250 K atmospheric temperature levels (Gulkis & De Pater 1984; De Pater et al. 1989, 1991). We expect C/N to have the solar value in these atmospheres (Fegley et al. 1991). Since the CH_4/H_2 mixing ratio is at least 30 times the solar value of C/H (Lutz et al. 1976; Baines & Smith 1990), a similar enhancement should occur for N/H, contrary to observations. As concerns Neptune, recent measurements of the planetary emission at 20 cm wavelength suggest that in the deep atmosphere, below the condensation level of NH_3 and below the cloud formation level, the N/H ratio is from $\sim 1/60$ (Romani, De Pater, & Atreya 1989) to $\sim 1/10$ (De Pater et al. 1991) of the solar value. The deficiency of NH_3 then amounts to $1/300$ to $1/1800$ of the expected abundance. (New work by Spilker [1991] on the NH_3 line shape does not remove this discrepancy (I. De Pater, private communication). The case of Uranus is more uncertain but the expected nitrogen enrichment is in any case ruled out. Explanations have included the suggestion that sulfur is grossly overabundant on these planets, thereby tying up the ammonia as NH_4SH , (Gulkis, Janssen, & Olsen 1978; De Pater et al. 1989, 1991) and the possibility that the ammonia is dissolved in water clouds or an ionic ocean (Atreya & Romani 1985). The results presented here suggest an alternative (initially proposed but considered unlikely by Romani et al. 1989): if the nitrogen is mainly in the form of N_2 , rather than NH_3 , the low microwave opacity is easily explained.

With ammonia suppressed instead of sulfur enhanced, it is possible to have clouds of NH_4SH overlain by clouds of H_2S ice, as some models for Uranus have suggested (De Pater et al. 1991; West, Baines, & Pollack 1991). The interesting question then is whether the formation of H_2S will occur under these conditions where we find that the conversion of CO to CH_4 is apparently inhibited, at least partially. In principle, nitrogen can be reduced to ammonia by the Haber's process ($\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$) in the interior of the planet at high temperatures (≥ 800 K) and high pressures (≥ 1000 atm). The process is, however, heterogeneous, requiring the presence of an iron catalyst to help widen the lattice and enlarge the active surface for reactions (Cotton & Wilkinson 1980). An ideal catalyst would be α -iron containing some oxide. Although iron is expected to be present in the core of Neptune, it may not be available as a catalyst if some separation of "rock" and "ice" has occurred in the deep interior of the planet. Such a possibility has been suggested in the case of Uranus (see Podolak, Hubbard, & Stevenson [1991] for a review). How different are the internal structures of Uranus and Neptune is debatable (Hubbard 1989). The lack of suitable catalysts may also effect the $\text{CO} \rightarrow \text{CH}_4$ conversion, leading to the orders of magnitude excess in the observed CO abundance compared with predictions of the model.

This analysis should apply to both Uranus and Neptune. We have no evidence about the presence of N_2 on Uranus, however, since HCN has not been detected there. As explained above, the absence of CO in the stratosphere of Uranus is consistent with expectations of inhibited vertical convection. This effect would also exclude N_2 . So if the same process that reduces the formation of NH_3 from N_2 on Neptune is operating on Uranus, one would conclude that there is a gross deficiency in nitrogen in the observable part of the Uranian atmosphere.

There is a further point to be made about abundances on Neptune. In a solar mixture, neon has nearly the same abundance as nitrogen. Hence an atmosphere containing as much as 0.3% N_2 should have 0.6% Ne. Neon would not condense at the tropopause and hence this amount of neon would make a significant contribution to the mean molecular weight derived from the *Voyager* observations.

The determination of mean molecular weight has been used to derive the atmospheric value of He/H_2 on both planets, under certain assumptions (Conrath et al. 1987, 1991). A detailed consideration of this problem taking into account the possibility of the presence of N_2 in the atmosphere of Neptune is beyond the scope of the present paper and will be presented elsewhere (Conrath et al. 1992). Here we simply wish to emphasize a few points.

Considering the uncertainties in these determinations, it is somewhat imprudent to derive firm conclusions about the possible difference between the He/H_2 values deduced for the two planets. However, if we assume mixing ratios of 0.3% for N_2 on Neptune (Conrath et al. 1992) and 0% on Uranus at the levels where the mean molecular weight is inferred, we would obtain the protosolar ratio for He/H_2 as the central value of the determinations for the two planets. That would rule out the scenario advocated by a number of authors (Fegley & Prinn 1986; Pollack & Bodenheimer 1989) which suggests that a detectable amount of hydrogen was initially consumed to form CH_4 and NH_3 from CO and N_2 contained in the core and/or in infalling planetesimals. [Note that the infalling planetesimal scenario would lead to the deposition of "rock" in the planetary envelopes, ending to promote catalysis of $\text{CO} \rightarrow \text{CH}_4$ (and

$N_2 \rightarrow NH_3$), which would tend to decrease the CO excess we have found]. A solar value of He/H also rules out the possibility of a solar ratio of Ne/C; i.e., neon cannot be contributed to the planets from the solid material that gave them their methane and nitrogen. That in turn suggests that this icy material was formed at temperatures above 20 K, or "backed out" to these temperatures when it was in granular form. At temperatures above 20 K, neon will not be trapped in ice (Bar-Nun et al. 1985). One then anticipates a solar value of $Ne/H = 2 \times 10^{-4}$, a negligible amount for calculations of the atmospheric mean molecular weight.

We conclude that the assumption of a protosolar value of He/H₂ on Uranus and Neptune is consistent with the following constraints:

1. Uranus has very low N₂ in its upper atmosphere, but the possibility of a substantial amount of N₂ in the deep interior (agrees with absence of HCN and CO and an absent or very weak internal heat source that severely limits deep, vertical convection).
2. Neptune has ~0.3% N₂ in its upper atmosphere (agrees with detection of HCN and CO, and a strong internal heat source that produces vigorous vertical convection).
3. Both Uranus and Neptune have solar value of Ne/H in upper atmosphere (agrees with core-ice formation temperature of $T > 20$ K).

We stress again, however, that uncertainties in the He/H₂ determination prevent us from reversing the argument and proving that these constraints are true evaluations of atmospheric composition. We are only able to establish consistency at this point.

7. CONCLUSION

The observations presented in this paper show that CO is present in both the troposphere and the stratosphere of Neptune, whereas HCN is present only in the stratosphere. We suggest that CO should originate from the interior of the planet, although its observed abundance is far greater than that predicted by current thermochemical models of the Uranus troposphere, which we assume to be applicable to Neptune. The formation of HCN in the stratosphere requires the presence of nitrogen atoms. Since both CO and N₂ are tracers of the convection, a logical conclusion is that N₂ also originates from the deep interior of the planet, is convected to the troposphere and the stratosphere with CO, and is subsequently dissociated by charged particles, probably Galactic cosmic rays. The role of magnetospheric charged particles cannot be fully ruled out either until the value of the auroral power input is firmed up. The excess of CO compared with model predictions may be the result of a partial inhibition of CO → CH₄ conversion owing to the lack of suitable catalysts. The same inhibition may exist in the case of N₂ → NH₃. In

other words, we suggest that nitrogen is mainly in the form of N₂ rather than in the form of NH₃ in the deep troposphere of Neptune. The same scenario should occur within Uranus, but the low convective activity presumably precludes vertical convection from the deep interior to the upper troposphere and the stratosphere, in agreement with the nondetection of CO and HCN on this planet.

Under the assumption of a high N₂ over NH₃ ratio in the tropospheres of both Uranus and Neptune, NH₄SH clouds would not form or would be less dense than previously envisaged, and a substantial amount of H₂S could be present above such clouds, as previously advocated by De Pater et al. (1991). H₂S ice clouds could be present at a pressure of 2.7 bars on both planets (West et al. 1991; De Pater et al. 1991). The same assumption permits a good fit of the microwave spectrum of Neptune, while accommodating with the expected enhancement of nitrogen.

An alternative scenario for HCN formation on Neptune is to invoke an external source, where nitrogen atoms escaping from Triton precipitate into Neptune; the observed HCN abundance, however, cannot be produced by the published nitrogen fluxes from Triton.

Finally, our analysis makes still more obvious the differences between the upper atmospheres of Uranus and Neptune previously revealed by *Voyager*. In this work we admit that chemistries of the deep atmospheres of the two planets are similar. However, Uranus and Neptune might exhibit strongly different composition and thermal structure in their deep interiors. Thermochemical models should then be drastically revised.

Additional work is needed to confirm our conclusions. Laboratory measurements on the rate constants, reaction products, and yields of reactions between nitrogen atoms and H₂ and CH₄ under appropriate environmental conditions for Neptune (pressures 0.1–100 mb, temperatures 50–100 K) will greatly enable proper modeling of the HCN production rate. Remote detections of tropospheric heavy element compounds, especially sulfur compounds, would provide further tests. Interior structure theories must be refined. The enigma of the very small internal heat of Uranus compared to that of Neptune must be solved.

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