THE CHEMICAL ATMOSPHERIC COMPOSITION OF THE GIANT PLANETS

T. ENCRENAZ
DESPA, Observatoire de Paris
F-92195 Meudon

Abstract

For a long time it was believed that the atmospheres of the giant planets, dominated by molecular hydrogen and helium, were similar in composition to the primordial nebula from which they formed. However, this image has strongly evolved over the past twenty years, due to new developments of ground-based infrared spectroscopy, coupled with the success of the Voyager space mission.

Significant differences were measured in the abundances of helium, deuterium and carbon of the four giant planets. The variations in the C/H and D/H ratios have given support to the "nucleation" formation scenario, in which the four giant planets first accreted a nucleus of about ten terrestrial masses, big enough to bind gravitationally the surrounding gaseous nebula; the helium depletion in Saturn has been interpreted as a differentiation effect in Saturn's interior; the apparent helium excess in Neptune, coupled with the recent unexpected detection of CO and HCN in this planet, might imply the presence of molecular nitrogen. In the case of Jupiter and Saturn, disequilibrium species have been detected (CO, PH_3, GeH_4, AsH_3), which are tracers of vertical dynamical motions.

In the future, significant progress in our knowledge of the Jovian composition, including the noble gases, should be obtained with the mass spectrometer of the Galileo probe. The ISO mission is expected to provide new far-infrared spectroscopic data which should lead to the detection of new minor species and a better determination of the D/H ratio.

1. Introduction

It has been known for many decades that the atmospheres of the giant planets were mostly composed of hydrogen and helium, with traces of minor compounds in a reduced form. Methane and ammonia were first detected from their near-infrared spectral signatures (Wildt, 1932); hydrogen, expected to be the dominant constituent (Herzberg, 1952) was detected almost thirty years later (Kiess *et al.*,1960). Helium, expected to be present at the 10% level, was indirectly inferred from the determination of the mean molecular weight, measured by a stellar occultation experiment (Baum and Code, 1953).

Earth, Moon, and Planets **67**: 77–87, 1995.

The hydrogen-rich composition of the giant planets was understood as an effect of their very high escape velocities. A molecule can escape an atmosphere if its kinetic velocity exceeds its escape velocity. This is more likely if the temperature is high and if the planet is small; in the case of the giant planets, the escape velocity is so high that even the lightest element, hydrogen, cannot escape over the lifetime of the Solar system (Spitzer, 1952). Since the giant planets were massive enough to keep all their constituents by gravitation, their atmospheres were thus expected to reflect closely the chemical composition of the primordial nebula from which they formed. Since abundances were assumed to be solar (or "cosmic") in the gaseous phase of the primordial nebula (with the exception of deuterium, continuously destroyed in stars), abundance ratios in the giant planets were more or less expected to follow the cosmic values.

From the early sixties to the mid-seventies, there was little progress in our knowledge of the atmospheric composition of the giant planets. Then, within a few years, a large number of minor species were detected (Table 1), due to the fast development of ground-based infrared techniques (see Atreya, 1986 and Encrenaz, 1990 for a review). The infrared spectral range is indeed best suited for studying the vibration-rotation bands of neutral molecules; in addition, these cold objects radiate a large fraction of their thermal energy in the infrared, beyond 5 µm. Infrared spectrosocopy at various wavelengths allowed astronomers to probe different altitude levels of the atmospheres; in particular, the 5-µm window, observable from the ground and free from methane and ammonia absorption, was very important for detecting minor tropospheric species on Jupiter (Ridgway *et al.*, 1976) and later Saturn (Prinn *et al.*, 1984). This method allowed the unexpected identification of disequilibrium species like PH_3, GeH_4, AsH_3 and CO in the tropospheres of Jupiter and Saturn.

Another major step was the Voyager mission with its two spacecraft which encountered Jupiter in 1979 and Saturn in 1980 and 1981; Voyager 2 encountered Uranus in 1986 and Neptune in 1989. Their infrared interferometers, named "IRIS", measured the infrared spectra of the four giant planets and Titan in the 5-50 µm range (200-2000 cm^{-1}), with a spectral resolution of 4.3 cm^{-1} (Hanel *et al.*, 1979a&b, 1981, 1982, 1986; Conrath *et al.*, 1990). These data, together with the radio-occultation Voyager measurements, allowed a simultaneous retrieval of the helium abundance and the vertical distribution of the thermal profiles on the four giant planets. Determinations of the C/H and D/H ratios on Jupiter and Saturn were also obtained from the study of the emission bands of CH_4 at 7.7 µm and CH_3D at 8.6 µm.

From all these results, a new picture has emerged, showing evidence for significant differences between the chemical composition of the giant planets (Table 1). An enrichment is observed, for both carbon and deuterium, from Jupiter to Neptune; the helium abundance strongly varies, with a minimum value in the case of Saturn and a maximum value in the case of Neptune. As a last example of these differences, CO and HCN have been detected recently in the stratosphere of Neptune (Marten *et al.*, 1991,1993; Rosenqvist *et al.*, 1992), but not in the stratospheres of the other giant planets; their abundances in Neptune are significantly higher than the predicted values.

These important results have been used to revisit the formation and evolution models of the giant planets. It now appears that the formation scenarios of the giant planets were likely to be much more complex than previously thought. By gathering all information coming from objects formed in this range of heliocentric distances (5 to 50 AU), including giant planets, satellites, Pluto and the comets, one should be able to proceed one step further in our knowledge of early formation and evolution processes in the outer solar system.

TABLE 1. Gaseous molecular species in the giant planets (summarized and updated from Atreya, 1986)

SPECIES	MIXING RATIOS (VERSUS H_2)			
	JUPITER	SATURN	URANUS	NEPTUNE
H_2	1	1	1	1
HD	6×10^{-5}	1×10^{-4}	***	***
He	0.11	0.03	0.18	0.23
CH_4	2×10^{-3}	4×10^{-3}	2×10^{-2}	4×10^{-2}
$^{13}CH_4$	2×10^{-5}	4×10^{-5}		
CH_3D	3×10^{-7}	4×10^{-7}	1×10^{-5}	3×10^{-5}
NH_3	3×10^{-4}	2×10^{-4}		
$^{15}NH_3$	1×10^{-6}			
C_2H_2	3×10^{-8} (*)	7×10^{-8} (*)	1×10^{-7}	$1\text{-}9 \times 10^{-7}$
$^{12}C^{13}CH_2$	3×10^{-9} (*)			
C_2H_6	2×10^{-6}	3×10^{-6}		3×10^{-6}
C_3H_4	3×10^{-9} (**)			
C_3H_8	6×10^{-7}(**)			
C_2H_4	7×10^{-9}(**)			
C_6H_6	2×10^{-9}(**)			
H_2O	1×10^{-6} (*)			
CO	1.5×10^{-9}(+)	2×10^{-9}(+)		6×10^{-7}(++)
PH_3	5×10^{-7}	1.5×10^{-6}		
GeH_4	7×10^{-10}	4×10^{-10}		
AsH_3	3 x 10-10	2.4×10^{-9}		
HCN	2×10^{-9}			3×10^{-10}(++)
H_3^+	(++)	(++)		

NOTES: Mixing ratios only indicate orders of magnitude

(*)	variable
(**)	in the north polar region
(***)	detected; mixing ratio is very uncertain
(+)	detected in the troposphere
(++)	detected in the stratosphere

2. Constraints in formation and evolution processes

The determination of elemental and isotopic ratios in the giant planets has provided significant constraints upon the formation and evolution of these objects. These ratios (D/H, C/H, N/H...) have been derived from the study of atmospheric species (HD, CH_4, NH_3), and the determination of their abundances and vertical distributions. The measurement of these quantities implies the simultaneous knowledge of the thermal profile T(P), which, in the case of the four giant planets, has been retrieved with good accuracy from the Voyager radio-occultation and far-infrared experiments. Once the thermal profile is known, vertical distributions of atmospheric species can be deduced from the measurement of their infrared spectroscopic bands, and a comparison made with synthetic models.

2.1 THE CARBON AND DEUTERIUM ABUNDANCES

Carbon was the first species for which an abundance variation was suspected among the four giant planets. The C/H ratio is derived from the CH_4/H_2 ratio, which, in the case of Jupiter and Saturn, is believed to be constant over the whole atmospheric range probed in the infrared. On Uranus and Neptune, saturation is expected to take place in the region of the upper troposphere and above, so that the CH_4 measurement, in order to be meaningful in terms of C/H determination, has to be performed in the deep troposphere. The first indication for a variation in CH_4 came from the analysis of the visible and near-infrared methane bands, which suggested a strong CH_4 enhancement on Uranus and Neptune, with respect to the two others (Encrenaz *et al.*,1974; Lutz *et al.*, 1976). In the case of Jupiter and Saturn, an accurate determination of C/H was obtained from the analysis of the 7.7 µm CH_4 band observed with the Voyager IRIS experiment (Gautier *et al.*, 1982; Courtin *et al.*, 1984). These data, coupled with other analyses in the near-IR range (Combes and Encrenaz, 1979; Buriez and de Bergh, 1981) provided definitive evidence for a carbon enrichment with respect to the solar value, by a factor of 2 in the case of Jupiter and around 4 (+/-2) in the case of Saturn. In the case of Uranus and Neptune the carbon enrichment is believed to be at least 10 times larger than for Jupiter; present analyses suggest a carbon enrichment in the range 25 to 60 (Baines and Bergstrahl, 1986; Baines and Smith, 1990; Fegley *et al.*, 1991; Gautier *et al.*, 1994).

The determination of a carbon excess which significantly increases from Jupiter to Neptune has given decisive support to the "nucleation" formation theory of the giant planets. Two decades ago, a "homogeneous" model was suggested, assuming giant homogeneous gaseous protoplanets with chemical compositions close to solar abundances. However, this model cannot account for the carbon abundance variations observed over the past ten years. In contrast, the nucleation models developed by Perri and Cameron (1974) and Mizuno (1980) does predict an enrichment in heavy elements. In this model, cores of heavy elements are formed first, in comparable masses for all giant planets (about 10 terrestrial masses). This mass is sufficient for the surrounding gaseous nebula to collapse. In the core formation, accretional heating leads to outgassing from ices (CO, CH_4, NH_3, H_2O...) and/or clathrates/hydrates, and a subsequent enrichment of the outer envelope in heavy elements like C, O, N, etc. As pointed out by Stevenson (1982), infalling planetesimals might also have contributed to the observed enrichment. Since the relative size of the core grows from Jupiter to Neptune, the C/H variations over the four planets are in qualitative agreement with this model (Gautier and Owen, 1989).

If the nucleation model is valid, all elements heavier than H, He and Ne (which are not expected to be trapped in ices) are expected to be enhanced in the atmospheres of the giant planets. We would thus expect to observe excesses of NH_3, H_2O, etc. However these measurements are very difficult, because these molecules condense in the four giant planets to form clouds, and a measurement below the clouds is very difficult by remote sensing spectroscopy. NH_3 seems to be enriched on Jupiter and Saturn (de Pater, 1986), but depleted on Uranus and Neptune (de Pater and Mitchell, 1993), which might be due to cloud chemistry, but is not completely understood at the present time (Gautier *et al.*,1994). H_2O has been detected in Jupiter only (Larson *et al.*, 1975); Carlson *et al.*, 1992); other sources of oxygen may exist, as illustrated by the detection of CO (Beer, 1975). Methane, which does not condense in Jupiter and Saturn, is considered as the best test for measuring the excess on heavy elements in the giant planets.

Deuterium is another isotope of particular interest for bringing constraints on formation scenarios. Unlike the other elements, the deuterium abundance in the protosolar nebula is higher than in the Sun, where deuterium is converted into helium. The protosolar value is about $3\ 10^{-5}$, as derived from ^3He solar wind measurements (Geiss, 1993). It is also expected to be higher than its value in the local interstellar medium today, because of the continuous destruction of deuterium in stars since the formation of the Solar system, 4.5 billion years ago. This variation of the D/H ratio as a function of time can actually be estimated from a modelling of the chemical evolution of galaxies (Delbourgo-Salvador *et al.*, 1985). The observed mean value of about 10^{-5} in the local interstellar medium (Linsky *et al.*, 1993) is consistent with these models.

Deuterium has been detected in the four giant planets, from both the HD and CH_3D molecules. The HD detection (Trauger *et al.*,1973; Macy and Smith, 1978) directly leads to D/H (the HD mixing ratio being twice the D/H ratio), but the HD lines appear in the visible region and are affected by scattering and blends with weak methane lines. In the case of Jupiter and Saturn, infrared bands of CH_3D (Beer *et al.*, 1972, Fink and Larson, 1978) provide a less model-dependent estimate of the CH_3D abundance, but its conversion into D/H is a function of the fractionation factor f through the equation $D/H = 1/4f \times (CH_3D/CH_4)$; f is a strong function of temperature (Fegley and Prinn, 1988). For Uranus and Neptune, near-infrared bands of CH_3D are used (de Bergh *et al.*, 1984, 1990). As a result, in spite of large error bars, the D/H in Jupiter and Saturn seems to be close to the primordial value of $3\ 10^{-5}$, while the Uranus and Neptune values are a factor of 5 to 10 larger (Gautier and Owen, 1989; Owen, 1992).

In the homogeneous formation model of the giant planets, one would expect the deuterium abundance in all giant planets to be similar to the primordial nebula value. In the nucleation model, in contrast, the deuterium coming from the core might be significantly enriched, as observed in molecules trapped in ices in other Solar system objects, like Titan (Owen *et al.*, 1986) and comet Halley (Eberhardt *et al.*, 1987). As first suggested by Owen *et al.* (1986), the origin of the D/H enrichment in this second deuterium reservoir could be ion-molecule reactions, as observed in the interstellar medium, which would have occurred before the formation of planetesimals. As discussed by Gautier and Owen (1989), the observed excess of D/H in Uranus and Neptune would be in qualitative agreement with both the nucleation model and the "ice reservoir" of deuterium proposed by Owen *et al.* (1986); however, more accurate data are needed before any firm conclusion can be drawn.

2.2 THE HELIUM ABUNDANCE

In the Big Bang theory, helium is assumed to have formed mostly in the first stage of the Universe. If there was no differentiation effect within the giant planets, a measurement of H_2/He in these objects would give a direct measurement of the protosolar helium abundance.

The He I resonance line at 584 A , detected on Jupiter, Saturn and Uranus from the Voyager spacecraft (Broadfoot *et al.*, 1981; Sandel *et al.*, 1982, Broadfoot *et al.*, 1986), is formed above the homopause and cannot be used for a determination of the helium relative abundance. The H_2/He ratio has been indirectly derived from a combination of two methods: the inversion of the far-infrared spectra of the giant planets, as measured with the IRIS Voyager experiment, and the determination of the mean molecular weight derived from the Voyager radio-occultation experiments. Large variations were observed in the helium mass fraction: the derived values were (assuming pure H_2-He atmospheres) 0.18 for Jupiter (Gautier *et al.*, 1981), 0.06 for Saturn (Conrath *et al.*, 1984), 0.26 for Uranus (Conrath *et al.*, 1987) and 0.32 for Neptune (Conrath *et al.*, 1991); the estimated value for the proto-Sun would be 0.28 (Sackman *et al.*, 1990). The helium depletion in Saturn was interpreted as a differentiation effect in Saturn's interior, due to the condensation, in metallic hydrogen, of helium droplets sinking toward the center and depleting the helium content of the outer envelope; the same effect might take place on Jupiter and explain its helium deficiency with respect to the primordial value. It would be less efficient than in the case of Saturn, as helium condensation is expected to have occurred later in the cooling process of both planets, Jupiter starting from a higher temperature. In the case of Uranus and Neptune, the pressure of their interiors does not seem sufficient for metallic hydrogen to be present, so that the helium condensation effect is not expected to take place (Gautier and Owen, 1989). Indeed, the Uranus value appears to be representative of the primordial helium abundance. The helium abundance of Neptune is marginally compatible with the primordial value. However, the value derived for a pure H_2-He atmosphere shows a slight excess with regard to this value. A possible explanation might be that molecular nitrogen is present in its interior at the 0.3% level, while the helium abundance would be, as in Uranus, primordial (Conrath *et al.*, 1993). This nitrogen abundance would explain the molecular weight excess possibly detected on Neptune, and could be responsible for the presence of stratospheric HCN in this planet (Gautier *et al.*,1994). This result, if confirmed, would have important implications upon the chemical nature of planetesimals from which the giant planets formed. Finally, an important question which remains to be solved is the origin of the difference between Uranus and Neptune: why are HCN and CO present in the stratosphere of Neptune, but not of Uranus? why would nitrogen be present in the troposphere of Neptune, but not of Uranus? As suggested by Conrath *et al.* (1993) and Hubbard *et al.* (1994), the origin might come from the difference in the internal energy sources of the two planets. In the case of Uranus, the internal heat flux is so small that convection might be inhibited in several layers of the troposphere, preventing upward movement of N_2 from the deep interior.

3. Spatio-temporal variations

Several processes can presently alter the chemical compositions of the giant planets, leading to non-uniform vertical mixing and spatio-temporal variations. These processes include condensation, photochemistry, interaction with the magnetosphere and general circulation.

As an example, the study of vertical motions in the giant planets can significantly benefit from the analysis of non-equilibrium species. These minor atmospheric compounds should not be observable on the basis of chemical equilibrium models, but are carried into visibility by upward vertical motions on timescales shorter than their chemical lifetime (Drossart *et al.*, 1989). The most abundant species of this kind is phosphine, which is present in solar abundance in Jupiter's deep troposphere (Ridgway *et al.*,1976), and is enriched by a factor about 3 in the case of Saturn (Bregman *et al.*, 1975). Other disequilibrium species include CO, GeH_4 and AsH_3, all detected at deep atmospheric levels in the 5 µm window (Beer, 1975; Noll *et al.*, 1986; Bézard *et al.*,1989; Noll *et al.*,1989). In the same way, spatio-temporal variations of condensable compounds such as H_2O and NH_3 can also be used for deriving information about vertical atmospheric motions (Lellouch *et al.*,1989).

The existence of aurorae on Jupiter and Saturn has been known for a long time from the Ly alpha emission of these planets (Clarke *et al.*, 1980, 1989; Broadfoot *et al.*, 1981). These regions were also characterized by a strong infrared emission in the bands of methane and various hydrocarbons (Caldwell *et al.*, 1980; Kim *et al.*,1985; Drossart *et al.*, 1986). This study has known a renewed interest with the detection of the H_3^+ ion in Jupiter's auroral regions (Drossart *et al.*,1989, 1992; Oka and Geballe, 1990), in the near-infrared range. These emissions appear to be powerful tracers of the thermal profile in the upper stratosphere (Drossart *et al.*, 1993).

4. Open problems and future studies

Our understanding of the giant planets has been completely renewed over the past decades. Following the exploration of the four planets by the Voyager spacecraft, and with the support of a very active ground-based observation program, we have successively discovered more and more differences, which are all indicators of their past or present history. In the light of these new results, there are still many important questions which remain to be solved.

One of the basic issues is a precise determination of C/H, D/H and H/He. Unfortunately, an improvement of the C/H determination on Uranus and Neptune seems difficult, because the thermal infrared range gives only access to the upper troposphere and the stratosphere, where methane is likely to condense. The case of deuterium, in contrast, is more favorable. A reliable determination of D/H on the four giant planets should be achievable through the HD rotational transitions, in particular with the spectrometers of the ISO satellite, to be launched in 1995 (Encrenaz and Kessler, 1992). These instruments also should provide an improved determination of the H_2/He ratio. A measurement of the noble gas abundances would be crucial for assessing new constraints upon formation scenarios; hopefully this will be performed in the case of Jupiter by the Galileo probe.

Global monitoring of the planets is necessary to understand the photochemical processes now governing their chemical compositions (photochemistry, general circulation). In addition to the exploration of Jupiter and Saturn by Galileo and Cassini respectively, one can foresee promising improvements in the field of ground-based imaging spectroscopy. Present developments include, in particular, infrared cameras with improved spatial resolution and sensitivity. The combination of a Fourier-Transform spectrometer with a bidimensional infrared camera will allow, in particular, a complete mapping of Jupiter and Saturn in the 5- µm window, and thus a continuous monitoring of their tropospheric compositions; the first adaptive optics instruments are now being developed (Saint-Pé *et al.*, 1993a&b), and will provide an improvement by a factor of 10 in the spatial resolution of the infrared images.

Finally, the spectrographs of the ISO mission could allow the detection of new minor species, especially in the far-infrared range. This search will also be possible from the ground, with the development of submillimeter interferometers and heterodyne receivers.

5. References

Atreya, S.K. (1986) *Atmospheres and ionospheres of the outer planets and their satellites*, Springer-Verlag.

Baines, K.H. and Bergstralh, J.T. (1986) The structure of the uranian atmosphere: Constraints from the geometric albedo spectrum and H_2 and CH_4 line profiles, *Icarus* **65**, 406-441.

Baines, K.H. and Smith, W.H. (1990) The atmospheric structure and dynamical properties of Neptune derived from ground-based and IUE spectrophotometry, *Icarus* **85**, 65-108.

Baum, W.A. and Code, A.D. (1953) A photometric observation of the occultation of s Arietis by Jupiter, *Astron. J.* **58**, 108-112.

Beer, R. (1975) Detection of carbon monoxide in Jupiter, *Astrophys.J.* **200**, L167-L169.

Beer, R., Farmer, C.B., Norton, R.H., Martonchik, J.V., and Barnes, T.G. (1972) Observation of deuterated methane in the atmosphere, *Science* **175**, 1360-1361.

Bézard, B., Drossart, P., Lellouch, E., Tarrago, G. and Maillard, J.P. (1989) Detection of Arsine in Saturn, *Astrophys.J.* **346**, 509-513.

Bregman, J.D., Lester, D.F., and Rank, D.M. (1975) Observation of the ν_2 band of PH_3 in the atmosphere of Saturn, *Astrophys. J.* **202**, L55-L56.

Broadfoot, A.L. *et al.* (1981) Overview of the Voyager ultraviolet spectrometry results through Jupiter encounter, *J. Geophys. Res.* **86**, 8259-8284.

Broadfoot, A.L. *et al.* (1986) Ultraviolet spectrometer observations of Uranus, *Science* **233**, 74-79.

Buriez, J.C. and de Bergh, C. (1981) A study of the atmosphere of Saturn based on methane line profiles near 1.1 µm, *Astron. Astrophys.* **94**, 382-390.

Caldwell, J., Tokunaga, A.T. and Gillett, F.C. (1980) Possible infrared aurorae on Jupiter, *Icarus* **44**, 666-675.

Carlson, B.E., Lacis, A.A. and Rossow, W.B. (1992) The abundance and distribution of water vapor in the Jovian troposphere as inferred from Voyager IRIS observations, *Astrophys.J.* **388**, 648-668.

Clarke, J.T., Moos, H.W., Atreya, S.K. and Lane, A.L. (1980) Observations from earth orbit and variability of the polar aurora on Jupiter, *Astrophys. J.* **241**, L179-L182.

Combes, M. and Encrenaz, T. (1979) A method for the determination of abundance ratios in the outer planets - Application to Jupiter, *Icarus* **39**, 1-27.

Conrath, B., Gautier, D., Hanel, R. and Hornstein, J.S. (1984) The helium abundance of Saturn from Voyager measurements, *Astrophys. J.* **282**, 807-815.

Conrath, B.J., Gautier, D., Hanel, R., Lindal, G. and Marten, A. (1987) The helium abundance of Uranus from Voyager measurements, *J. Geophys. Res.* **92**, 15003-15010.

Conrath, B.J., Gautier, D., Lindal, G., Samuelson, R.E. and Shaffer, W.A. (1991) The helium abundance of Neptune from Voyager measurements, *J. Geophys. Res.* **96**, 18907-18919.

Conrath, B.J., Gautier, D., Owen, T. and Samuelson, R.E. (1993) Constraints on N_2 in Neptune's atmosphere from Voyager measurements, *Icarus* **101**, 168-171.

Conrath, B. *et al.* (1989) Infrared observations of the Neptunian system, *Science* **246**, 1454-1459.

Courtin, R., Gautier, D., Marten, A., Bézard, B. and Hanel, R. (1984) The composition of Saturn's atmosphere at northern temperate latitudes from Voyager IRIS spectra : NH_3, PH_3, C_2H_2, C_2H_6, CH_3D, CH_4 and the Saturnian D/H isotopic ratio, *Astrophys.J.* **287**, 899-916.

Delbourgo-Salvador, P., Gry, C., Malinie, G. and Audouze, J. (1985) Effects of nuclear uncertainties and chemical evolution of the standard big bang nucleosynthesis, *Astron. Astrophys.* **150**, 53-61.

de Bergh, C., Lutz, B., Owen, T. and Chauville, J. (1988) Monodeuterated methane in the outer solar system. II. Its detection on Uranus at 1.6 µm, *Astrophys. J.* **311**, 501-510.

de Bergh, C., Lutz, B., Owen, T. and Maillard, J.P. (1990) Monodeuterated methane in the outer solar system. IV. Its detection and abundance on Neptune, *Astrophys. J.* **355**, 661-666.

de Pater, I. (1986) Jupiter's Zone-Belt structure at radio-wavelengths. II. A comparison of observations with model-atmosphere calculations, *Icarus* **68**, 344-365.

de Pater, I. and Mitchell, D.L. (1983), Microwave observations of the planets : The importance of laboratory measurements, *J. Geophys. Res. Planets* **98**, 5471-5490.

Drossart, P., Bézard, B., Atreya, S.K., Lacy, J., Serabyn, E., Tokunaga, A.T. and Encrenaz, T. (1986) Enhanced acetylene emission near the north pole of Jupiter, *Icarus* **66**, 610-618.

Drossart, P., Courtin, R., Atreya, S. and Tokunaga, A. T. (1989) Variations in the Jovian atmospheric composition and chemistry, in M.Belton, R.West and J.Rahe (edts), *Time-variable phenomena in the Jovian system*, NASA SP-494, pp.344-362.

Drossart, P., Maillard, J.P., Caldwell, J., Kim, S.J., Clarke, J., Waite, H., and Wagener, R. (1989) Detection of H_3^+ in Jupiter, *Nature* **340**, 539-541.

Drossart, P., Prangé, R. and Maillard, J.P. (1992) Morphology of infrared H_3^+ emissions in the auroral regions of Jupiter, *Icarus* **97**, 10-25.

Drossart, P., Maillard, J.P., Caldwell, J. and Rosenqvist, J. (1993) Line-resolved spectroscopy of the Jovian H_3^+ auroral emission at 3.5 micrometers, *Astrophys.J.* **402**, L25-L28.

Eberhardt, P., Dolder, U., Schulte, W., Krankowsky, D., Lämmerzahl, P., Hoffman, J.H., Hodges, R.R., Berthellier, J.J. and Illiano, J.M. (1987) The D/H ratio in water from comet P/Halley, *Astron. Astrophys.* **187**, 435-437.

Encrenaz, T. (1990) Remote sensing of the atmospheres of Jupiter, Saturn and Titan. *Rep. Prog. Phys.* **53**, 793-836.

Encrenaz, T. and Kessler, M.F. (1992) *Infrared Astronomy with ISO*, Nova Science.

Encrenaz, T., Hardorp, J., Owen, T. and Woodman, J. H. (1974) Observational constraints on model atmospheres for Uranus and Neptune. In A.Woscyk and I. Iwaniszewska (edts) *Exploration of the Planetary Systems*, Dortrecht : D.Reidel, pp.487-496.

Fegley, M.B. and Prinn, R.G. (1988) The predicted abundances of deuterium-bearing gases in the atmospheres of Jupiter and Saturn, *Astrophys.J.* **326**, 490-508.

Fegley, B., Gautier, D, Owen, T. and Prinn, R.G. (1991) Spectroscopy and chemistry of the atmosphere of Uranus, in *Uranus* J.T.Bergstralh *et al.* edts, Univ. of Arizona, 147-203.

Fink, U. and Larson, H.P. (1978) Deuterated methane observed on Saturn, *Science* **201**, 343-345.

Gautier, D., Bézard, B., Marten, A., Baluteau, J. P., Scott, N., Chédin, A., Kunde, V. and Hanel, R. (1982) The C/H ratio in Jupiter from the Voyager IRIS investigation, *AstrophysJ.* **257**, 901-912.

Gautier D and Owen T (1989) The composition of outer planet atmospheres, in S. Atreya, J. Pollack and M. Matthews (edts) *Origin and evolution of planetary and satellite atmospheres*, pp.487-512.

Gautier, D., Conrath, B., Flasar, M., Hanel, R., Kunde, V., Chedin, A. and Scott,N. (1981) The helium abundance of Jupiter from Voyager, *J. Geophys. Res.* **86**, 8713-8720.

Gautier, D., Conrath, B. J., Owen, T., de Pater, I. and Atreya, S. K. (1994), *The troposphere of Neptune*, in *Neptune*, ed. D.Cruikshank *et al.*, The University of Arizona Press, Tucson (in press).

Geiss, J. (1993) Primordial abundances of hydrogen and helium isotopes, in N. Prantzos *et al.* (edts) *Origin and evolution of the elements*, Cambridge, pp. 89-106.

Hanel, R. *et al.* (1979a) Infrared observations of the Jovian system from Voyager 1, *Science* **204**, 972-976.

Hanel, R. *et al.* (1979b) Infrared observations of the Jovian system from Voyager 2, *Science* **206**, 952-956.

Hanel, R. *et al.* (1981) Infrared observations of the Saturnian system from Voyager 1, *Science* **212**, 192-200.

Hanel, R. *et al.* (1982) Infrared observations of the Saturnian system from Voyager 2, *Science* **215**, 544-548.

Hanel,R. *et al.*, Infrared observations of the Uranus sytem, *Science* **233**, 70-74.

Herzberg, G. (1952) in G.P. Kuiper (edt) *The Atmospheres of the Earth and Planets*, Chicago.

Hubbard, W.B., Pearl, J.C., Podolak, M. and Stevenson, D.J. (1994), *The interior of Neptune*, in *Neptune*, D.Cruikshank *et al.* (edt), The Univ. of Arizona Press (in press).

Kiess, C.C., Korliss, C.H. and Kiess, H.K. (1960) High-dispersion spectra of Jupiter, *Astrophys. J.* **132**, 221-231.

Kim, S.J., Caldwell, J., Rivolo, A.R., Wagener, R. and Orton, G.S. (1985) Infrared Polar Brightening of Jupiter : III- Spectrometry from the Voyager 1 IRIS Experiment, *Icarus* **64**, 233-248.

Larson, H.P., Fink, U., Treffers, R. and Gautier, T.N. (1975) Detection of water vapor on Jupiter, *Astrophys. J.* **197**, L-137-L140.

Lellouch, E., Drossart, P. and Encrenaz, T. (1989) A new analysis of the Jovian 5-μm Voyager IRIS spectra, *Icarus* **77**, 457-465.

Linsky, J.L., Brown, A., Gaylay, K., Diplas, A., Savage, B.D., Ayres, T.R., Landsman, W., Shore, S.N. and Heap, S.R. (1993) Goddard high-resolution spectrograph observations of the local interstellar medium and the deuterium/hydrogen ratio along the line of sight toward Capella, *Astrophys. J.* **402**, 694-709.

Lutz, B. L., Owen ,T. and Cess, R. D. (1976) Laboratory band strengths of methane and their application to the atmospheres of Jupiter, Saturn, Uranus, Neptune and Titan, *Astrophys. J.* **203**, 541-551.

Macy, W.W. and Smith, W.H. (1978), Detection of HD on Saturn and Uranus and the D/H ratio, *Astrophys. J.* **222**, L137-L140.

Marten , A., Gautier, D., Owen, T., Sanders, D., Tilanus, R.T., Deane, J. and Matthews, H. (1991) First detections of CO and HCN in the atmosphere of Neptune, *B.A.A.S* **23**, 1164.

Marten, A., Gautier, D., Owen,T., Sanders, D.B., Matthews, H.E., Atreya, S.K., Tilanus, R.P.J., and Deane, J.R. (1993) First observations of CO and HCN on Neptune and Uranus at millimeter wavelengths and their implications for atmospheric chemistry, *Astrophys. J.* **406**, 285-297.

Mizuno, H. (1980) Formation of the giant planets, *Prog. Theor. Phys.* **64**, 544-557.

Noll, K.S., Knacke, R.F., Geballe, T.R. and Tokunaga, A.T. (1986) Detection of carbon monoxide in Saturn, *Astrophys. J.* **309**, L91-L94.

Noll, K.S., Geballe, T.R. and Knacke, R.F. (1989) Arsine in Saturn and Jupiter, *Astrophys. J.* **338**, L71-L74.

Oka, T. and Geballe, R.T. (1990) Observation of the 4 µm fundamental band of H_3^+ in Jupiter, *Astrophys. J.* **351**, L53-L56.

Owen, T (1992), Deuterium in the Solar System, in P. Singh (edt.) *Astrochemistry of cosmic phenomena*, Dordrecht-Kluwer, pp. 97-101.

Owen, T., Lutz, B. L. and de Bergh, C. (1986) Deuterium in the outer solar system: Evidence for two distincts reservoirs, *Nature* **320**, 244-246.

Perri, F. and Cameron, A.G.W. (1974) Hydrodynamic instability of the solar nebula in the presence of a planetary core, *Icarus* **22**, 416-425.

Prinn, R.G., Larson, H.P., Caldwell, J.J and Gautier, D. (1984), *Composition and Chemistry of Saturn's Atmosphere*, in *Saturn*, T. Gehrels and M.S. Matthews (edts.), Univ. of Arizona, 88-149

Ridgway, S.T., Larson, H.L. and Fink, U. (1976), *The Infrared Spectrum of Jupiter*, in "Jupiter", T. Gehrels (edt.), Univ. of Arizona, 384-417

Rosenqvist, J., Lellouch, E., Romani, P., Paubert, G. and Encrenaz, T. (1992) Millimeter-wave observations of Saturn, Uranus et Neptune : CO and HCN on Neptune, *Astrophys. J.* **392**, L99-L102.

Sackman, I.J., Boothroyd, A.I. and Fowler, W.A. (1990) Our Sun. I. The standard model : successes and failures, *Astrophys. J.* **360**, 727-736.

Sandel, B.R. *et al.* (1982) Extreme ultraviolet observations from the Voyager 2 encounter with Saturn, *Science* **215**, 548-553.

Saint-Pé, O., Combes, M., Rigaut, F., Tomasko, M. and Fulchignoni, M. (1993a) Demonstration of adaptive optics for resolved imagery of Solar-system objects : Preliminary results on Pallas and Titan, *Icarus* **105**, 263-270.

Saint-Pé, O., Combes, M. and Rigaut, F. (1993b) Ceres surface properties by high-resolution imaging from Earth, *Icarus* **105**, 271-281.

Spitzer, L. (1952), in G.P. Kuiper (edt.), *The Atmospheres of the Earth and Planets*, Chicago.

Stevenson, D.J. (1982), Formation of the giant planets, *Planet. Space Sci.* **30**, 755-764.

Trauger, J., Roesler, F., Carleton N,P, and Traub, W.A. (1973) Observation of HD on Jupiter and the D/H ratio, *Astrophys. J.* **184**, L137-L141.

Wildt, R. (1932) Veröff Univ. Sternwarte Göttingen 2 22 171