

THE COMPOSITION OF PLANETARY ATMOSPHERES

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During the past 10 years, great progress has been made in our knowledge of the planetary atmospheres, mainly due to the recent development of infrared techniques and space astronomy.

Three steps can be considered in the research development of planetary atmospheres from infrared spectroscopy: (1) detection of molecules; (2) determination of thermal profiles; (3) determination of abundance ratios. The third point, which requires the achievement of both (1) and (2), is the most important from an astrophysical point of view, since abundance ratios are a basic tool for cosmogonical and cosmological studies.

Infrared spectroscopy has led to the discovery of minor molecules and isotopes on Mars and Venus. Nevertheless the most accurate abundance ratios have been derived from in situ measurements (mass spectrometry, chromatography).

IR observations have proven to be efficient for the detection of thin atmospheres on faint objects (Triton, Pluto, Io). Also, they were especially successful for the determination of the chemical atmospheric composition of the giant planets and for the related determination of abundance ratios in these planets. Jupiter is the most extensively studied, and IR spectroscopy has led to the discovery of a large number of molecules and to the determination of major abundance ratios: H_2/He , D/H , $^{12}C/^{13}C$, $^{15}N/^{14}N$, N/H , P/N , C/H . The authors' conclusion is that these ratios are close to the cosmic values while other authors conclude to a significant enrichment of most of the elements with respect to H. This controversy is reviewed and analyzed. Concerning the other outer planets, the H_2/He ratio, in spite of large uncertainties, seems to be solar, too, and the C/H ratio, following most of the studies, is significantly enriched on Uranus and Neptune.

TABLE I
Observed Molecules in the Atmosphere of Jupiter

Molecule	Spectral Range	Reference
He	584 Å	Judge and Carlson (1974)
HD	7460 Å	Trauger et al (1973)
H ₂	0.8 μm 2.5 μm 1.25 μm	Kiess et al. (1960) Martin et al. (1976) De Bergh et al. (1977)
CH ₄	0.8 μm 1 - 2 μm 1.1 μm 8 μm	Wildt (1932) Kuiper (1952) Walker and Hayes (1967), Maillard et al. (1973) Gillett et al. (1969)
¹³ CH ₄	1.1 μm	Fox et al. (1972), De Bergh et al. (1976)
CH ₃ D	5 μm	Beer et al. (1972)
NH ₃	Visible 1 - 2 μm 10 μm 50 - 200 μm	Wildt (1932) Kuiper (1952) Aitken and Jones (1972) Furniss et al. (1978), Erickson et al. (1978), Baluteau et al. (1978,1980)
¹⁵ NH ₃	10 μm	Encrenaz et al. (1978)
H ₂ O	5 μm	Larson et al. (1975)
CO	5 μm	Beer (1975)
GeH ₄	5 μm	Fink et al. (1978)
PH ₃	2 μm 5 μm 10 μm	Larson and Fink (1977) Larson et al. (1977) Ridgway (1974)
C ₂ H ₂	13 μm	Ridgway (1974), Combes et al. (1974), Aumann and Orton (1976)
C ₂ H ₆	12 μm	Ridgway (1974), Combes et al (1974), Tokunaga et al. (1976)

I. INTRODUCTION

Two main reasons can explain the huge progress achieved during the past decade in our knowledge of the composition of planetary atmospheres. First, in situ measurements from space vehicles (Mariner, Pioneer, Venera, ...) have provided basic data on the atmospheric composition of terrestrial planets. Second, the recent and spectacular development of infrared astronomy, from the ground and in space, has drastically improved our knowledge of the atmospheric composition of such fainter objects as the Giant Planets and their satellites.

In the case of Jupiter, infrared spectroscopy is responsible for the discovery of most of the minor molecules (see Table I). While H_2 , CH_4 , and NH_3 were the only detected constituents known in 1970, a dozen new molecules have been identified during the past decade. Most of these molecules have been detected in the near IR range ($1\mu m < \lambda < 3\mu m$) or in the far infrared range ($\lambda > 5\mu m$). Infrared astronomy is also responsible for the discovery of an internal source of energy on Jupiter, Saturn, and Neptune (Armstrong et al. 1972; Gautier and Courtin 1979). In the case of Titan our present understanding of its atmosphere is mainly built upon infrared spectroscopic observations.

The success of infrared astronomy for the study of planetary atmospheres is easy to understand if we keep in mind that the planets of the solar system are typical infrared objects. There are two kinds of infrared radiation coming from the planets; a solar photon in the visible and near IR range entering the planetary atmosphere can be either scattered by the molecules and/or the particles and sent back to the Earth at the same wavelength, or absorbed by one of the atmospheric constituents and converted into thermal heat. Knowing the size of the planet, its mean visible albedo and its distance to the Sun, it is easy to calculate the effective temperature expected for the planet (Table II) and thus the spectrum of its infrared radiation (Figure 1). In the case of the giant planets, the value of the albedo is close to 0.5 which means that approximately one half of the solar incoming flux is scattered back in the visible and near IR range, and the other half is thermal radiation, approximately corresponding to the backbody curve of its effective temperature. As seen on Table II and Figure 1, the wavelength of maximum thermal emission ranges from $13\mu m$ in the case of the Earth, to $110\mu m$ in the case of Neptune.

Apart from the favorable shape of their spectra, the planets have another advantage: they are extended objects. Their diameters can reach one arcmin for Venus, 44 arcsec for Jupiter. For these two reasons Venus, Mars, and Jupiter are, apart from the Sun and the Moon, the brightest infrared sources in the sky, and are consequently observed in all the astronomical infrared experiments, at least as calibration sources.

Concerning the infrared experiments devoted to planetary observations, various types of instruments are used. In the terrestrial

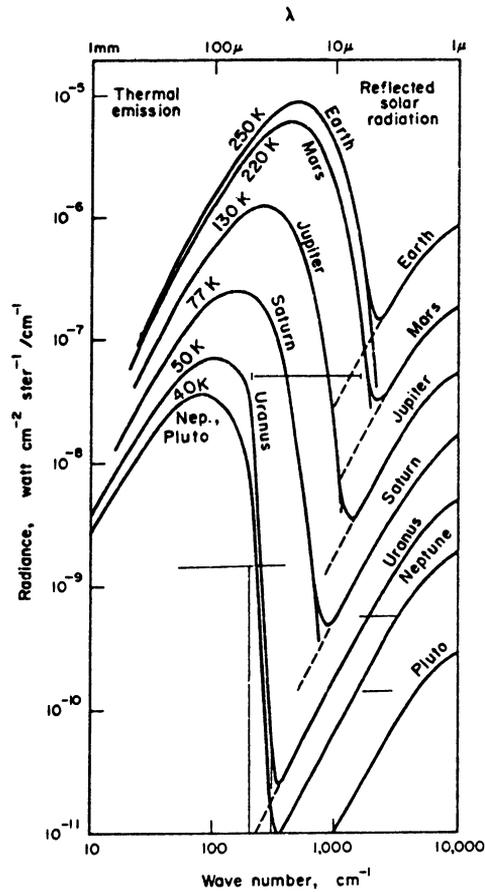


Figure 1. Thermal emission and reflected solar radiation of the planets (from Encrenaz 1979).

TABLE II

Thermal Emission of the Giant Planets

(NB: The difference in Columns I and III indicates the existence of an internal source of energy on Jupiter, Saturn, and Neptune.)

Planet	T_e (expected) (°K)	λ_{\max} (expected) (μ)	T_e (observed) (°K)
Jupiter	105	50	125
Saturn	77	66	90 - 95
Uranus	55	80	57
Neptune	45	110	~ 55

atmospheric windows (5 μ m, 10 μ m, 20 μ m), the use of ground-based large telescopes, associated with high sensitivity detectors, gives--in the case of the brightest planets--a signal-to-noise ratio high enough to allow high spectral resolution. With Fourier Transform Spectrometers, the resolving power can reach 10^5 in the near IR range (Maillard et al. 1973; Lecacheux et al. 1976) and 10^4 at 5 μ m (Larson 1980) and 10 μ m (Tokunaga et al. 1979b). An even higher resolving power (10^6) is obtained with the heterodyne technique at 10 μ m, which has been developed during the past 5 years (Abbas et al. 1976) and applied to planetary observations (Mumma et al. 1979). The development of airborne observations has opened the available spectral range, especially toward longer wavelengths ($\lambda > 50\mu$ m). However, the resolving power is most often limited to 100 or less, due to the smaller telescope, the shorter integration time and the decrease in flux relative to shorter wavelengths. Nevertheless these far infrared planetary observations have proven to be very useful in particular for the determination of the H₂/He ratio on the giant planets (Gautier et al. 1977; Courtin et al. 1978, 1979). In contrast, most of the detection of minor molecules has been obtained in the near infrared range or in the 5 μ m and 10 μ m atmospheric window with high resolution spectroscopy.

In this paper, we first discuss the astrophysical information which can be derived from infrared planetary spectra (Part II). In Part III, we present the results obtained in the identification of atmospheric constituents. Part IV briefly reports the contribution of IR spectroscopy in the determination of the thermal profile T(P). In Part V we present and analyze the astrophysical implications: determination of abundance ratio, physical processes involved in the vertical profiles of non-uniformly mixed constituents. Perspectives and conclusions are discussed in Part VI.

II. THE ASTROPHYSICAL OBJECTIVES

The planetary atmospheres constitute a basic tool for our understanding of the origin and the evolution of our Solar System. The terrestrial planets, because of their small size and relative proximity to the Sun, have been unable to retain their primitive atmospheres; a comparative study of the elemental and isotopic relative abundances derived from the composition of their atmospheres and/or their surfaces is the only way to understand the early stages of planetary formation in the vicinity of the Sun. In contrast, the giant planets, which are cold and large objects, must have retained in their atmospheres the composition of the primordial solar nebula. The study of their atmospheric composition is of major interest for understanding the composition and physical conditions of the primordial nebula at the time of the solar system formation.

The first astrophysical result which can be derived from the reduction of infrared planetary spectra is the detection of minor molecules. This determination requires only the knowledge

of the frequencies of the lines of multiplets. The infrared range is especially well adapted for this work, because most of the molecules exhibit strong vibration-rotation bands (mostly fundamentals) between 1 and 20 μm . In contrast with the visible range, the structure of these bands is relatively simple and they have been extensively studied in the laboratory. They are sufficiently separated from one another and they present a large number of individual lines, which allows unambiguous determinations.

The mechanism of line formation in a planetary atmosphere depends upon the kind of radiation which is considered. In the near infrared range, the solar radiation is either absorbed or scattered by a molecule or a particle. Thus, in this spectral range, molecular lines in a planetary spectrum usually appear in absorption, apart from the case of nonthermal effects. In contrast, in the far infrared range where thermal emission takes place the measured flux refers in a first approximation to the atmospheric level where the optical depth is equal to one; the probed atmospheric regions most often correspond to pressures larger than 1-10 bars, where L.T.E. takes place. The far IR measured flux is thus a strong function of the thermal atmospheric profile, and the molecular lines or bands can appear either in emission or in absorption, as a function of the temperature lapse rate in the formation region.

It clearly appears that, even when the absolute intensities of the molecular bands are known in the laboratory, it is usually not possible to derive the abundance of an atmospheric constituent from a planetary spectrum. In the far infrared range, this determination requires the knowledge of the thermal profile; in the near-infrared range, it requires the T(P) profile and also all the scattering parameters (scattering probabilities, scattering phase functions) which are usually unknown. However, in the latter case, a rough estimate of the absorber abundance can be derived with the hypothesis of the "reflecting layer model" which assumes no scattering above a purely reflecting layer (cloud or surface). This assumption is reasonable in the case of a tenuous atmosphere, as Mars; it has been used also for a long time in the case of the giant planets, in the absence of any other information; the validity of the method in this case will be discussed in more detail below.

The second step in the interpretation of planetary spectra is thus the determination of the thermal profile (e.g., Figure 2), which is needed in all cases to derive abundance measurements and, later on, abundance ratios. Various methods can be used for the determination of the temperature-pressure (T(P)) relationship. In the case of Mars, Venus, and Jupiter, thermal profiles have been derived from radio-occultation experiments aboard space vehicles (Mariner, Pioneer: Kliore et al. 1972; Kliore and Woiceshyn 1976), and also, on Mars and Venus, from *in situ* measurements. In the case of the giant planets, most of our information about the T(P) profile comes from their infrared spectrum, as is discussed in detail by Dr. G. Orton in the present

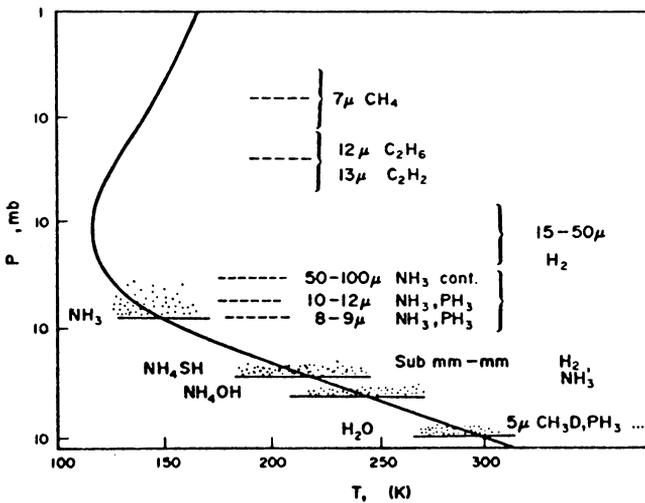


Figure 2. Jovian atmospheric layers probed in the far IR range (from Encrenaz 1979).

volume. On Jupiter, Hanel et al. (1979a,b) have obtained a set of thermal profiles on various points of the Jovian disk, from interferometric measurements at 4 cm^{-1} resolution between 200 and 2000 cm^{-1} (5–50 μm). For the other giant planets all the information comes from ground-based observations (Gautier et al. 1977a; Courtin et al. 1978, 1979).

Once the first two steps are achieved, it becomes possible to derive from infrared planetary spectra information which is of much higher astrophysical interest. Indeed, once the thermal profile is known, abundance ratios can be derived and, in the case of non-uniformly mixed constituents, vertical distribution profiles can be obtained. First, these determinations allow us to study the physical and chemical processes involved in the planetary atmospheres (photochemistry, condensation, circulation, chemical reactions,...), and to learn the nature and the evolution of the cloud structure, and then to start understanding the climate of these planets. But these planetary studies also have a more general implication. The elemental and isotopic ratios derived in the giant planets actually reflect, in many cases, the composition and physical conditions of the primordial nebula at the time of the solar system formation. Comparison with data obtained in the interstellar medium can give information about the general problem of star formation. On the other hand, comparative studies of the basic ratios on the four giant planets may show evidence for an inhomogeneous distribution of the elements as a function of their distance from the Sun. The study of some stable isotopes ($^{12}\text{C}/^{13}\text{C}$, $^{14}\text{N}/^{15}\text{N}$) can give information about the chemical evolution of the Galaxy; finally, precise determinations of D/H, H/He, $^3\text{He}/^4\text{He}$ in

the solar system (and in particular in the giant planets) are basic tools for discriminating among different cosmological models.

III. DETECTION OF MOLECULES

In spite of the major role of *in situ* measurements for the determination of the atmospheric composition on Mars or Venus, it is worthwhile to recall what has been the contribution of infrared spectroscopy in the identification of molecular species. Tables III and IV give a list of molecules detected on Venus and Mars by infrared spectroscopy.

TABLE III

Observed Molecules in the Atmosphere of Venus

Molecule	Spectral Range	Resolution	Reference
CO ₂	0.9 - 1.8 μm	5 x 10 ⁻³ μm	Kuiper (1952)
	750 - 1250 cm ⁻¹	1.25 cm ⁻¹	Hanel et al. (1968)
CO ₂ , H ₂ SO ₄	450 - 1250 cm ⁻¹	0.67 cm ⁻¹	Samuelson et al. (1975)
" "	" "	0.25 cm ⁻¹	Kunde et al. (1977)
	500 - 800 cm ⁻¹	3.2 cm ⁻¹	Orton and Aumann (1977)
CO ₂	900 - 1100 cm ⁻¹	10 ⁻³ cm ⁻¹	Mumma et al. (1980)
HCl } HF } CO }	5000 - 6000 cm ⁻¹	0.1 cm ⁻¹	Connes et al. (1967) Connes et al. (1968)
H ₂ O	35 - 55 μm		Taylor et al. (1980)
CO ₂ , H ₂ SO ₄	1 - 4 μm	0.04 μm	Pollack et al. (1974)

Carbon dioxide was first identified spectroscopically in the near infrared range (Kuiper 1952) on Mars and Venus where it is the most abundant element. Other determinations were made later on at 8700 Å on Mars (Kaplan et al. 1964; Spinrad et al. 1966) with a first measurement of the CO₂ abundance. In the case of Venus, the amount of carbon dioxide was obtained from *in situ* measurements (Venera 4, 5, and 6; Vinogradov et al. 1968; Avduevsky et al. 1970).

Water vapor was first spectroscopically identified on Mars at 8700 Å (Kaplan et al. 1964); these observations already indicated a variation of H₂O with the seasons on Mars. The amount of H₂O on Mars was later monitored by the IRIS experiment during the Mariner 9

mission (Conrath et al. 1973). On Venus, water vapor was detected from the earth in the red range (Schorn et al. 1969), but did not appear in the near IR (Connes et al. 1967) nor in the 8-22 μm range (Kunde et al. 1977). Further information on H_2O was provided by the infrared radiometer experiment (VORTEX) of Pioneer Venus which has identified H_2O in its far infrared channel (35-55 μm) (Taylor et al. 1980; Beer 1980; McCleese 1980).

TABLE IV

Observed Molecules in the Martian Atmosphere

Molecule	Resolution (cm^{-1})	Spectral Range (cm^{-1})	Abundance	Reference
CO_2	0.2	9530	68 ± 26 m-atm	Belton and Hunten (1966)
"		700 - 1200		Sinton and Strong (1960)
"	20	"	65 ± 30 m-atm	Verdet et al. (1972)
"		4000 - 12500		Kuiper (1952)
"	2.4	200 - 2000		Conrath et al. (1973)
CO_2	}	"		Maguire (1977)
$\text{C}^{16}\text{O}^{18}\text{O}$				
$\text{C}^{16}\text{O}^{18}\text{O}$				
$^{13}\text{CO}_2$				
$^{13}\text{CO}_2$	10^{-3}	1000		Peterson et al. (1974)
CO_2	"	"		Mumma et al. (1975); Betz (1975)
H_2O	2.4	200 - 2000		Conrath et al. (1973)
CO	0.1	4000 - 6500	5.6 cm-am	Kaplan et al. (1969)
O_2 (O_3)	0.02	7850 - 7900		Noxon et al. (1976) Traub et al. (1977)

Infrared spectroscopy has proven to be especially useful in the near infrared (1 - 2.5 μm) with the use of the high resolution Fourier Transform spectrometer built by P. and J. Connes (Connes and Connes 1966): with this instrument, HCl , HF , CO , H_2SO_4 have been identified on Venus, CO and O_2 on Mars. Another powerful instrument has been the IRIS Michelson interferometer working between 5 μm and 50 μm , flown on

the Mariner 9 mission: H_2O , CO_2 and its isotopes have been identified on Mars (Maguire 1977). A third kind of result which has to be mentioned is the high resolution (10^6) profiles of CO_2 obtained at $10\ \mu\text{m}$ with a new heterodyne spectrometer (Mumma et al. 1975; Betz 1975; Mumma et al. 1980).

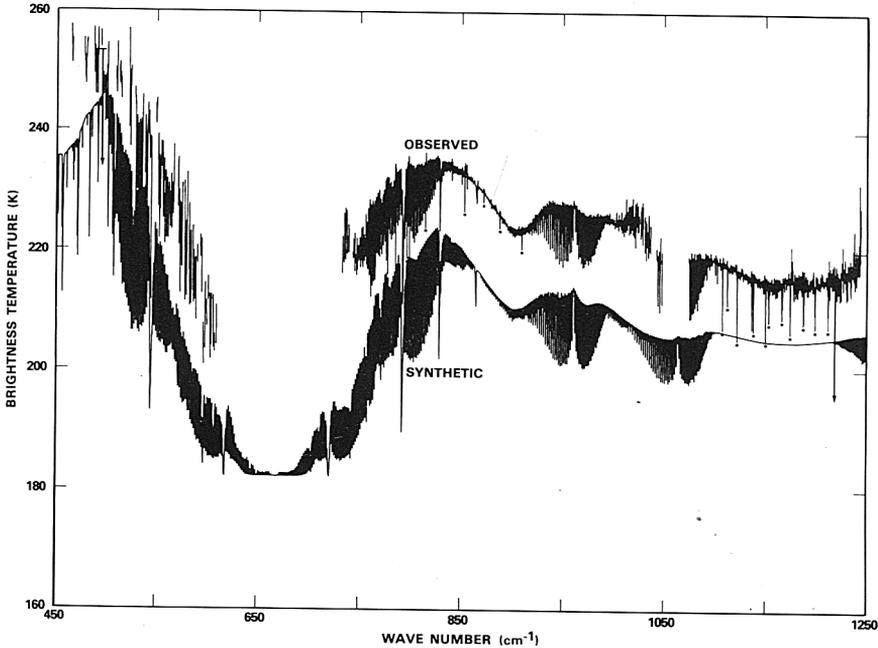


Figure 3. Synthetic and observed spectra of Venus, by Kunde et al. (1977). The broad absorption feature around $900\ \text{cm}^{-1}$ is attributed to H_2SO_4 haze.

The infrared range is also most suitable for searching for particles and droplets. Spectroscopic experiments can identify the nature of these particles and droplets by the observation of their broad infrared absorptions, while polarimetry measurements can give information upon their size. A haze of H_2SO_4 has been identified on Venus between 870 and $930\ \text{cm}^{-1}$ (Figure 3) (Kunde et al. 1977). On Mars, the silicate absorption at $10\ \mu\text{m}$ is present in a ground-based spectrum recorded during the dust storm (Verdet et al. 1972) and on the Mariner 9 IRIS spectra (Figure 4) (Hanel et al. 1972). The IRIS experiment also identified around $800\ \text{cm}^{-1}$ broad absorption features due to H_2O ice clouds on some points of the Martian disk. In the case of giant planets, all the molecular identifications are the results of infrared spectroscopic experiments, apart from He and HD on Jupiter

(Table I). Most of these observations have been made with Fourier Transform spectrometers with a resolving power better than 10^3 (Figure 5). On Jupiter H_2 , $^{13}CH_4$, CH_3D , C_2H_2 , C_2H_6 , CO , PH_3 , $^{15}NH_3$ have been detected from the ground while H_2O and GeH_4 were observed from the Kuiper Airborne Observatory at $5 \mu m$. NH_3 ice was also identified on Jupiter at $8 - 9 \mu m$ (Orton 1975b; Encrenaz et al. 1980). This illustrates the major role played by ground-based astronomy in the terrestrial atmospheric windows, especially $5 \mu m$, $7 - 13 \mu m$ (Figure 6), and the near IR range. In the case of Saturn (Table V) the interpretation of its spectrum at $10 \mu m$ has been controversial: the features appearing between 930 and 990 cm^{-1} were attributed either to PH_3 in absorption (Bregman et al. 1975) or to C_2H_4 in emission (Encrenaz et al. 1975). The recent spectrum recorded by Tokunaga et al. (1980) demonstrates that Bregman et al.'s interpretation was right. The absence of C_2H_4 on Saturn can be related to the absence of C_2H_4 on Jupiter (Encrenaz et al. 1978). In contrast, the presence of C_2H_4 has been suggested on Titan from the observation of an emission feature at $10.5 \mu m$ (Gillett 1975).

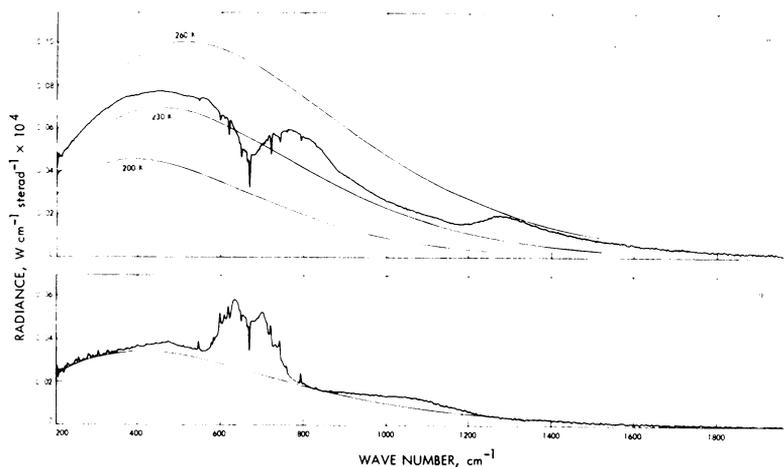


Figure 4. Thermal spectra of Mars (A: non polar; B: polar), with the Mariner 9 IRIS experiment. The figure is taken from Hanel et al. (1972).

Concerning Uranus and Neptune (Table VI), the detection of molecules comes from the visible and near infrared range when strong CH bands are present. In addition, an emission feature has been detected at $8 \mu m$ and $12 \mu m$ on Neptune, corresponding to CH_4 and C_2H_6 respectively, but not on Uranus (Gillett and Rieke 1977; Macy and Sinton 1977). As will be discussed below, this difference in the spectra of Uranus and Neptune in the $8 - 12 \mu m$ range is explained by different thermal profiles in the upper atmospheres of Uranus and Neptune.

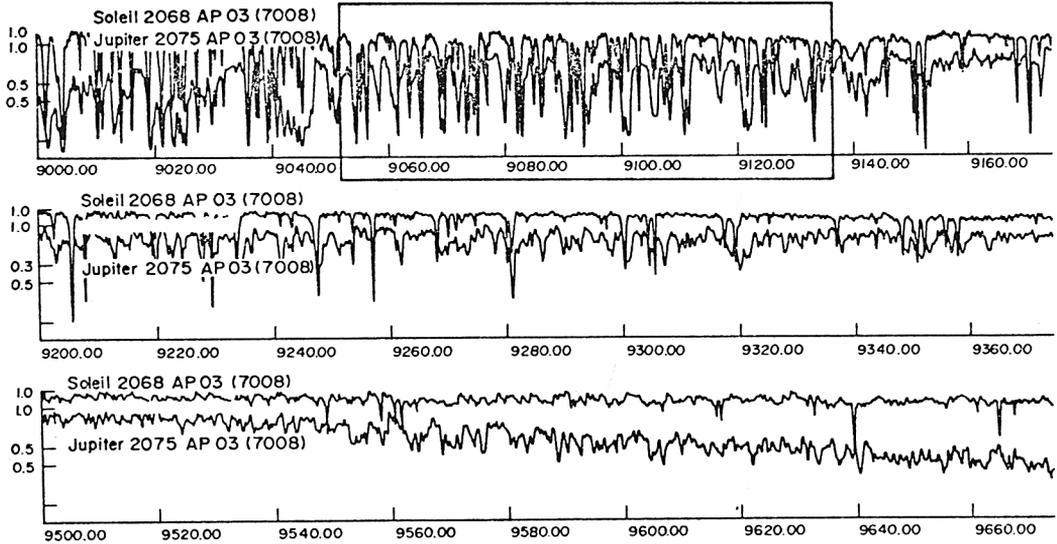


Figure 5. The spectrum of Jupiter (heavy line) and the solar comparison spectrum (light line) in the region of the $3\nu_3$ CH_4 band ($9000\text{--}9700\text{ cm}^{-1}$). This figure is taken from Maillard et al. (1973).

TABLE V

Observed Molecules in the Atmosphere of Saturn

Molecule	Spectral Range	Reference
H_2	0.8 μm 1.25 μm	Kiess et al. (1960) DeBergh et al. (1977)
HD	6064 \AA	Macy and Smith (1978)
CH_4	0.8 μm , 1–2 μm 1.1 μm	Wildt (1932); Kuiper (1952) DeBergh et al. (1973)
$^{13}\text{CH}_4$	1.1 μm	Combes et al. (1975)
CH_3D	5 μm	Fink and Larson (1977)
NH_3	6450 \AA	Encrenaz et al. (1974)
PH_3	3 μm , 5 μm 10 μm	Fink and Larson (1977) Bregman et al. (1975); Tokunaga et al. (1980)
C_2H_6	12 μm	Tokunaga et al. (1975)

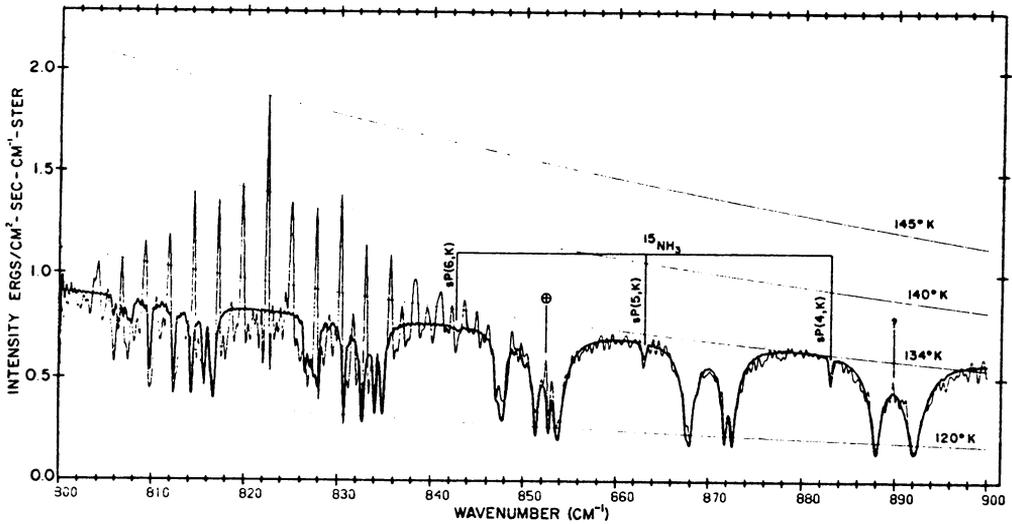


Figure 6. The spectrum of Jupiter in the 11-12.5 μm range, from Tokunaga et al. (1979b).

TABLE VI

Observed Molecules on Uranus, Neptune, and Titan

Planet/Satellite	Molecule	Spectral	Reference
Uranus	H ₂	0.6 - 0.8 μm	Giver and Spinrad 1966
	CH ₄	Visible	Kuiper (1952)
	HD	Visible	Macy and Smith (1978)
Neptune	H ₂	0.6 - 0.8 μm	Trafton (1972)
	CH ₄	Visible	Kuiper (1952)
	"	8 μm	Macy and Sinton (1977)
	C ₂ H ₆	12 μm	Gillett and Rieke (1977)
Titan	H ₂	6400 Å	Trafton (1974)
	C ₂ H ₆	Visible	Kuiper (1944)
	"	1.1 μm	Trafton (1975)
	"	8 μm	Gillett et al. (1973)
	C ₂ H ₂ , C ₂ H ₆ CH ₃ D, C ₂ H ₄	10 - 13 μm	Gillett (1975)

There are three satellites of major planets where an atmosphere has been detected at the present time. The most fascinating of them is probably Titan which fills at least two conditions favorable for the development of the early stages of life: a surface and a reducing atmosphere. The atmosphere of Titan has been known since 1944 (Kuiper 1944). Methane was detected in the visible, then the $3\nu_3$ band of CH_4 at $1.4 \mu\text{m}$ was observed by Trafton (1975). The identification of H_2 , first suggested by Trafton (1972), is still tentative (Munch et al. 1977). The other molecular determinations have been done in the $7 - 13 \mu\text{m}$ region by Gillett (1975): emission features have been tentatively identified as C_2H_2 , C_2H_6 , C_2H_4 , and CH_3D . The far infrared spectrum of Titan ($16 - 30 \mu\text{m}$) recorded by McCarthy et al. (1980) has been interpreted by the authors in terms of a thin dust haze high in the atmosphere. The peculiar interest presented by Io and its volcanoes has been spectacularly demonstrated by the imaging experiment of the Voyager mission. At the same time, a detection of SO_2 has been made at 1350 cm^{-1} with the IRIS interferometer (Pearl et al. 1979). The apparent discrepancy with the upper limit of SO_2 derived from IUE in the ultraviolet range (Butterworth et al. 1980) can be resolved if the SO_2 atmosphere is confined to the vicinity of the volcanoes, or if the SO_2 abundance on Io is variable with time. It is interesting to mention that the volcano eruptions on Io seem to be correlated with $5 \mu\text{m}$ outbursts, which could be due to vapor eruptions of liquid sulfur (Sinton 1979).

The first indication of methane atmospheres on Triton, satellite of Neptune, and Pluto, was given by Cruikshank and Silvaggio (1979, 1980) who reported the observation of broad absorption features at $2.2 \mu\text{m}$ and $1.7 \mu\text{m}$ respectively. The Pluto absorption was attributed to a combination of gaseous and solid methane, in agreement with the previous CH_4 ice identification of Cruikshank et al. (1976). Trafton, using model calculations, reported later that the existence of gaseous CH_4 on Pluto requires the presence of a heavier and more abundant gas (Trafton 1979b). The Triton absorption was attributed to a tenuous CH_4 atmosphere. In both cases, more measurements are required for determining the nature and the density of these tenuous atmospheres.

IV. DETERMINATION OF THE THERMAL PROFILE

In this part, we give a few examples of the contribution of infrared spectroscopy in the determination of the thermal planetary structure, especially in the case where this information is absolutely needed for our understanding of the atmospheric composition.

The first method consists in the determination of the $T(P)$ profile using the thermal infrared spectrum of the planet in a spectral range where the main atmospheric constituent is absorbing. The method consists of choosing a set of frequencies corresponding to well separated atmospheric levels where the radiation comes from (in a first approximation the levels of optical depth equal to 1). From the measurement

of the thermal flux at these wavelengths, it is possible to generate an iterative method which converges toward the true profile $T(P)$. This method has been used in the case of Venus, in the CO_2 absorption region at $15 \mu\text{m}$, by the VORTEX experiment on the Pioneer Orbiter mission (Taylor et al. 1980). In the case of the giant planets, the method has been used in a slightly different way: two absorbers are responsible for most of the far IR spectrum between 15 and $50 \mu\text{m}$: hydrogen and helium, in a relative abundance ratio which must be determined also. Since the absorption coefficient is a function of this H_2/He ratio, it is possible to generate a double-iterative method, which converges toward both the true $T(P)$ profile and the true H_2/He ratio. This method is presented and discussed in detail by Orton (1980) in the present symposium. It was first applied to Jupiter (Orton 1975a, 1977; Wallace and Smith 1977; Gautier et al. 1977a) then to the other giant planets (Gautier et al. 1977b; Courtin et al. 1978, 1979) from ground-based observations. The same method was used on Jupiter by the IRIS experiment during the Voyager mission (Hanel et al. 1979a, b). This determination has the advantage of requiring no high spectral resolution: for the giant planets, a resolving power of 10 to 50 is sufficient. The measurement of the H_2/He mixing ratio derived from this method will be discussed in more detail below. Figure 2 shows a typical thermal profile in the case of Jupiter. It can be shown that the four profiles are characterized by a convective zone where the measured lapse rate seems very close to the adiabatic value, a minimum value at a pressure around 0.03 bar, and apart from Uranus, a strong increase of temperature as a function of altitude in the lower stratosphere.

In another way, spectroscopic observations in the thermal range ($\lambda > 5 \mu\text{m}$) can provide constraints on the temperature profile. The reason is, as explained above, the close relationship between the measured brightness temperature (T_B) and the true temperature of a given atmospheric level. As an example, the measured T_B cannot be smaller than the minimum value of the temperature profile: this remark has been used to derive an upper limit of the Jovian minimum temperature from the observation of the NH_3 absorption line centers at $10 \mu\text{m}$ (Combes et al. 1976). Another example is given by the emission bands of CH_4 at $7.7 \mu\text{m}$ and, at $12 - 13 \mu\text{m}$, C_2H_2 and C_2H_6 . The first observation of the high flux measured at $8 \mu\text{m}$ on Jupiter by Gillett et al. (1969) was the first element in favor of a temperature inversion on Jupiter. Later on, the observation of C_2H_2 and C_2H_6 gave another experimental support to this idea (Ridgway 1974; Combes et al. 1974; Orton and Aumann 1977). Information upon $T(P)$ from the lower Jovian stratosphere has also been derived from the far infrared Jovian spectrum in the NH_3 rotational spectrum (Vapillon et al. 1977; Goorvitch et al. 1979); however, there is another unknown parameter which is the upper NH_3 density distribution. In the case of Saturn, infrared observations at $20 \mu\text{m}$ along the central meridian were used to derive $T(P)$ distributions at the equator and at the poles (Tokunaga et al. 1978).

TABLE VII

Abundance Ratios on Venus

Molecule/Ratio	Measured Value	Atmospheric Level	Reference
$^{12}\text{C}/^{13}\text{C}$	Terrestrial		Connes et al. (1968) (Ground-based Sp.)
<u>Upper Atmosphere</u>			
CO_2	$6 \times 10^9 \text{ cm}^{-3}$	135 km	Von Zahn et al. (1979)
He	$5 \times 10^6 \text{ cm}^{-3}$	} > 155 km	Mass spectr. "
CO_2	$1.1 \times 10^9 \text{ cm}^{-3}$		
CO	$2.4 \times 10^8 \text{ cm}^{-3}$		
N_2	$2.1 \times 10^8 \text{ cm}^{-3}$		
O	$6.6 \times 10^8 \text{ cm}^{-3}$		
He	$2 \times 10^6 \text{ cm}^{-3}$		
$\left. \begin{array}{l} ^{12}\text{C}/^{13}\text{C} \\ ^{16}\text{O}/^{17}\text{O} \\ ^{16}\text{O}/^{18}\text{O} \end{array} \right\}$	Terrestrial		Niemann et al. (1979) Mass spectr. (probe)
<u>Lower Atmosphere</u>			
$^{36}\text{Ar}/^{12}\text{C}$	10^{-4}		Hoffman et al. (1979) Mass spectr. (probe)
$\text{S}_2, \text{S}_8, \text{COS}, \text{H}_2\text{S}$			
CO_2	$96.4 \pm 1.03\%$	} 24 km	Oyama et al. (1979) Gas chromat. (probe)
N_2	$3.41 \pm 0.02\%$		
H_2O	< 0.06%		
O_2	$69.3 \pm 1.3 \text{ ppm}$		
Ar	18.6 ± 2.4		
Ne	$4.3 (+5.5, -3.9)$		
SO_2	$186 (+349, -156)$		

V. ATMOSPHERIC COMPOSITION AND ABUNDANCE RATIOS

A. Venus and Mars

Results on abundance ratios measured in the atmospheres of Venus and Mars are listed in Tables VII and VIII. In the case of Venus, apart from a $^{12}\text{C}/^{13}\text{C}$ determination from infrared ground-based spectroscopy, the information comes entirely from space missions. Abundances were measured by mass spectrometers and gas chromatographs aboard the probes of the Pioneer Venus mission and the Venera 11 and 12

missions. These *in situ* measurements have shown that the Venus atmosphere is governed by sulfur chemistry. In the upper oxidizing atmosphere (40 - 90 km), sulfur is present in H_2SO_4 and, at lower levels, SO_2 and O_2 are detected (Sill 1979). In the lower reducing atmosphere near the surface S_2 , S_8 , COS , and H_2S have been detected by the Pioneer mass spectrometer (Hoffman et al. 1979). Sulfur is expected to condense in droplets near 32 km. The CO molecule has been detected in the upper atmosphere above 150 km (Niemann et al. 1979), in agreement with millimetric ground-based measurements at $2.6 \mu m$ (Schloerb et al. 1979; Muhleman et al. 1979; Wilson and Klein 1979). In the case of Mars, the isotopic ratios previously estimated by ground-based experiments and by Mariner 9 IRIS data have been remeasured with high accuracy with the Viking mass spectrometer experiment (Nier et al. 1976; Biemann et al. 1976). In particular, a ^{15}N enhancement by a factor of 75% has been found (Table VIII). This enrichment is attributed to selective escape from the Martian upper atmosphere, implying that Mars must have lost an appreciable amount of N_2 to space during its history (McElroy et al. 1976).

TABLE VIII

Abundance Ratios on Mars

Ratio	Method	Measured Value	Reference
$^{12}C/^{13}C$	Ground-based Sp.	Terrestrial	Kaplan et al. (1969)
"	"	"	Young (1971)
"	Mariner 9 (IRIS)	89 ± 13	Maguire (1977)
"	Viking Mass Sp.	85 ± 9	Biemann et al. (1976)
	"	87 ± 3	Nier et al. (1976)
$^{16}O/^{17}O$ $^{16}O/^{18}O$	Mariner 9 (IRIS)	Terrestrial	Maguire (1977)
$^{16}O/^{18}O$	Viking Mass Sp	526 ± 50	Biemann et al (1976)
$^{14}N/^{15}N$	"	175 ± 25	"
$^{36}Ar/^{38}Ar$	"	(75% ^{15}N enrich.) $4 - 7$	"

B. The Giant Planets and Their Satellites

In what follows, two cases can be considered. If the constituents are homogeneously mixed with hydrogen, their vertical distribution is defined by a single parameter, which is the ratio of the corresponding element to hydrogen. In the case of nonhomogeneously mixed constituents, we have to determine their vertical distributions independently at different atmospheric levels, in order to understand the physical processes involved.

TABLE IX. ABUNDANCE RATIOS IN THE GIANT PLANETS

Ratio	Spectral Range	Jupiter	Saturn	Uranus	Other*
H ₂	thermal radiation	0.897±0.030 (1)†	>0.5 (2)	0.9±0.1 (3)	(☉) 0.89 (4) (PN) 0.871±0.02(5)
C	scattering model (visible+NIR)	2-3×10 ⁻³ (6)		3-10×10 ⁻³ (7)	(☉) 4.7 ^{+1.2} _{-1.0} ×10 ⁻⁴ (9)
H	scattering model (1-2 μm)	8×10 ⁻⁴ (8)	1.15×10 ⁻³ (8)	2×10 ⁻³ (8)	(Neptune) 9×10 ⁻⁴ (8)
	scattering model (1.1 μm)	1.5±0.7×10 ⁻³ (10)	2±1×10 ⁻³ (10)		
	visible+NIR	6.2±2.1×10 ⁻⁴ (11)		~10 ⁻² (12)	(Neptune) ~10 ⁻² (12)
	thermal radiation	7×10 ⁻⁴ (13) <10 ⁻³ (14) 7.0±2.2×10 ⁻⁴ (15)			
D	HD/H ₂	5.1±0.7×10 ⁻⁵ (16)	5.5±2.9×10 ⁻⁵ (17)	3.0±1.2×10 ⁻⁵ (17)	(PN) 2.5×10 ⁻⁵ (18)
H	(visible)	<2.3×10 ⁻⁵ (11)		1-2×10 ⁻⁵ (19)	(LIM) 1-2×10 ⁻⁵ (20)
CH ₃ D	5 μm	5×10 ⁻⁷ (21)			
H ₂	10 μm	2.5×10 ⁻⁷ (22) ≤2×10 ⁻⁷ (14) 5×10 ⁻⁷ (15)			
¹² C/ ¹³ C	1.1 μm	89 ⁺¹² ₋₁₀ (23)	89 ⁺²⁵ ₋₁₈ (23)		(☉) 89±5 (24)
¹⁵ N/ ¹⁴ N	10 μm	0.0037±0.0015 (25) 0.003 - 0.006 (26)			(☉) 0.0037 (4)

*Other: (☉)=Sun; (PN)=Primordial Nebula; (LIM)=Local Interstellar Medium; (☉)=Earth.

†REFERENCES:

- (9) Lambert 1978
- (10) Gautier et al. 1980
- (11) Gautier et al. 1977b
- (12) Courtin et al. 1978
- (13) Cameron 1974
- (14) Lequeux et al. 1979
- (15) Wallace and Hunten 1978
- (16) Benner and Fink 1980
- (17) Fink and Larson 1979
- (18) Geiss and Reeves 1972
- (19) Encrenaz and Combes 1978
- (20) Laurent 1978
- (21) Beer and Taylor 1978
- (22) Kunde et al. 1979
- (23) Combes et al. 1977
- (24) Hall et al. 1972
- (25) Encrenaz et al. 1978
- (26) Tokunaga et al. 1979b

a) The case of homogeneously mixed components

The abundance ratios which have been determined from homogeneously mixed constituents are H_2/He , C/H , D/H , $^{12}C/^{13}C$ and $^{14}N/^{15}N$.

H_2/He . The H_2/He ratio has been derived on Jupiter by the inversion of the Jovian far infrared spectrum, as explained above (Part IV). The first ground-based determinations resulted in a solar value of H_2/He (Orton 1975a, 1977; Wallace and Smith 1977; Gautier et al. 1977a): $He/(H_2 + He) = 0.89 \pm 0.06$. After the Voyager IRIS measurement, the error bar was divided by two (Rouan et al. 1980; Gautier et al. 1980). As shown on Table IX, the Jovian He/H_2 value is equal to the solar value, and--what is more significant--slightly smaller than the primordial value estimated by Lequeux et al. (1979) (Gautier et al. 1980). In the case of the other giant planets, the same method could apply in theory; however, in the case of Saturn and Neptune, the uncertainty in the present data is too large so that no information is obtained on H_2/He ; only T(P) is derived (Gautier et al. 1977b; Courtin et al. 1979). In contrast, H_2/He was obtained on Uranus, in good agreement with Jupiter's value: $H_2/(H_2 + He) = 0.9 \pm 0.1$ (Courtin et al. 1978).

C/H . Since the CH_4 spectrum extends from the visible to $8 \mu m$, it is possible to obtain estimates of C/H from both the near IR and the far IR range, at least on Jupiter where both sets of data exist.

The first C/H estimates on Jupiter were made some 10 years ago in the visible and near infrared range, where data were first available. As mentioned above, the simple "reflecting layer model" (RLM) was used, in the absence of any information about the Jovian atmospheric scattering. However, it is easy to demonstrate that the RLM approximation is not valid for the dense atmospheres of the giant planets: the ratios derived from different lines or bands of CH_4 vary by a factor of 3. Another attempt to solve the problem is the use of a scattering model; however, too many parameters, still unknown, are involved in this model, so that the solution is not unique: as summarized by Wallace and Hunt (1978) the derived C/H ratio ranges from the solar value to 3 or 4 times the solar value; in particular the recent study by Buriez and de Bergh (1980a), from the $3\nu_3CH_4$ band at $1.1 \mu m$, concludes that carbon is enriched by a factor 2 to 4. A different approach is used by Fink and Larson (1979) who prefer to use the CH_4 weak bands at longer wavelengths (1.2 and $1.6 \mu m$) because they may be used for the four giant planets and Titan, and also because the effect of scattering is minimized. They derive a C/H ratio enriched by a factor 2 relative to the solar value. A third method is defined by Combes and Encrenaz (1979), which consists of eliminating, as much as possible, the effects of scattering by defining appropriate conditions in the selection of the lines or bands used for the abundance ratio. Applying their method to Jupiter, they conclude that carbon is enriched by a factor 1.3.

Simultaneously, C/H estimates of Jupiter have been derived from its $7 - 8 \mu m$ spectrum. The first tentative estimate was made by Orton

(1977) corresponding to an enrichment of 1.5. This result is confirmed by the upper limit derived from the absence of the CH_4 absorption feature at $8 - 9 \mu\text{m}$, corresponding to a carbon enrichment smaller than 2 on Jupiter (Encrenaz et al. 1980). Finally, the carbon enrichment by a factor 1.5 on Jupiter is also confirmed by the Voyager IRIS experiment (Rouan et al. 1980; Kunde et al. 1980).

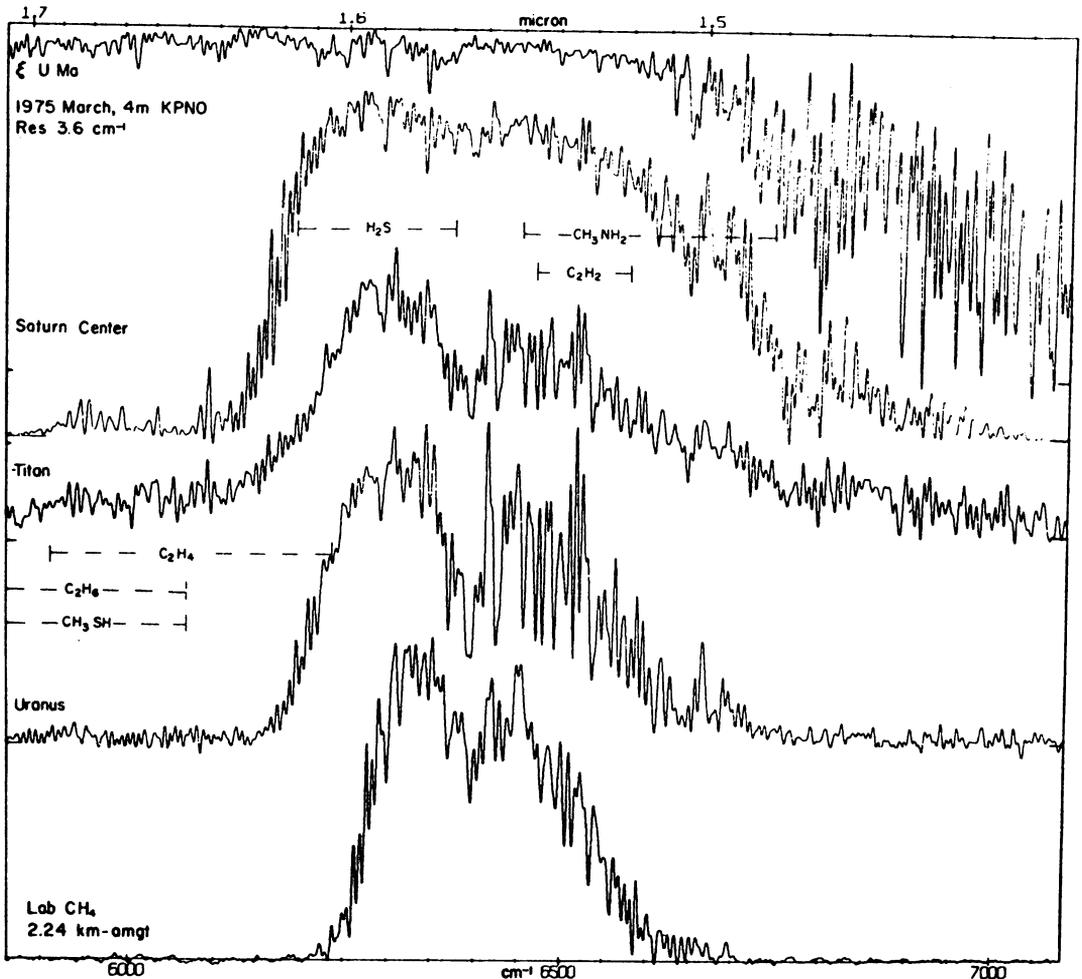


Figure 7. Spectra of Saturn, Uranus and Titan in the 6400 cm^{-1} methane window. The figure is taken from Fink and Larson (1979).

In conclusion, in spite of the apparent contradiction among the various determinations of the Jovian C/H ratio, some general considerations can be drawn. As shown in Table IX, there are basically two classes of results: (1) the Jovian C/H values derived from visible and near IR data, based on scattering model calculations, ranging from 2 to 5 times the solar value; (2) the values corresponding to a Jovian carbon enrichment less than a factor 2, which are based upon two methods: the use of the thermal spectrum between 7 and 9 μm , and the use of visible or near IR range data without scattering models, where the lines and bands have been chosen in order to eliminate as much as possible scattering effects. We have no explanation at the present time to explain this discrepancy. However, we strongly favor the second set of C/H values--implying a small carbon enrichment on Jupiter--for the following reasons. First, this low enrichment is derived from two completely independent methods. Second, the thermal infrared range is, in our opinion, more reliable because the physics involved is much simpler, since the effect of scattering is much less important than in the visible and near infrared ranges. Third, the variety of C/H results obtained from scattering models illustrates the non-uniqueness of the solution, because too many unknown parameters are involved in the calculations.

In the case of the other giant planets, the only data come from the visible and near infrared ranges. Here again a discrepancy exists between the values derived by Fink and Larson (1979) from the 1 - 2 μm range (see Figure 7), implying a constant carbon enrichment on the four giant planets, and other estimates implying higher carbon enrichments on Saturn (Boriez and de Bergh 1980b) or Uranus and Neptune (Lutz et al. 1976). With the improvement in quality of far infrared spectra, it should be possible to derive in the near future C/H estimates based upon thermal radiation, at least for Saturn and Neptune.

Finally, the case of Titan is especially puzzling. While methane has been detected in large amounts, the H_2 identification is too tentative to allow a reliable C/H ratio to be derived. Another difficulty comes from the very high CH_4 abundances derived on Titan from the near infrared bands, relative to the CH_4 amounts obtained from the visible CH_4 bands. In any case the H_2 abundance seems to be small compared to methane but another inert gas, such as N_2 , could be present in large abundance so that the uncertainty about the surface pressure ranges from 11 mb (Fink and Larson 1979) to 1 bar or more, according to various models (Trafton 1979a; Rages et al. 1979; Giver et al. 1979; Hunten 1978).

In conclusion, it should be mentioned that the solar C/H ratio itself is very uncertain: the derived value has been varying by a factor of 2 during the past 5 years (Cameron 1974; Mount and Linsky 1975; Pagel 1977; Lambert 1978). In the preceding discussion we have adopted the most recent value (4.7×10^{-4}), in agreement with Pagel (1977) and Lambert (1978).

$^{12}\text{C}/^{13}\text{C}$. The $^{13}\text{CH}_4$ molecule has been discovered in the $3\nu_3$ band at $1.1\ \mu\text{m}$ on both Jupiter and Saturn (Fox et al. 1972; de Bergh et al. 1976; Combes et al. 1975). The first $^{12}\text{C}/^{13}\text{C}$ values were derived with the RLM assumption and had no internal consistency: the choice of different lines led to different results: for Jupiter, 110 ± 35 (Fox et al. 1972) and 70_{-15}^{+30} (de Bergh et al. 1976); for Saturn, 35_{-15}^{+40} (Lecacheux et al. 1976).

Combes et al. (1977) applied to $^{12}\text{C}/^{13}\text{C}$ the method described later in detail by Combes and Encrenaz (1979) for eliminating the effect of scattering by a proper selection of the lines used in the ratio determination. This method led to new $^{12}\text{C}/^{13}\text{C}$ determinations on Jupiter and Saturn, 89_{-10}^{+12} and 89_{-18}^{+25} , respectively. As in the case of Mars and Venus, these ratios are in good agreement with the solar value. There is no determination of $^{12}\text{C}/^{13}\text{C}$ on Uranus and Neptune at the present time.

$^{14}\text{N}/^{15}\text{N}$. In this case, the only determination comes from the thermal radiation at $10\ \mu\text{m}$. The presence of $^{15}\text{NH}_3$ on Jupiter was first suggested by Lacy (1977, private communication) and definitely identified by Encrenaz et al. (1978). The derived $^{14}\text{N}/^{15}\text{N}$ Jovian ratio was found in agreement with the terrestrial value, but with a large uncertainty, mainly due to the noise of the spectrum. Tokunaga et al. (1979b) recorded later a high quality spectrum of the same spectral range and derived a ^{15}N enrichment on Jupiter with an error bar which still includes the terrestrial value. The error bar is still large because the authors show that it is not possible to find a $^{15}\text{N}/^{14}\text{N}$ ratio which fits the observations for all the $^{15}\text{NH}_3$ multiplets. More $^{15}\text{NH}_3$ laboratory measurements are needed to solve this problem. There is no $^{15}\text{N}/^{14}\text{N}$ determination at the present time on the other outer planets.

D/H. The D/H ratio on the giant planets is probably the most interesting number to determine, in view of its astrophysical implications. As in the case of C/H, its measurement is still strongly controversial.

Basically two methods can be used for determining the D/H ratio. The HD molecule can be used in the visible, associated with H_2 or CH_4 measurements in the same spectral range. The CH_3D molecule can also be used in the thermal range; the $\text{CH}_3\text{D}/\text{H}_2$ ratio is thus derived from thermal models.

From the HD observation on Jupiter at $7460\ \text{\AA}$, Trauger et al. (1973, 1977) derived for the Jovian D/H, with the RLM approximation, a value of $5.1 \pm 0.7 \times 10^5$, which corresponds to a deuterium enrichment around 2 relative to the expected value of the primordial nebula (estimated from other measurements in the local interstellar medium). This value was later reestimated by Combes et al. (1978) and Combes and Encrenaz (1979) in order to avoid the RLM approximation and minimize the effects of scattering. Instead of determining the Jovian D/H directly, they

choose to measure D/C, because the visible HD and CH₄ lines were more appropriate to give a reliable ratio. By using their determination of C/H (see above) they derived D/H $\leq 2.3 \times 10^{-5}$, which implies no deuterium enrichment. This method has the advantage of avoiding the use of the H₂ quadrupole lines, which are very difficult to measure in the laboratory. In the case of Saturn and Uranus, D/H values have been obtained by Macy and Smith (1978), in the RLM approximation, in the same range as Trauger et al.'s value for Jupiter. The Combes-Encrenaz method could not be used on these planets, in the absence of appropriate data.

In the thermal emission range, estimates of the Jovian CH₃D/H₂ ratio were obtained at 5 μm and 10 μm . From 5 μm observations, Beer and Taylor (1978) derived a value of 5×10^{-7} in the deep Jovian atmosphere. Since the CH₃D/H₂ is proportional to the product (D/H)x(C/H), their result implied a significant enrichment in deuterium and/or carbon. However, from Voyager IRIS data at 5 μm , the best fit corresponded to CH₃D/H₂ = 2.5×10^{-7} (Kunde et al. 1979). At 8 - 9 μm , from the absence of CH₃D features in the Jovian spectrum, Encrenaz et al. (1980) found an upper limit of 2×10^{-7} for CH₃D/H₂ which implies, with their C/H value, an upper limit of 4×10^{-5} for D/H. More recently Kunde et al. (1980) have derived a CH₃D/H₂ ratio of 5×10^{-7} in the same spectral range from the Voyager IRIS data. Discrepancies between the results obtained at 5 μm and 10 μm may be explained by the differences of atmospheric levels: the 5 μm measurements refer to a much deeper level than the 10 μm observations do, and the conditions of line formation may not be identical if the cloud structure is different. We cannot explain the differences in the results which have been done in the same range. It can be mentioned, however, that at 10 μm the determination is difficult because the CH₃Dv₂ band is located in the wings of NH₃ and PH₃ absorption bands, which may vary over the disk and with time. In both cases, the CH₃D band itself is not observed, and the derived CH₃D/H₂ is chosen by finding the best fit for the continuum at medium resolution. We must also notice that when we use the CH₃D/H₂ ratio another uncertainty in the D/H determination comes from the fractionation factor for deuterium exchange between methane and hydrogen, which is strongly a function of the temperature. The value used for Jupiter has been estimated by Beer and Taylor (1978). In conclusion the determination of the D/H ratio--on Jupiter and on the other planets--is not solved, and more measurements are needed, both in the visible and in the far infrared ranges.

b) The case of nonuniformly mixed components

Various physical processes may be at the origin of a departure from the hydrostatic law in the vertical distribution of an atmospheric constituent. Condensation can deplete a density distribution according to the corresponding saturation law: it occurs in the case of NH₃ on all the giant planets, CH₄ and C₂H₂ probably on Uranus and Neptune. Photodissociation by solar UV radiation is active in the upper atmospheres and strongly depletes the CH₄ and NH₃ upper profiles. Vertical

circulation and chemical reactions may also alter the distribution of a constituent, as may be the case of PH_3 .

NH_3 . NH_3 follows its saturation law below the level of minimum temperature on the four giant planets. Above this level ammonia would follow a hydrostatic law in the absence of photodissociation. In the case of Jupiter, it is now demonstrated that NH_3 is strongly depleted in the upper atmosphere. This information comes from Jovian spectra recorded in the rotational NH_3 band (40 - 110 μm) and in the 10 μm NH_3 band, where no thermal emission appears in the center of the NH_3 emission multiplets (Figure 8) (Goorvitch 1978; Goorvitch et al. 1979; Baluteau et al. 1978,1979; Gautier et al. 1979; Marten et al. 1980). The NH_3 photodissociation has also been demonstrated from UV observations with IUE (Combes et al. 1980). It has to be mentioned that emission lines of NH_3 were observed at Jupiter's pole by heterodyne technique at 10 μm (Kostiuk et al. 1977) with a line width smaller than the Doppler width. However, this NH_3 emission which is of non-thermal origin cannot be simply correlated to the NH_3 distribution of the upper atmosphere.

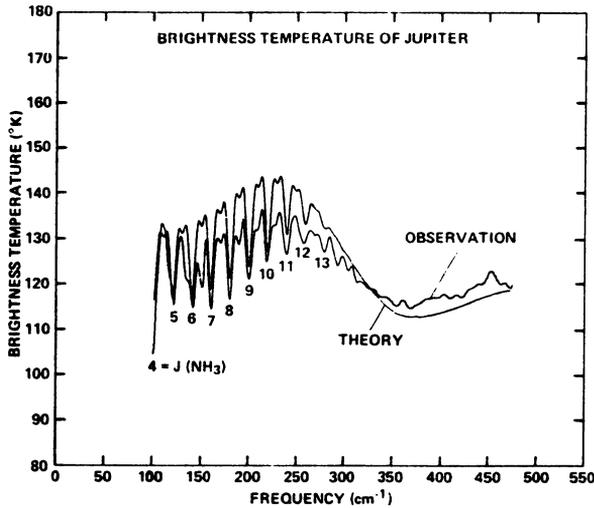


Figure 8. The far IR spectrum of Jupiter in the NH_3 rotational band (Erickson et al. 1978; Goorvitch et al. 1979).

Below the temperature minimum of Jupiter, the NH_3 distribution is probed in the NH_3 ν_2 band at 9 μm and 10 μm . Combes et al. (1976) and Encrenaz et al. (1978,1980) found a good agreement with the NH_3 saturation curve, while Tokunaga et al. (1979b), with an improved Jovian spectrum at 10 - 13 μm , find a better fit if the NH_3 density in the troposphere is 0.5 times the saturated vapor pressure density. The same conclusion is reached by Marten et al. (1980).

Below the NH_3 cloud level around 145 K, different results of the NH_3/H_2 ratio are derived. From visible data and using a scattering model, Sato and Hansen (1979) conclude that nitrogen is enriched by a factor around 1.5 - 2. From near infrared data, Encrenaz and Combes (1977) and Combes and Encrenaz (1979) derive an N/H value depleted by a factor 2 and suggest that nitrogen may be trapped at lower levels in some icy components (NH_4SH , NH_4OH). A similar conclusion is reached by Marten et al. (1980) who observe a difference in the NH_3/H_2 ratios below and above the region 250-330 K, and interpret this difference in terms of a cloud of nitrogen compounds at this level.

In the case of Saturn, very little is known about its NH_3 distribution. Ammonia was observed in the visible range (Encrenaz et al. 1974) but not in the near infrared range where the NH_3 bands are stronger (Owen et al. 1977; Larson et al. 1979): this illustrates again the effects of scattering in Saturn's atmosphere. Marten et al. (1980) derived, below the cloud level, a NH_3/H_2 ratio which includes the solar value. On Uranus and Neptune, Gulkis et al. (1977) and Olsen and Gulkis (1978) found an NH_3 depletion in the deep atmosphere from the millimetric spectra.

PH₃. The presence of phosphine in the atmospheres of the giant planets is of major interest for the study of dynamics on these planets. According to thermochemical equilibrium calculations (Lewis 1969; Barshay and Lewis 1978) phosphine should not be observable on the outer planets, because PH_3 is expected to react with H_2O below a temperature of 2000 K. Its discovery on Jupiter and Saturn at 2 μm , 5 μm , and 10 μm (Ridgway 1974; Larson et al. 1977; Ridgway et al. 1976; Tokunaga et al. 1980) was entirely unexpected. It was suggested by Prinn and Lewis (1975) that PH_3 was probably carried from deep atmospheric levels where it is stable, up to the atmospheric regions where it has been observed: for Jupiter, the 200-230 K level at 5 μm and the 130 K-145 K level at 9 - 10 μm ; the time needed for the transportation would have to be short enough for PH_3 to be observed at the top of the current before it has completely reacted with H_2O . The same mechanism could be also responsible for the observation of GeH_4 and CO. If this explanation is right, we would eventually expect to measure a P/H ratio smaller than the solar value. In the case of Jupiter, various estimates have been derived: at 10 μm , Ridgway et al. (1976) found a P/H close to the solar value, Tokunaga et al. (1979b) estimated a P/H value depleted by a factor 4, in agreement with Encrenaz et al. (1980), Fink and Larson (1977) at 2 μm , and Beer and Taylor (1979) at 5 μm . In the case of Saturn, the first observation of Bregman was consistent with a solar P/H value, but the recent result of Tokunaga et al. (1980) implies a phosphorus enrichment by a factor 3 at least. Similarly, Larson et al. (1980) derive a PH enhancement by a factor of 2 from 2 - 5 μm observations. As suggested by the authors, rapid convection is probably not sufficient to account for this large amount of phosphine. Larson et al. (1980) indicate some mechanisms which could explain the observed PH_3 amount: the reaction of PH_3 with H_2O may be slower than previously thought (Sill 1979); moreover, according to

Strobel (1977) photodissociation of PH_3 is expected to be inhibited by the absence of gaseous NH_3 , as is the case on Saturn. This last argument could possibly explain the quantitative difference between the PH_3 abundances on Jupiter and Saturn.

C_2H_2 , C_2H_6 . Another surprising result was the discovery of C_2H_2 and C_2H_6 in the infrared spectrum of Jupiter (Ridgway 1974). This result gave the first observational evidence for CH_4 photodissociation by the solar UV radiation in the upper Jovian atmosphere. C_2H_6 was present in all the following observations (Combes et al. 1974; Tokunaga et al. 1976; Encrenaz et al. 1976; Aumann and Orton 1976; Encrenaz et al. 1978) but C_2H_2 seemed to be absent on some observations (Tokunaga et al. 1976; Encrenaz et al. 1976) which may suggest a possible variation of C_2H_2 with time. This variation could be explained by condensation of C_2H_2 in the region of the temperature minimum.

Density profiles of C_2H_2 and C_2H_6 have been obtained by the Voyager IRIS experiment (Hanel et al. 1979b), on different points of the Jovian disk from the equator to the South Pole; the C_2H_2 amount appears to be significantly depleted at the South Pole, which could again be due to an atmospheric cooling. Moreover, Hanel et al. (1979b) report a significant change in the $\text{C}_2\text{H}_2/\text{C}_2\text{H}_6$ ratio between the two encounters; this result may be a confirmation of the possible C_2H_2 variation suggested from ground-based observations.

On Saturn, only C_2H_6 was detected (Tokunaga et al. 1975); the absence of acetylene is probably due to condensation. In contrast, C_2H_2 has been tentatively identified on Titan, with C_2H_6 and C_2H_4 (Gillett 1975); this seems to imply a higher temperature on Titan at the level of formation.

The presence of C_2H_6 on Neptune was especially useful because it provided evidence for a warm upper stratosphere in contrast with Uranus. The difference of thermal profiles on these two planets has to be correlated with the absence of an internal heat source on Uranus, which itself remains unexplained.

VI. PERSPECTIVES AND CONCLUSIONS

In conclusion, we can try to summarize what is known and what has still to be studied in the composition of planetary atmospheres. The atmospheric composition and structure of Mars and Venus have been studied extensively by in situ experiments. In the case of Jupiter we now have a good knowledge of the mean atmospheric parameters (temperature, pressure) and we start with the results of Voyager 1 and 2 to have some spatial resolution of the thermal and cloud structure. However a large uncertainty still exists on some basic elemental and isotopic ratios, as C/H and D/H. This uncertainty is even larger on the other outer planets. However, in the case of Jupiter, in view of the results summarized in Table IX, we believe that the enrichment in

helium, deuterium, and carbon is moderate and not sufficient at the present time to definitely imply an inhomogeneous interior of Jupiter.

What progress can we expect in our knowledge of the giant planets within the next decade? In the case of Jupiter the main event will be the Galileo mission. Apart from the mass spectrometer experiment aboard the probe, information on the atmospheric composition will come, in particular, from the Near Infrared Mapping Spectrometer which will record 0.6 - 5.2 μm scans with moderate spectral resolution (~ 100 -200) but high spatial resolution. In the case of Saturn--and possibly Uranus--the Voyager mission will provide, as in the case of Jupiter, the T(P) distribution and the H_2/He ratio. Day and night measurements of Titan with the IRIS experiment will give valuable information about the atmospheric cooling of Titan, and thus about its density. The same kind of information will possibly be obtained from the reduction of observations of Titan during the 1980 eclipses.

In the case of Uranus and Neptune, which will probably not be objectives of space missions in the near future, the contribution of Voyager and ground-based infrared spectroscopy should be of major interest within the next decade. From aircraft measurements, a better H_2/He value will be derived while estimates of C/H and D/H will probably be obtained from the ground in the near infrared (as already started by Fink and Larson (1979) and at 5 μm and 10 μm). The upper atmospheres of Titan, Uranus, and Neptune will be studied in more detail with better observations of the CH_4 and C_2H_6 emission lines around 10 μm . All this progress will help us to solve two important questions: (1) the evidence for a difference in the atmospheric abundance ratios from Jupiter to Neptune, and (2) the nature of Titan's atmosphere. In conclusion we can expect that infrared astronomy will still provide us new and exciting results on planetary atmospheres within the next few years.

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DISCUSSION FOLLOWING PAPER DELIVERED BY T. ENCRENAZ

ORTON: A correlation of the Pioneer 11 Infrared Radiometer results at Saturn with the Radio Science occultation experiment to determine the structure of the neutral atmosphere has given a mixing ratio for H_2 of 0.90 ± 0.03 (assuming the rest to be He). This determination used a technique similar to that used by Gautier et al. (1980) to determine the same parameters from Voyager data.

JOSEPH: Is it possible to describe, simply, how thermal radiation is used to derive the C/H ratio?

ENCRENAZ: We use the CH_3D band and thermal profile models. For a given temperature profile, we can estimate at which level the CH_3D lines are formed. The observed band is then fit to synthetic spectra calculated for given CH_3D to H_2 ratios.

R. CAYREL: How important are considerations of non-LTE in the interpretation of observational data for planetary atmospheres?

ENCRENAZ: Fortunately, the atmospheric region we are probing has pressures above 10 or 100 mbar, and we are not bothered by problems of non-LTE. In contrast, in the UV region non-LTE must be accounted for.