Chapter 5
Saturn: Composition and Chemistry

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Abstract The chapter reviews our current knowledge of the molecular, elemental, and isotopic composition and atmospheric chemistry in Saturn’s shallow atmosphere, i.e., between the cloud levels and the homopause. We do not restrict the review to Cassini’s results, as past and current ground-based or Earth-based observations are still fundamental to draw a complete picture of the planet. We address the global composition and its importance in studying the origin of the planet, and the meridional and vertical gradients in composition, stressing their insights into Saturn’s dynamics. We present the current 1D thermochemical and photochemical models, how these models fare to reproduce the observed composition, and the first attempts to design 2D chemical models. We present some directions to improve our knowledge of Saturn’s composition both from observations, modelling and laboratory experiments.

5.1 Introduction

Atmospheric composition and chemistry directly determine Saturn’s horizontal and vertical structure, dynamics and visible appearance. Composition affects the thermal structure through the radiative balance between solar energy deposition and thermal infrared emission. Condensation of volatiles and photochemistry determine the cloud structure, hence the visible appearance of the planet. Chemistry, either photochemistry or thermochemistry, strongly shapes the molecular composition, and vertical, meridional and seasonal gradients in composition are observed. In turn, gradients in chemical constituent abundances and latent heat release by condensibles contribute to thermal and density gradients that power atmospheric dynamics, which feeds back to affect the composition and thermal structure. Hence, observations of the atmospheric composition provide constraints on the present-day chemistry, dynamics, energy balance, appearance and other phenomena, whilst also providing a window into the past, to the conditions at the time of formation and evolution of the gas giants. Indeed, the elemental abundances of carbon, oxygen, nitrogen, and sulfur are key parameters needed for planetary formation scenarios. In this chapter, we address the chemical composition and the chemistry of the atmosphere from the homopause level down to below the cloud base. The composition and the structure of the interior of the planet are reviewed in Chapter 4, while the composition above the homopause level is covered in Chapter 8.

Without any in situ measurements to probe Saturn’s composition, we have to rely exclusively on remote sensing, and more specifically on spectroscopy which provides the most powerful way to quantitatively measure gaseous composition. The full electromagnetic spectrum, from the ultraviolet to radio wavelengths, is used in order to cover the greatest possible vertical range. The early spectrometric studies of Saturn’s atmosphere are reviewed in Chapter 2. However, the impact of Cassini on our knowledge of Saturn’s chemical composition is still relatively immature except in some specific areas. For this reason, we do not restrict our review to Cassini results, but extend our discussion to ground-based and space-based observations up to 20 years ago, when relevant, in order to present a comprehensive and consistent picture of Saturn’s composition. Ground-based observations concomitant with the Cassini mission can also prove very useful. In parallel with observations, modelers have been developing chemical models, involving either thermochemistry or photochemistry, in order to interpret and to understand the reasons for the observed composition. Many of these models were put together prior to Cassini’s arrival at Saturn and need refinements in light of the newest Cassini and ground-based studies.

The chapter is divided into two large sections. Section 5.2 reviews the observed composition, starting with the problem of the global composition in helium (Section 5.2.1.1). Then, we gather the different results on the carbon (Section 5.2.1.2), nitrogen and sulfur (Section 5.2.1.3) compositions,
while the isotopic composition is discussed in Section 5.2.1.4. We stress that Saturn’s global oxygen content still cannot be determined from remote sensing studies at present. Section 5.2.2 reviews our current measurements of species that are not in thermodynamic equilibrium at the cloud level, but are rather rapidly transported from the deep interior. In Section 5.2.3 we discuss how photochemistry affects the observed composition. First we address the upper troposphere, then we present the family of detected hydrocarbons in the middle atmosphere and how their abundances vary horizontally and vertically. Section 5.2.4 reviews the oxygen-bearing species observed to be present in the stratosphere, which implies an external oxygen flux to Saturn. Section 5.3 presents the current status of modelling the observed composition, starting with the tropospheric chemistry, either due to thermochemical reactions (Section 5.3.1.1) or photochemical reactions (Section 5.3.1.2). In Section 5.3.2 we discuss the hydrocarbon stratospheric photochemistry. We discuss the important chemical reactions and how one-dimensional models fare in terms of reproducing the observed composition. We then describe the one-dimensional seasonal models and the first attempts to design two-dimensional models and their difficulties in fitting the observed meridional gradient in hydrocarbons abundances. Finally, Section 5.3.4 reviews our current understanding of the oxygen chemistry induced in the stratosphere by the external flux.

5.2 Observed Composition

5.2.1 Major Gases or Bulk Composition

The enrichment of Saturn in heavy elements relative to the Sun constitutes an essential constraint for formation scenarios. If our views on Saturn’s composition have been improving over recent years and during the Cassini prime mission, our knowledge of the solar elemental composition has also evolved significantly. In the literature, different authors have compared Saturn’s composition with different solar values, without explicitly stating their reference, making intercomparisons difficult. In addition, authors have also used the term mixing ratio both for volume mixing ratio and for the mixing ratio relative to H$_2$, different by about 20%. To avoid such a caveat in this Chapter, we quote all the measurements in Saturn in terms of mole fraction, or the equivalent volume mixing ratio. The mole fractions are then converted in terms of enrichment relative to the Sun, using the solar composition proposed by Grevesse et al. (2007). Hence, our values for Saturn enrichment may not correspond to the values quoted in the cited references, which used an earlier solar composition.

Note, however, that some caveats on the solar enrichment value still exist because of the necessity of making assumptions about the partitioning of the elements into different molecular species (e.g., some oxygen may be tied up in non-H$_2$O condensates in Saturn’s deep atmosphere so that water may not represent the full complement of Kronian oxygen, Visscher and Fegley 2005, and other similar assumptions for the other elements come into play).

5.2.1.1 Helium Abundance

Knowledge of the helium abundance in the giant planets is important for studies of the evolutionary history of these bodies. During their formation, hydrogen and helium were acquired from the primitive solar nebula. Consequently, the volume mixing ratio of helium to molecular hydrogen [He]/[H$_2$] is believed to have been initially uniform and equal to the protosolar value. During the evolution of Jupiter and Saturn, fractionation processes have modified this distribution. In particular, the immiscibility of helium in metallic hydrogen with resulting gravitational separation in the interiors of these planets is expected to have resulted in enhancement of helium in their deep interiors with depletion in the outer, molecular envelope. Measurements of [He]/[H$_2$] in the observable atmosphere can strongly constrain evolutionary theories of these bodies.

A combination of Voyager infrared spectrometer (IRIS) and radio occultation (RSS) measurements were used to determine the helium abundance in the upper tropospheres of all four giant planets. Analysis of the RSS data yields a profile of $T/m$, the ratio of the temperature to the mean molecular mass. For an assumed atmospheric composition, the mean molecular mass and microwave refractivity coefficient can be calculated, and a profile of temperature versus barometric pressure $T(p)$ can be obtained. A radiative transfer code is used with this profile to calculate a theoretical thermal emission spectrum that is compared with measured spectra acquired near the occultation point on the planet. With this approach, a helium-to-hydrogen mixing ratio [He]/[H$_2$] of $0.110 \pm 0.032$, corresponding to a mass fraction $Y = 0.18 \pm 0.04$, was obtained for Jupiter (Gautier et al. 1981; Conrath et al. 1984), representing a modest depletion with respect to the protosolar value $Y = 0.28$ (Profitt 1994), while a remarkably low value of $0.034 \pm 0.024 (Y = 0.06 \pm 0.05)$ was found for Saturn (Conrath et al. 1984). Subsequent in situ measurements of He from the Galileo probe gave a value of [He]/[H$_2$] = $0.157 \pm 0.003$ on Jupiter (von Zahn et al. 1998; Niemann et al. 1998). The Voyager Jupiter result can be made consistent with the Galileo result only if the nominal radio occultation profile (Lindal 1992) is made cooler at all atmospheric levels by $\sim 2$ K (Conrath and Gautier 2000). This suggests the presence of systematic errors in the Voyager
measurements for Jupiter and raises the possibility of similar errors in the helium determination for Saturn.

The detailed shape of the thermal emission spectrum in the far infrared ($\nu < 600 \text{ cm}^{-1}$) provides an additional constraint on the helium abundance. The differential spectral dependence of the $S(0)$ and $S(1)$ collision-induced absorption lines and translational continuum of $H_2$ is a function of the relative contribution of $H_2$–$H_2$ and $H_2$–$He$ interactions. Conrath and Gautier (2000) used this dependence to obtain a new determination of the Saturn He abundance using Voyager IRIS measurements only. In addition to helium, this portion of the spectrum is also sensitive to the vertical thermal structure and the molecular hydrogen ortho/para ratio, and it is necessary to simultaneously retrieve the temperature profile, and the para $H_2$ profile along with the He abundance. Separation of these parameters is dependent on relatively subtle effects of each on the shape of the collision-induced $H_2$ spectrum. As a consequence, the retrieval problem is highly “ill-posed” and requires the use of a priori constraints in the inversion algorithm. These take the form of low-pass filtering of the temperature and para $H_2$ profiles. Because of the weak separability of the parameters, the results are strongly dependent on these constraints, and only rather broad limits can be set on the He abundance. Using this approach, Conrath and Gautier (2000) obtained values of $[\text{He}]/[\text{H}_2]$ in the range 0.11–0.16 (corresponding to a helium mass fraction range 0.17–0.24), significantly larger than the value obtained with the IRIS/RSS approach. The IRIS/RSS method is strongly sensitive to systematic errors in the RSS and/or the IRIS measurements, while the IRIS-only inversion approach is sensitive to any factors that can affect the differential spectral shape such as spectrally dependent tropospheric aerosol opacities that are poorly constrained. Given these uncertainties in the Voyager results, a new determination of the Saturn helium abundance became a major Cassini science objective. The primary approach used in the Cassini analysis makes use of Composite Infrared Spectrometer (CIRS) measurements along with Cassini RSS results in a manner similar to the Voyager IRIS/RSS analysis. The range of latitudes and observational geometries covered by the Cassini radio occultations can lead to a better understanding of the limitations and possible error sources associated with this method. As an additional constraint, direct inversions of CIRS spectra are also being pursued. The extended spectral range to lower wavenumbers, along with the large spatial and temporal coverage available from Cassini, permits better separation of the parameters affecting the shape of the CIRS spectrum, which may lead to better constraints on the helium abundance with the CIRS-only approach than was possible with IRIS.

During the course of the Cassini prime mission, Saturn atmospheric radio occultations have been acquired over a range of latitudes and occultation geometries, along with near-simultaneous CIRS spectral measurements. Preliminary results based on eleven low-latitude occultation points, all within Saturn’s equatorial jet, give a mean value of $[\text{He}]/[\text{H}_2] = 0.08$, corresponding to a He mass fraction of 0.13 or a mole fraction of 0.07 (Gautier et al. 2006). An example of a spectral fit is shown in Fig. 5.1. In this analysis, it was assumed that only hydrogen, helium, and methane contribute significantly to the mean molecular mass and mean refractivity coefficient, and a methane-to-hydrogen mixing ratio $[\text{CH}_4]/[\text{H}_2] = 4.86 \times 10^{-3}$ was used. Initial results from the CIRS-only approach of direct spectral inversion yield somewhat higher values, consistent with the Voyager

![Fig. 5.1](image-url) Spectra calculated from an RSS $T/m$ profile at $7.4^\circ S$, illustrating the sensitivity of the CIRS/RSS method to helium. The value of $[\text{He}]/[\text{H}_2]$ assumed in each case is indicated. An average of 450 CIRS spectra acquired near the occultation point is shown for comparison. Only the spectral region between 220 and 500 cm$^{-1}$ is used in the analysis.
IRIS-only results of Conrath and Gautier (2000). However, the apparent discrepancy between the CIRS/RSS results and the CIRS-only results once again suggests the possibility of systematic errors. A detailed error analysis is in progress. Error sources considered include uncertainties in the absolute calibration of CIRS, gaseous absorption coefficient errors, effects of additional opacity sources such as clouds and hazes, uncertainties in radio frequency refractivity coefficients, and uncertainties in the gravitational potential surfaces used in the RSS analyses. Of particular concern is the sensitivity of the retrieved radio occultation $T/m$ profiles to perturbations in the gravitational potential surfaces associated with the wind field. In a preliminary study of this sensitivity, two different wind models have been used. In one model, the shape of the potential surfaces is based on the Voyager cloud-tracked winds, assumed to be uniform parallel to the planetary rotation axis (barotropic). The second model assumes no winds and yields a temperature profile $\sim$2 K warmer for a given molecular mass, resulting in a value of $[\text{He}]/[\text{H}_2]$ that is $\sim$0.02 smaller than that obtained with the barotropic model (Flasar et al. 2008). Further investigations into the effects of the wind field are being carried out using radio occultations and CIRS spectra acquired at higher latitudes away from the equatorial jet. Although major uncertainties remain to be resolved, the preliminary values from both the CIRS/RSS and CIRS-only analyses fall within the He mass fraction range 0.11–0.25 suggested by evolutionary modeling results (see for example Hubbard et al. 1999; Guillot 1999), and imply at least some depletion from the proto solar value.

Some constraints on the helium abundance can also be supplied by Cassini UVIS occultation data. Preliminary UVIS results are presented in Chapter 8.

### 5.2.1.2 The Para Fraction of Molecular Hydrogen

Molecular hydrogen comes in two states, the ortho state, corresponding to odd rotational quantum numbers, and the para state corresponding to the even quantum rotational numbers. At deeper atmospheric levels, the ortho-para ratio approaches its 3:1 high temperature limit. In the shallow atmosphere, molecular hydrogen can depart from its thermodynamic equilibrium ortho-para ratio because of the slow conversion between the ortho and para states. An upwelling air parcel tends to retain its initial para hydrogen fraction ($f_p$) corresponding to the warmer temperatures of the deeper levels. As a consequence, its value of $f_p$ can be smaller than the equilibrium value ($f_{pe}$) associated with the cooler temperatures of the upper troposphere. Hence, the hydrogen para fraction is of considerable interest to trace the dynamics in Saturn’s upper troposphere. Since the ortho-para conversion rate can be shortened through surface catalytic processes, $f_p$ can also be influenced by the distribution of atmospheric aerosols. The para hydrogen fraction can be measured by remote sensing using the collision-induced H$_2$ continuum. Conrath et al. (1998) and Fletcher et al. (2007a) both retrieved Saturn’s $f_p$ in the upper troposphere, between 400 and 100 mbar, respectively from Voyager/IRIS and Cassini/CIRS. The different patterns are not easy to interpret as the difference $f_{pe} - f_p$ changes sign with altitude and latitude. Conrath et al. (1998) found a $f_p$ minimum near 60°S and a $f_p$ maximum near 15°S, consistent with upward motion near 60°S and downwelling in the tropics. The northern hemisphere, just emerging from winter, had higher $f_p$. In contrast, Fletcher et al. (2007a) found the lowest $f_p$ at the equator, a summer Southern Hemisphere with $f_{pe} - f_p > 0$ and a winter Northern Hemisphere with $f_{pe} - f_p < 0$. Since the seasons probed by Voyager and Cassini are similar, closer agreement might be expected. Because of the low upper tropospheric lapse rate on Saturn, especially in the summer hemisphere, the spectral information content on $f_p$ is limited. As a consequence, the retrievals are strongly dependent on the a priori constraints assumed in the inversion algorithms, which may account for these differences, at least in part. This topic remains to be investigated in detail. As Cassini CIRS data continue to be acquired, hemispheric asymmetries associated with changing seasonal conditions will be better characterized.

#### 5.2.1.3 Carbon Elemental Composition

The elemental composition of carbon is determined through the measurements of the methane mole fraction, since methane is well-mixed, does not condense, and is expected to be the thermodynamically stable form of carbon throughout the atmosphere. Before the review by Prinn et al. (1984), all the methane measurements in Saturn had been obtained in the solar reflected spectral range. Although all the measurements concluded that carbon was enriched with respect to the solar composition, the magnitude of the enrichment varied widely from one study to another. Since 1984, the quest to measure Saturn’s C/H ratio in the visible and in the near-infrared spectral regions has continued. The principle remains the same: one needs to observe simultaneously an H$_2$ and a CH$_4$ absorption of similar strength and, if possible, close to each other in the spectral range. With this technique, the two gaseous absorptions probe similar pressure levels and can be modeled with the same cloud structure.

Recent studies have taken advantage of the improved knowledge of methane absorption coefficients, and of new and more efficient methods in multiple scattering numerical modeling. However, the large dispersion, and the incompatibility of the different measurements within their respective error bars, has not disappeared, as shown in Table 5.1. This large dispersion in methane mole fraction inferred from solar
The measurements in the thermal infrared are the most reliable, the value measured by Fletcher et al. (2009a) being the most accurate. The methane mole fraction of $4.7 \pm 0.2 \times 10^{-3}$, averaging over a larger number of CIRS observations.

In contrast, studies in the thermal infrared range have clustered their results around a methane mole fraction of $4.5 \times 10^{-3}$. Analysis in this spectral range requires first the determination of the vertical temperature profile, then, assuming this profile, the adjustment of the volume mixing ratio until the observed methane thermal emission is reproduced. Courtin et al. (1984) were the first to carry out such a measurement. They used the temperature profile determined from the Voyager radio occultation experiment along with the stratospheric $\text{CH}_4 \nu_4$ emission observed by IRIS to infer a volume mixing ratio of $(4.3^{+2.2}_{-1.3}) \times 10^{-3}$. Fifteen years later, the Short Wavelength Spectrometer (SWS) aboard the Infrared Space Telescope (ISO) observed the 8–11 $\mu$m region. Although, this spectral region is dominated by $\text{PH}_3$ absorptions, micro-windows between 10 and 11 $\mu$m allowed Lellouch et al. (2001) to measure the tropospheric temperature, while the $\nu_4$ wings in the 8.15–8.5 $\mu$m range probed the $\text{CH}_4$ tropospheric mixing ratio. Now, Cassini/CIRS observes for the first time the methane rotational lines (Fig. 5.2). These lines, formed on the $\text{H}_2$ collision-induced continuum that probes the tropospheric temperature, are well isolated from other gaseous absorption. Hence, they allow a very precise measurement. Fletcher et al. (2009a) obtain the most accurate measurement, $(4.7 \pm 0.2) \times 10^{-3}$.
This mole fraction corresponds to a carbon enrichment of 10.4 with respect to the solar abundance, assuming that a negligible amount of carbon is tied up in constituents other than CH\textsubscript{4}. Cassini hence definitely demonstrates that Saturn lies in between Jupiter, and Uranus and Neptune, in terms of carbon elemental enrichment. This has important implications for the giant planets formation scenarios reviewed in the Formation Chapter.

5.2.1.4 Nitrogen, Sulfur and Oxygen

About ten astronomical units from the Sun, Saturn is a cold world. For this reason, the clouds form at large pressures (about 20 bars for the water cloud, a few bars for the chemical NH\textsubscript{3}SH cloud, and around the 2-bar level for NH\textsubscript{3} cloud). In this situation, it is extremely difficult for a remote observer to measure the deep, global abundance of the condensibles below their associated clouds. Only observations in the centimeter range, between 6 and 70 cm, are able to probe molecular species that deep. Unfortunately, the interpretation of such observations is difficult for several different reasons. First, the absolute calibration uncertainties are large in this wavelength range, not better than 20%. Second, the lineshapes of the gaseous absorbers are not very well known, although progress has been made recently. Finally, the various absorbers, gas, liquids, or solids, have broad, relatively featureless spectra; hence the measurements in the centimeter range do not contain independent information on both temperature and composition.

For all these reasons, the published values must be taken with caution. The most convincing results have been obtained by Briggs and Sackett (1989). Their Very Large Array (VLA) and Arecibo observations were best fit by a deep ammonia volume mixing ratio of \(4.8 \pm 1 \times 10^{-4}\), hence 4.5 \pm 1.0 times the solar abundance. Moreover, Briggs and Sackett (1989), (see also Killen and Flasar 1996; van der Tak et al. 1999), found that the brightness temperature in the 2–6 cm range points toward a low ammonia relative humidity between 2 and 4 bars. They interpreted this depletion of NH\textsubscript{3} as an evidence for a large H\textsubscript{2}S abundance, equal to a volume mixing ratio of 4.1 \times 10^{-4}, that served as a sink of NH\textsubscript{3} through the formation of a dense NH\textsubscript{3}SH cloud. Such an abundance corresponds to 17 times the solar composition. It is hoped that measurements from the Cassini Radio Science Subsystem will improve the absolute calibration of Saturn’s observation in the 2–14 cm range. Combined with the CIRS temperature profiles, a more accurate determination of the N/H and S/H ratios could be obtained.

Although tropospheric water has been detected by ISO in the 5-\mu\text{m} band (de Graauw et al. 1997), the inferred abundance is highly subsolar: ISO observations probe only pressure levels (2–4 bars) where water vapor condenses out. This situation precludes any measurement of the O/H ratio in Saturn, which constitutes an important missing piece of information for constraining the delivery of volatiles to the planet. Unfortunately, we cannot expect any progress on this issue from Cassini and will have to wait for a deep entry probe.

5.2.1.5 Isotopic Composition

The isotopic composition, especially the D/H ratio, is important for constraining the fraction of solids relative to gases that were accreted to form Saturn. The majority of D/H determinations in Saturn’s atmosphere have been derived from the comparative abundance of methane and deuterated methane (CH\textsubscript{3}D). Besides the uncertainty on CH\textsubscript{4} itself, the interpretation of the CH\textsubscript{3}D measurements in terms of the bulk deuterium abundance (i.e., in H\textsubscript{2}) is complicated by the existence of an isotopic exchange reaction between H\textsubscript{2} and CH\textsubscript{4} (HD + CH\textsubscript{4} \leftrightarrow CH\textsubscript{3}D + H\textsubscript{2}) whose thermodynamics, kinetics and coupling with atmospheric dynamics are uncertain. According to different studies (Lecluse et al. 1996; Smith et al. 1996), the fractionation coefficient \(f\):

\[
f = \frac{(D/H)_{\text{CH}_4}}{(D/H)_{\text{H}_2}}
\]

lies in the range \(f = 1.34 \pm 0.19\).

Deuterated methane was first detected by Fink and Larson (1978) in its \(v_2\) band at 4.7 \mu\text{m}. Owen et al. (1986) and de Bergh et al. (1986) were the first to publish an abundance of CH\textsubscript{3}D, using high spectral resolution observations of the \(3v_2\) band at 1.55 \mu\text{m} (see Table 5.2 for the values). Another determination in the solar reflected range was obtained by Kim et al. (2006), between 2.87 and 3.10 \mu\text{m} (CH\textsubscript{3}D \(v_3 + v_2\) band), with a low abundance of \(2.5 \times 10^{-7}\). Noll and Larson (1991) used the 4.7-\mu\text{m} spectral region, that probes deep in Saturn’s troposphere, to determine a volume mixing ratio of \((3.3 \pm 1.5) \times 10^{-7}\). This spectral region, difficult to analyse due to some strong PH\textsubscript{3} absorption, yielded a similar result from ISO/SWS observations. CH\textsubscript{3}D abundance can also be measured in the 8.6-\mu\text{m} region using the \(v_6\) thermal emission. Three studies focused in this spectral region with medium resolution observation (between 4.3 and

<table>
<thead>
<tr>
<th>(\text{D}/\text{H}_{\text{H}_2})</th>
<th>Method</th>
<th>Reference</th>
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<tbody>
<tr>
<td>((1.6^{+0.7}_{-1.2}) \times 10^{-5})</td>
<td>CH\textsubscript{3}D at 8 \mu\text{m}</td>
<td>Courin et al. (1985)</td>
</tr>
<tr>
<td>((1.7^{+0.5}_{-0.8}) \times 10^{-5})</td>
<td>CH\textsubscript{3}D at 1.6 \mu\text{m}</td>
<td>de Bergh et al. (1986)</td>
</tr>
<tr>
<td>((1.1 \pm 1.3) \times 10^{-5})</td>
<td>CH\textsubscript{3}D at 4.7 \mu\text{m}</td>
<td>Noll and Larson (1991)</td>
</tr>
<tr>
<td>((2.3^{+1.1}_{-0.6}) \times 10^{-5})</td>
<td>HD R(1)</td>
<td>Griffin et al. (1996)</td>
</tr>
<tr>
<td>((1.85^{+0.85}_{-0.60}) \times 10^{-5})</td>
<td>HD R(2) &amp; R(3)</td>
<td>Lellouch et al. (2001)</td>
</tr>
<tr>
<td>((2.0^{+0.7}_{-0.6}) \times 10^{-5})</td>
<td>CH\textsubscript{3}D at 8 \mu\text{m}</td>
<td>Lellouch et al. (2001)</td>
</tr>
<tr>
<td>((1.6 \pm 0.2) \times 10^{-5})</td>
<td>CH\textsubscript{3}D at 8 \mu\text{m}</td>
<td>Fletcher et al. (2009a)</td>
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0.5 cm\(^{-1}\)): Courtin et al., 1984 using Voyager/IRIS data, Lellouch et al. (2001) with ISO/SWS data, and Fletcher et al. (2009a) with Cassini/CIRS spectra. Overall, the different measurements cluster around a value for the D/H ratio in methane of \(1.8 \times 10^{-5}\). Given the above estimate of the fractionation coefficient \(f\), this gives a low estimate for the D/H in H\(_2\)\:_ about \(1.5 \times 10^{-5}\). Ground-based, high-resolution spectroscopic observations that resolved the stratospheric cores of the \(v_6\) CH\(_3\)D lines would be of great interest to improve the Cassini determination.

The first, and to date only, direct measurement of the D/H ratio in molecular hydrogen was obtained with the ISO telescope. Griffin et al. (1996) observed the R(1) rotational line at 56 \(\mu\)m with the Long Wavelength Spectrometer (LWS) aboard ISO. However, their measurement (Table 5.2) must be taken with caution, as the ISO/LWS data were difficult to calibrate for the very large flux of the giant planets. Lellouch et al. (2001) used ISO/SWS to observe the HD R(2) and R(3) rotational lines. From this, they derive a D/H ratio of \((1.85^{+0.07}_{-0.06}) \times 10^{-5}\). Combining HD and CH\(_3\)D measurements, Lellouch et al. (2001) concluded to \((D/H)_{\text{HD}} = (1.70^{+0.75}_{-0.35}) \times 10^{-5}\). This value is not accurate enough to distinguish Saturn from Jupiter ((D/H)\(_{\text{HD}}\) = \((2.25 \pm 0.35) \times 10^{-5}\)) and from the local interstellar medium ((D/H)\(_{\text{HD}}\) = \((1.5 \pm 0.1) \times 10^{-5}\)). In this respect, Saturn does not seem to obey the trend of increasing D/H from Jupiter to Neptune. Improvements on this determination should come in the near future from the Herschel satellite when it observes the R(0) line at 2680 GHz, and from better calibrated Cassini/CIRS R(1) line observations.

Very few authors have focused on the \(^{12}\)C/\(^{13}\)C ratio in Saturn. Combes et al. (1977) observed \(^{13}\)CH\(_4\) and \(^{12}\)CH\(_4\) lines of the \(v_3\) band at 1.1 \(\mu\)m to determined a \(^{12}\)C/\(^{13}\)C ratio of \(89^{+25}_{-18}\). This ratio was later corrected to \(71^{+25}_{-18}\) by Brault et al. (1981), who revised the \(^{13}\)CH\(_4\)/\(^{12}\)CH\(_4\) intensity ratio in the \(v_3\) band based on laboratory spectra of methane. Sada et al. (1996) measured recently a \(^{12}\)C/\(^{13}\)C ratio of 99\(^{+0.25}_{-0.23}\) in ethane. Although C\(_2\)H\(_6\) is not the major carbon reservoir in Saturn, we do not expect significant isotopic fraction for this species.

Hence, before the Cassini arrival, the Kronian \(^{12}\)C/\(^{13}\)C ratio was compatible with the terrestrial value \((89.9^{+2.6}_{-2.4}\)) but the measurements were not very constraining. The high quality of the CIRS dataset over the prime Cassini mission has allowed Fletcher et al. (2009a) to obtain a much more precise value. They use the \(v_4\) band thermal stratospheric emission to infer a \(^{12}\)C/\(^{13}\)C ratio of \(91.8^{+5.5}_{-5.3}\), still compatible with the terrestrial and the jovian values, but different from the Titan value (Niemann et al. 2005). This difference shows that methane on Titan has suffered from isotopic fractionation either at its formation or through its evolution.

### 5.2.2 Thermochemical Products

Some chemical species have been detected at shallow atmospheric levels with abundances that largely exceed the abundances predicted by thermodynamical equilibrium. As explained in detail in Section 5.3.1.1, the explanation for the observed abundances involves rapid convective transport from the deep, hot, atmosphere where the equilibrium abundances of these species are relatively large. The observed mixing ratios are then representative of quenching levels (300–500 bars) where the time constants of the conversion reactions become equal to or greater than the timescale for convective mixing. Below this level, thermochemical equilibrium prevails, whereas above, chemical destruction is inhibited so that the mole fractions remain constant in an uplifted air parcel. The distribution of thermochemical products is an important tracer of dynamical processes in the troposphere, and has been given a lot of attention. Hereafter, we describe the measurements of such disequilibrium species: phosphine, germane, and arsine. (The specific case of carbon monoxide, with two different possible origins, is detailed in Section 5.2.4.) All of these measurements were obtained in the 5-\(\mu\)m window of Saturn’s spectrum (Fig. 5.3). The low opacity of the major gases in this spectral region offers the opportunity to probe pressure levels of several bars. This long path length allows the detection of trace constituents, while at these pressure levels the measured mixing ratios are unaffected by photochemical destruction, hence revealing the abundances of the observed species at the quench level.

The first spectrum of Saturn in the 5-\(\mu\)m window was obtained by Larson et al. (1980) using the Fourier

![Fig. 5.3 Observed ISO-SWS spectrum (upper curve) and synthetic spectrum of Saturn (lower curve) in the 5\(\mu\)m region. Spectral absorptions are due to NH\(_3\), PH\(_3\), AsH\(_3\), GeH\(_4\), CH\(_3\)D and H\(_2\)O. In the lower curve, the narrow line corresponds to a calculation without H\(_2\)O. Adapted from de Graauw et al. (1997) ](image-url)
Transform Spectrometer on the Kuiper Airborne Observatory (KAO/FTS). The absorption features of phosphine were evident in this moderate spectral resolution spectrum, but a more quantitative analysis had to await higher spectral resolution observations. Bézard et al. (1989) and Larson and Noll (1991) both demonstrated that the abundance of PH$_3$ in the lower troposphere of Saturn, with a volume mixing ratio in the range $(4-10) \times 10^{-6}$, was larger than the value in Jupiter. ISO observations confirmed this value, with de Graauw et al. (1997) deriving a global volume mixing ratio of $4.4 \times 10^{-6}$. Saturn’s PH$_3$ global abundance corresponds to an elemental enrichment of a factor of 10 in comparison with the solar abundance (assuming all phosphorous is tied up in PH$_3$ on Saturn). It would be interesting to know whether this deep mixing ratio varies with latitude, as it would indicate a meridional difference in the strength of convection from the interior. From CIRS observations, Fletcher et al. (2007b) are unable to disentangle deep variations from variations above the radiative-convective boundary. The Visual and Infrared-Mapping Spectrometer (VIMS) aboard Cassini is in position to study such a meridional variation in the lower troposphere, but no results have been released yet.

The first evidence for germane in Saturn came from observations near 4.7 $\mu$m obtained at the United Kingdom Infrared Telescope (UKIRT). Noll et al. (1988) used these data to determine a GeH$_4$ volume mixing ratio of $(4 \pm 2) \times 10^{-10}$. However, the analysis of spectra in the 4.7-$\mu$m region is complicated by the presence of strong PH$_3$ absorptions and by an equal balance between solar reflection and thermal emission. This situation has led Noll and Larson (1991) to conclude that their 4.7-$\mu$m Infrared Telescope Facility (IRTF) observations favored the presence of GeH$_4$ in Saturn, but that they could not exclude its absence. The confirmation of the presence of germane in Saturn hence came recently, from ISO observations. Although of moderate spectral resolution, ISO spectra achieved signal-to-noise ratios in the 5-$\mu$m region much larger than that of previous observations. Using these data, de Graauw et al. (1997) measured a deep germane volume mixing ratio of $2 \times 10^{-9}$ (corresponding to 0.2 times the solar abundance), and found evidence for a decreasing mixing ratio above the 1-bar pressure level, possibly due to photolysis in the upper troposphere.

Arsine was detected independently by two different teams: Bézard et al. (1989) used the Fourier Transform Spectrometer mounted on the Canada-France-Hawaii Telescope (FTS/CFHT), while Noll et al. (1989) used the UKIRT. Noll and Larson (1991) at the IRTF and more recently de Graauw et al. (1997) using ISO data confirmed the detection. Two AsH$_3$ vibration bands are observed in the 4.7-$\mu$m region, the $v_1$ and $v_3$. The two bands allow the authors to probe the arsine vertical profile between ~4 bars and 0.2 bar. In the deep atmosphere, the published volume mixing ratios clustered around $(2.5 \pm 1) \times 10^{-9}$, while Bézard et al. (1989) measured a mixing ratio of $(3.9^{+2.1}_{-1.3}) \times 10^{-10}$ in the upper troposphere. The deep mixing ratio corresponds to a global As elemental abundance equal to five times the solar abundance. In the upper troposphere, AsH$_3$ may be subject to photochemical destruction as is the case for PH$_3$ and GeH$_4$. VIMS is also in position to derive a meridional distribution of the deep AsH$_3$ abundance.

Not all elements experience enhancements in the upper troposphere, revealing different chemistries. For example, Teanby et al. (2006) used far infrared spectra (10-600 cm$^{-1}$) from the Cassini Composite InfraRed Spectrometer (CIRS) to determine the best-to-date upper limits of hydrogen halides HF, HCl, HBr, and HI. These authors obtained 3-$\sigma$ upper limits on HF, HCl, HBr, and HI mole fractions of $8.0 \times 10^{-12}$, $6.7 \times 10^{-11}$, $1.3 \times 10^{-10}$, and $1.4 \times 10^{-9}$, respectively, at the 500-mbar pressure level. These upper limits confirm sub-solar abundances of halide species for HF, HCl, and HBr in Saturn’s upper atmosphere, consistently with predictions from thermochemical models. We note that the upper limit for HCl derived by Teanby et al. (2006) is 16 times lower than the tentative detection at $1.1 \times 10^{-9}$ reported by Weisstein and Serabyn (1996).

### 5.2.3 Photochemical Products

#### 5.2.3.1 Evidence for Photochemistry in the Upper Troposphere

Several molecules are known to be affected by photolysis in the upper troposphere. Weisstein and Serabyn (1994) were the first to demonstrate, from high spectral resolution of the 1–0 rotational line observations, that a cutoff in phosphine abundance exists at a pressure between 13 and 140 mbar. Orton et al. (2000, 2001), also using rotational line observations, showed that the PH$_3$ abundance dropped from $7.4 \times 10^{-6}$ at 645 mbar down to $4.3 \times 10^{-7}$ at 150 mbar. Such a behaviour was also consistent with ISO/SWS observations, as Lellouch et al. (2001) measured a profile with mole fractions of $6 \times 10^{-6}$ up to the 600-mbar level, decreasing to $4 \times 10^{-6}$ at 250 mbar, and $3 \times 10^{-7}$ at 150 mbar. Since phosphine does not condense at the tropopause of Saturn, such a decrease with altitude can only be explained by photolysis. However, none of the products of this phosphine photochemistry has been detected to date. In this context, the monitoring of the meridional phosphine gradient is a powerful tracer of differences in vertical mixing, although it should be mentioned that aerosol opacity in the ultraviolet also strongly affects the phosphine gradient and caution should be used when trying to disentangle the relative effects of aerosol shielding and vertical mixing. In fact, phosphine photolysis may itself constitute a source of haze.
Fletcher et al. (2007b, 2008, 2009b) use the Cassini/CIRS spectra (Fig. 5.4, bottom panel) to measure the phosphine abundance as a function of latitude. Baines et al. (2005) also publish preliminary PH₃ meridional variations above the cloud top as retrieved from VIMS data. At 150 mbar their results are in line with previous studies, but at 250 mbar their abundance is lower than that of Lellouch et al. (2001) anywhere on the planet. Reasons for this disagreement have not been investigated. The Cassini results are summarized as follows (see also Table 5.3 and Fig. 5.4, Top panel).

1. The equatorial region presents the highest PH₃ abundance in the upper troposphere, which is consistent with the elevated equatorial haze, the cold temperature and the sub-equilibrium H₂ para fraction measured in this region.
2. Tropical latitudes (±23°) present the lowest PH₃ abundance, consistent with upwelling at the equator and downwelling in the neighbouring equatorial belts.
3. Mid-Latitudes at ±42° presents local maximum followed by a local minimum at ±57°.
4. Polar regions are enhanced in phosphine relative to tropical and mid-latitudes, but a sharp phosphine depletion occurs within ±2-3° of the poles, suggestive of subsidence over the high-temperature polar cyclones.
5. The northern hemisphere shows lower PH₃ abundance than the southern hemisphere. This is in opposition with a simple prediction based on the higher photolysis rate.

Fig. 5.4 Top panel: The phosphine mole fraction as a function of latitude and pressure as retrieved from Cassini/CIRS data. Bottom panel: CIRS spectrum of the equatorial region in the range 900–1400 cm⁻¹, compared with synthetic spectra showing the sensitivity the phosphine mole fraction at 500 mbar. Adapted from Fletcher et al. (2009)

Table 5.3 PH₃ vertical profiles measured from Cassini/CIRS mid-IR spectra, averaged in latitude regions (from Fletcher et al. (2007b))

<table>
<thead>
<tr>
<th>Latitude</th>
<th>q₈₅H₃ at 250 mbar (in ppb)</th>
<th>q₈₅H₃ at 150 mbar (in ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Polar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65–85 °N</td>
<td>820 ± 380</td>
<td>220 ± 200</td>
</tr>
<tr>
<td>North Temperate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15–65 °N</td>
<td>390 ± 100</td>
<td>62 ± 34</td>
</tr>
<tr>
<td>Equatorial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15°S–15 °N</td>
<td>1700 ± 200</td>
<td>470 ± 90</td>
</tr>
<tr>
<td>South Temperate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65–15 °S</td>
<td>660 ± 80</td>
<td>84 ± 27</td>
</tr>
<tr>
<td>South Polar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>85–65 °S</td>
<td>990 ± 130</td>
<td>160 ± 40</td>
</tr>
</tbody>
</table>
in the summer hemisphere compared to that in the winter hemisphere, but maybe explained by a enhanced shielding by aerosols in the southern hemisphere.

In the upper troposphere the ammonia volume mixing ratio decreases with altitude due to the combined effect of condensation and photolysis. The NH$_3$ vertical profile is slightly subsaturated around the 700-mbar pressure level (Courtin et al. 1984; Burgdorf et al. 2004), and highly subsaturated above that, hence showing evidence for photolysis at lower pressures, reaching an abundance of $10^{-9}$–$10^{-8}$ around 300–400 mbar (Kerola et al. 1997; Kim et al. 2006). In the upper troposphere, evidence for photolysis of arsine and germane has been found by Bézard et al. (1989) and de Graauw et al. (1997).

### 5.2.3.2 Stratospheric Products

In the upper stratosphere, methane is photodissociated by ultraviolet solar emission to produce CH, CH$_2$, and CH$_3$ radicals. Subsequent chemical reactions between the photolysis products and other atmospheric molecules yield several heavy hydrocarbons: to date, acetylene (C$_2$H$_2$), ethylene (C$_2$H$_4$), ethane (C$_2$H$_6$), propane (C$_3$H$_8$), methylacetylene (CH$_3$C$_2$H), diacetylene (C$_4$H$_2$), and benzene (C$_6$H$_6$) have been detected; the lighter radical CH$_3$ has also been observed.

C$_2$H$_6$ and C$_2$H$_2$ are the two most abundant species and, not surprisingly, were the first to be detected: acetylene in the UV range (Moos and Clarke 1979), and ethane in the thermal infrared (Tokunaga et al. 1975). Courtin et al. (1984), using Voyager/IRIS observations, were the first to determine reliable abundances: $(3.0 \pm 1.1) \times 10^{-6}$ from the ethane $v_3$ band at 821 cm$^{-1}$, and $(2.0 \pm 1.4) \times 10^{-7}$ from the C$_2$H$_2$ $v_5$ band at 729 cm$^{-1}$. From ground-based observations in the thermal infrared, Noll et al. (1986b) and Sada et al. (2005) found slightly larger values (the different measurements are summarized in Fig. 5.5). Using ISO/SWS observations, de Graauw et al. (1997) and Moses et al. (2000a) were the first to demonstrate that the C$_2$H$_2$ volume mixing ratio actually increases with altitude, as expected from photochemical models. Indeed, the emissions from the $v_4 + v_5 + v_4$ hot band detected by ISO probed higher altitudes than the $v_3$ band. Moses et al. (2000a) inferred a mixing ratio of $(1.2^{+0.9}_{-0.8}) \times 10^{-6}$ at 0.3 mbar and $(2.7 \pm 0.8) \times 10^{-7}$ at 1.4 mbar. For ethane, as all lines have approximately the same strength, vertical profile information cannot be obtained; from ISO/SWS data, a volume mixing ratio at 0.5 mbar alone was determined: $(9 \pm 2.5) \times 10^{-6}$.

Ethane and acetylene spectral features have also been unambiguously detected in the reflected infrared around 3 μm by Bjoraker et al. (1981) and Kim et al. (2006) (respectively the $v_3 + v_9 + v_{11}$ of ethane and the $v_3$ of acetylene). These studies suggested a cut-off in the vertical distributions at about 10–15 mbar, but the uncertainties on the band strengths in this spectral region make the inferred mole fractions less reliable than from the thermal infrared. Kim et al. (2006) also detected ethane emissions in its $v_3$ band originating from μbar levels. However, since collision relaxation parameters are not known with enough accuracy for this band, the observations could only be crudely analyzed yielding no reliable estimates of the ethane abundance.

As products of methane photolysis, ethane and acetylene abundances might be expected to exhibit meridional

![Fig. 5.5 Hydrocarbon mole fractions as a function of pressure in Saturn's upper atmosphere, as derived from the “Model C” 1-D steady-state photochemical model of Moses et al. (2005). The solid curves represent the model profiles for the individual hydrocarbons (as labeled), and the symbols with associated error bars represent various infrared and ultraviolet observations.](image-url)
and seasonal variations. The observations mentioned above were unable to access this geographical dimension as they were either disk-averaged, or targeted to a specific position. The work by Greathouse et al. (2005) hence opened the era of meridional hydrocarbon study. Using Texas Echelon Cross Echelle Spectrograph (TEXES) observations in the thermal infrared, they showed that the C$_2$H$_2$ volume mixing ratio at 1.16 and 0.12 mbar decreased by a factor of 2.5 from the equator towards the south pole (Fig. 5.6). In contrast, ethane was found to be stable within error bars, with 2.3-mbar mixing ratios of $(7.5^{+2.2}_{-1.7}) \times 10^{-7}$ at the equator and $(1.0^{+0.7}_{-0.5}) \times 10^{-5}$ at 83°S. Cassini/CIRS now measures both the C$_2$H$_2$ and C$_2$H$_6$ abundance from nadir observations (Howett et al. 2007), and from limb soundings (Fouchet et al. 2008; Guerlet et al. 2009). CIRS also extends the meridional coverage towards the northern hemisphere that was hidden by the rings to Greathouse et al. (2005). Cassini results confirm that the C$_2$H$_4$ mole fraction remains latitudinally constant at 1 mbar (although Howett et al. find a suspicious increase southward of 50°S), and that C$_2$H$_2$ decreases towards both poles (Fig. 5.6). This behaviour can be attributed to the different chemical timescales of the two molecules, C$_2$H$_6$ being a long-lived species compared to C$_2$H$_2$. Hence, the former can be horizontally transported and homogenized while the latter reflects the mean meridional solar irradiation. However, this interpretation is not validated by chemical models (see Section 5.3.2.4).

The Cassini/CIRS limb soundings also reveal some dynamical features in the hydrocarbon meridional profiles. At 1 mbar, Guerlet et al. (2009) find that the C$_2$H$_2$ profiles present a sharp and narrow maximum centered at the equator, not shown by C$_2$H$_6$. They interpret this feature as a signature of a dynamical process, the descent of air between 0.1 and 1 mbar associated with the equatorial oscillation. This descent transports C$_2$H$_2$ more efficiently than C$_2$H$_6$, as the former molecule shows a stronger vertical gradient than the latter. At lower pressures ($p < 0.1$ mbar), that can only be probed by limb soundings or occultations, Guerlet et al. (2009) find that the C$_2$H$_2$ and C$_2$H$_6$ mole fractions are the largest at mid-northern latitudes, and the lowest at mid-southern latitudes. This situation is in complete opposition with photochemical model predictions of an abundance following the solar
irradiance at these pressure levels. The observations thus suggest the existence of a strong meridional circulation, transporting molecules from the summer hemisphere across the equator towards the winter hemisphere.

In the upper stratosphere, ethane, ethylene, and acetylene have been detected from spacecraft ultraviolet observations. The Ultraviolet Spectrometer (UVS) on Voyager 1 and 2 recorded six solar and stellar occultations (Broadfoot et al. 1981; Sandel et al. 1982; Festou and Atreya 1982; Smith et al. 1983; Vervack and Moses 2009). The Vervack and Moses (2009) study is the only one to analyze all six occultations. Vertical profiles for C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$ have been derived from this analysis, and Vervack and Moses (2009) confirm that the mixing ratios for all three species have a peak at high altitudes, with a decreasing mixing ratio with decreasing altitude away from this high-altitude peak. The variability of the results from the six UVS occultations also demonstrates that the pressure level of the peak mixing ratio varies with latitude and/or time on Saturn, which has interesting implications with respect to atmospheric transport. To date, the Cassini Ultraviolet Imaging Spectrograph (UVIS) has also performed 15 stellar occultations and 7 solar occultations (see Shemansky and Liu 2009, and Chapter 8). The results from some of these occultations are presented by Shemansky and Liu (2009), who derive C$_2$H$_2$ and C$_2$H$_4$ profiles and further confirm the distinct mixing-ratio peak and the meridional variability. The ultraviolet occultation results are discussed in more detail in Chapter 8.

The ISO/SWS instrument, due to its unprecedented sensitivity in the thermal infrared, has allowed the detection of several complex hydrocarbons. de Graauw et al. (1997) reported the detection of CH$_3$C$_2$H and C$_2$H$_2$ in the range 615–640 cm$^{-1}$. The emissions are optically thin, and only column densities can be derived: (1.1 ± 0.3) $\times$ 10$^{15}$ molecules cm$^{-2}$ for CH$_3$C$_2$H, and (1.2 ± 0.3) $\times$ 10$^{14}$ molecules cm$^{-2}$ for C$_2$H$_2$ were reported from the ISO/SWS analysis of Moses et al. (2000a). Bézard et al. (2001a) reported the detection of benzene, from emission at 674 cm$^{-1}$, with a column density of (4.7$^{+2.1}_{-1.1}$) $\times$ 10$^{13}$ molecules cm$^{-2}$. Cassini/CIRS is in position to derive meridional distributions for these species, but no results have been published in the refereed literature yet. ISO/SWS also unveiled the v$_2$ emission from CH$_3$ at 16.5 μm. Bézard et al. (1998) derived a CH$_3$ column density in the range 1.5–7.5 $\times$ 10$^{13}$ molecules cm$^{-2}$, taking into account uncertainties in the data calibration, the CH$_3$ band strength, and the temperature and methyl vertical profiles. Given recent updates in the measured line strengths of the of v$_2$ fundamental of CH$_3$ (Stancu et al. 2005), the Bézard et al. (1998) CH$_3$ column abundance should be increased by a factor of ~2. Similarly, updates in our understanding of Saturn’s thermal structure at the time of the ISO observations (e.g., Lellouch et al. 2001) and of spectral line parameters (e.g., Vander Auwera et al. 2007; Jacquot-Husson et al. 2005) necessitate some updates to the above quoted abundances from Moses et al. (2000a).

Finally, ground-based thermal infrared observations with the high-resolution TEXES spectromter have allowed Bézard et al. (2001b) and Greathouse et al. (2006) to detect ethylene and propane, respectively. The inferred C$_2$H$_4$ column abundance lies between 2–3 $\times$ 10$^{15}$ molecules cm$^{-2}$. For the C$_2$H$_6$ abundance, Greathouse et al. (2006) reported 5-mbar volume mixing ratios of (2.7 ± 0.8) $\times$ 10$^{-8}$ at 20°S and (2.5$^{+1.7}_{-0.8}$) $\times$ 10$^{-8}$ at 80°S latitude, suggesting that propane, like ethane, does not present any meridional variations of its abundance. However, from Cassini/CIRS limb soundings, Guerlet et al. (2009) find that the propane volume mixing ratio does increase from the northern winter hemisphere towards the southern summer hemisphere. This contradiction remains to be resolved by future ground-based and Cassini/CIRS observations.

### 5.2.4 External Oxygen Flux

An external oxygen influx to Saturn has long been postulated, originating either from micrometeoroid precipitation, large cometary impacts or from Saturn’s rings and satellites. A flux of oxygen in the reducing atmosphere of Saturn can have a conspicuous effect on the stratospheric chemistry by forming new molecules, attenuating the UV flux or providing condensation nuclei. The first observational basis for such an oxygen source was presented by Winkelstein et al. (1983). These authors had to introduce a 1.6 $\times$ 10$^{17}$ cm$^{-2}$ column density of water in the stratosphere in order to fit their IUE spectrum in the 150–300 nm range. Using HST data covering a similar spectral range, Prangé et al. (2006) showed that the large water abundance inferred by Winkelstein et al. (1983) resulted from their assumption of a vertically uniform acetylene profile. Using a C$_2$H$_2$ vertical profile compatible with infrared observations and photochemical models (see Sections 5.2.3.2 and 5.3.1.2), Prangé et al. (2006) showed that only upper limits on the H$_2$O abundance can be derived from UV spectra. Water was first firmly detected by Feuchtgruber et al. (1997) using ISO observations. Rotational lines of H$_2$O were clearly detected at 30.90, 35.94, 39.37, 40.34, 43.89, 44.19, and 45.11 μm, yielding a stratospheric column density of (1.4 ± 0.4) $\times$ 10$^{15}$ cm$^{-2}$ (Moses et al. 2000b). ISO observations also allowed de Graauw et al. (1997) to detect the stratospheric emission of the CO$_2$ v$_2$ band at 14.98 μm for the first time. This emission is modeled with a CO$_2$ column abundance of (6.3 ± 1.0) $\times$ 10$^{14}$ cm$^{-2}$ (Moses et al. 2000b).

Carbon monoxide can also act as a tracer of an external oxygen flux. Indeed, oxygen-bearing molecules are photochemically converted to CO in the stratosphere, and the CO
photochemical lifetime is long compared with a saturnian year or other hydrocarbon lifetimes. However, CO can also originate from Saturn’s interior as do PH$_3$, GeH$_4$, and AsH$_3$. To discriminate between both possible sources, observers need to retrieve the CO vertical profile: a stratospheric abundance larger than that in the troposphere constitutes the signature of an external flux. CO was first detected by Noll et al. (1986a) in the (1–0) vibration band near 4.7 µm. Noll and Larson (1991) observations of the 4.5- to 5-µm region at the IRTF superseded that of Noll et al. (1986a). About 10 CO-lines from the (1-0) band can be clearly identified in the former spectrum. As demonstrated by Moses et al. (2000b), line intensities are mostly sensitive to the CO column abundance between 100 and 400 mbar, yielding a tropospheric volume mixing ratio of (1 ± 0.3) × 10$^{-9}$, i.e. a column abundance of (0.7–1.5) × 10$^{17}$ cm$^{-2}$. However, the observations could also be accommodated by a stratospheric volume mixing ratio of 2.5 × 10$^{-8}$; i.e. a column abundance of ~6 × 10$^{17}$ cm$^{-2}$. Both distributions fit equally well the observations, with the exception of the P14 line at 2086.3 cm$^{-1}$, which is best matched by a tropospheric distribution. Unfortunately, this line is entangled with phosphine absorption and is not well reproduced by the model spectra in any case, hence undermining the conclusion.

Due to their high spectral resolution, millimetric and sub-millimetric heterodyne observations are well suited to discriminate between the narrow stratospheric emission and the broad tropospheric absorption. After several fruitless attempts (Rosenqvist et al. 1992; Cavalié et al. 2008), Cavalié et al. (2009) obtain the first detection of the CO(3-2) line in Saturn using the James Clerk Maxwell Telescope. They find that the CO line is best matched with a stratospheric mole fraction of 2.5 × 10$^{-8}$ at pressures smaller than 15 mbar, and of 10$^{-10}$–10$^{-9}$ at higher pressures. This profile favors an external origin for carbon monoxide, due to a cometary impact about 200–300 years ago. However, the water observed in Saturn’s stratosphere still needs to be provided by a continuous source, so that both a continuous source and a sporadic source of oxygen seem to be active in Saturn.

Herschel and the Atacama Large Millimeter Array (ALMA) will observe stronger CO and H$_2$O lines at other frequencies, providing further constraints on the vertical profiles of these species. Unfortunately Cassini can contribute very marginally to the observations of oxygenated species. Water rotational lines are difficult to detect at the spectral resolution of CIRS. Hence, many spectra will have to be averaged, at the expense of meridional resolution. For CO$_2$, it should be possible to extract a meridional profile from CIRS limb observations at high spectral resolution, but only a few observations were performed, and have not yet been analyzed.

5.3 Chemistry

5.3.1 Tropospheric Chemistry

5.3.1.1 Thermochemistry

In the deep troposphere of Saturn, well below the regions that can be probed by remote-sensing techniques, temperatures become high enough (i.e., ≥1000 K) that energy barriers to chemical kinetic reactions can be overcome. Chemical reactions in these high-temperature regions therefore proceed rapidly, and the atmosphere is expected to attain thermochemical equilibrium. The thermochemical-equilibrium composition is strongly dependent on temperature and weakly dependent on pressure, as well as being dependent on the relative abundance of the different elements. Fegley and Prinn (1985) presented the first comprehensive thermochemical-equilibrium calculations for Saturn. In this model, the large background atmospheric H$_2$ abundance allows CH$_4$ to be the dominant carbon-bearing molecule throughout Saturn’s atmosphere, with all other carbon species having abundances much less than CH$_4$. Carbon monoxide is expected to have an exceedingly low abundance in the observable regions of the upper troposphere but becomes more and more abundant with increasing temperature and depth. Similarly, H$_2$O, NH$_3$, and H$_2$S are the dominant forms of oxygen, nitrogen, and sulfur throughout the pressure-temperature regimes found in Saturn’s troposphere. Updates to the major-element thermochemical-equilibrium calculations for Saturn can be found in Fegley and Lodders (1994), Lodders and Fegley (2002), Visscher and Fegley (2005), and Visscher et al. (2006), although the qualitative conclusions of Fegley and Prinn (1985) still hold.

Fegley and Prinn (1985) expect P$_2$O$_5$ vapor (formed from the oxidation of PH$_3$ by water) to be the thermodynamically stable form of phosphorus in the ~400–900 K region on Saturn, with PH$_3$ becoming dominant only at deeper levels for temperatures in excess of ~1000 K. At temperatures below ~400 K (i.e., still well below the water cloud), the P$_2$O$_5$ vapor is expected to be converted to a solid NH$_4$H$_2$PO$_4$ condensate, and gas-phase phosphorous-bearing species are expected to have low abundances in the upper troposphere of Saturn under thermochemical-equilibrium conditions. The phosphorus results are somewhat uncertain due to uncertain thermodynamic parameters and elemental ratios: Borunov et al. (1995) suggest that PH$_3$ could be the dominant equilibrium form throughout Jupiter’s atmosphere at all temperatures greater than ~500 K, at which point a NH$_4$H$_2$PO$_4$ condensate forms; they expect Saturn’s thermochemistry to be similar. The latest phosphorus equilibrium calculations for Saturn (Visscher and Fegley 2005) produce results qualitatively similar to that of Fegley and Prinn (1985) in terms
of the phosphorus speciation, with some small quantitative differences in the temperature levels at which the different major species take over.

Based on thermochemical equilibrium modeling, both GeH4 and AsH3 are expected to be relatively abundant at depth on Saturn (Fegley and Prinn 1985; Fegley and Lodders 1994) but fall to negligible quantities in the upper troposphere due to condensate formation (e.g., Ge, GeS, GeTe, and As solid phases). Gas-phase HF is expected to be the dominant form of fluorine until the temperature drops below ~300 K, at which point NH4F condenses. Similarly, HCl, HBr, and HI are expected to be major gas-phase species at temperatures below ~1000 K, until condensation of NHCl, NHBr, and NH4I occurs in the 350-450 K region (Fegley and Lodders 1994).

The observed abundance of CO, PH3, GeH4, and AsH3 (see Section 5.2) greatly in excess of thermochemical-equilibrium predictions provides clear evidence that thermochemical equilibrium cannot be maintained in the colder regions of Saturn’s troposphere. Based on arguments first presented by Prinn and Barshay (1977), the observed disequilibrium tropospheric composition is likely caused by strong convective motions in giant-planet tropospheres that allow gas species to be mixed vertically at a rate more rapid than the chemical kinetic destruction can keep pace. As a gas parcel is transported upwards, the equilibrium composition is “quenched” or “frozen in” at the level at which the vertical mixing time scale drops below the chemical kinetic time scale of conversion between different forms of the element. The observed upper tropospheric abundance then represents equilibrium conditions at a much deeper level, with that level being dependent on the strength of vertical mixing and the kinetic rate coefficients. Because the quench level is not well constrained from theoretical arguments, the relative partitioning between different molecules containing P, Ge, and As at the quench level is uncertain, and the observed abundances of PH3, GeH4, and AsH3 represent lower limits to the bulk abundances of these elements.

If one assumes the elemental abundances on Saturn are well known and the kinetics well understood, the observed abundances of these disequilibrium species can be used to back out transport time scales and one-dimensional eddy diffusion coefficients in Saturn’s troposphere (e.g., see Fegley and Prinn 1985; Fegley and Lodders 1994, who derive eddy diffusion coefficients of order 10^6–10^9 cm^2 s^{-1} at the tropospheric quench levels based on model comparisons with CO and PH3 abundances). Conversely, if one makes assumptions about the convective time constants from mixing-length theory (e.g., Stone 1976; see also Smith 1998) and the chemical time constants from the rate-limiting kinetic reactions for the conversion mechanisms of a particular molecule (e.g., Prinn and Barshay 1977; Yung et al. 1988; Bézard et al. 2002), the observed disequilibrium abundances can be used to back out the deep-atmospheric abundance of the element in question. Visscher and Fegley (2005; see also the Bézard et al. 2002 calculations for Jupiter) attempt to get the deep oxygen abundance from this method, as the deep O/H ratio on Saturn cannot be directly measured by any of the Cassini or Voyager instruments. Because the bulk elemental abundances have important implications for giant-planet formation scenarios (e.g., Lunine et al. 2004), such calculations are of great interest for understanding the origin of the solar system. In practice, however, current uncertainties in the tropospheric CO abundance on Saturn and in the kinetics and rate coefficients of the CO-CH4 interconversion mechanisms are preventing reliable estimates of the deep oxygen abundance on Saturn from being obtained using this method (cf. the Jupiter study of Bézard et al. 2002). That situation could change in the near future with tighter observational constraints on tropospheric CO from high-resolution ground-based observations and with expanded laboratory or theoretical investigations of appropriate rate coefficients and thermodynamic parameters.

5.3.1.2 Photochemistry in the Troposphere

Rapid atmospheric mixing is not the only disequilibrium process that affects the composition of Saturn. Photochemistry, or the chemistry that is initiated when an atmospheric constituent absorbs a photon, plays a major role in controlling the abundances of trace species. For details of tropospheric photochemistry on Saturn and the other giant planets, see Atreya et al. (1984), Prinn et al. (1984), and Strobel (1975, 1983, 2005). Although Rayleigh scattering, molecular absorption, and aerosol and cloud opacity limit the depth to which solar ultraviolet photons can penetrate in Saturn’s atmosphere (e.g., Tomasko et al. 1984; Pérez-Hoyos and Sánchez-Lavega 2006; see also Chapter 7 in this volume), photochemical processes can occur in the few-hundred mbar region and above. In that region, water has already been removed through condensation at depth, and NH3H and ammonia clouds have formed, but the vapor pressure of NH3 may be high enough at the cloud tops (and the overlying haze opacity sufficiently low) that NH3 may interact with ultraviolet photons with wavelengths <220 nm. Ammonia photochemistry may therefore occur in Saturn’s upper troposphere (e.g., Strobel 1975, 1983; Atreya et al. 1980), with ammonia being photolyzed at the cloud tops to form predominantly H atoms and NH2 radicals. The NH2 radicals can recombine with each other to form hydrazine (N2H4) or with H to reform NH3. The hydrazine will condense to form an aerosol, but some may be photolyzed or react with H to form N2H3 and eventually produce N2.

Phosphine does not condense at Saturnian temperatures, and it will also participate—and likely dominate—tropospheric photochemistry. The upper tropospheric haze is relatively
optically thick on Saturn (see Chapter 7), which helps to shield the ammonia from photolysis in its condensation region. Phosphine, on the other hand, can diffuse upward until haze opacity is low enough for PH$_3$ photolysis to occur, and phosphine photochemistry is therefore guaranteed at some atmospheric level, no matter what the haze opacity. The coupled photochemistry of phosphine and ammonia on Saturn has been studied by Kaye and Strobel (1983c, 1984). Phosphine is photodissociated by photons with wavelengths less than $\sim 235$ nm. The dominant photolysis products are PH$_2$ and H. Analogous with NH$_3$ photochemistry, two PH$_2$ radicals can combine to form P$_2$H$_4$, which can condense at the cold Saturnian temperatures, or the PH$_2$ can combine with H to reform PH$_3$. The ammonia photolysis products NH$_2$ and H can also react with PH$_3$ to provide addition mechanisms for PH$_3$ production and PH$_3$ destruction. The yield of N$_2$H$_4$, N$_2$, and other nitrogen-bearing products is therefore reduced when PH$_3$ is present. Dominant products of the coupled PH$_3$-NH$_3$ photochemistry are expected to be P$_2$H$_4$, condensed red phosphorous, NH$_2$PH$_2$, N$_2$H$_4$, and N$_2$. Diphosphine (P$_2$H$_4$) is a leading candidate for the upper tropospheric haze. Appropriately designed laboratory experiments investigating the photolysis of PH$_3$ or NH$_3$-PH$_3$ mixtures (e.g., Ferris and Morimoto 1981; Ferris et al. 1984; Ferris and Khwaja 1985) have been valuable in elucidating the nature of the coupled phosphine-ammonia chemistry of the giant planets.

The possibility of chemical coupling between hydrocarbons and NH$_3$ or PH$_3$ is a more controversial topic. Methane is photolyzed at high altitudes on Saturn, well removed from the ammonia and phosphine photolysis regions. Numerous laboratory experiments over the years on “simulated” giant-planet atmospheres (e.g., Sagan et al. 1967; Woeller and Ponomarova 1969; Ferris and Chen 1975; Raulin et al. 1979; Ferris and Morimoto 1981; Bossard et al. 1986; Ferris and Ishikawa 1988; Ferris et al. 1992; Guillemin et al. 1995a) have addressed the possible formation of HCN and other nitriles and organo-nitrogen compounds or organophosphorus compounds, but the relative gas abundances or other conditions in those experiments have not always been good analogs for giant-planet tropospheres. Kaye and Strobel (1983a, b) have used a photochemical model to study several possible mechanisms for coupled carbon-nitrogen chemistry on Jupiter. One pathway involves CH$_3$ radicals produced from the reaction of methane with hot hydrogen atoms that were produced from PH$_3$ and NH$_3$ photolysis; the CH$_3$ combines with NH$_2$ to form methylamine (CH$_3$NH$_2$), which can photolyze to form a small amount of HCN. A second pathway involves reaction of NH$_3$ with C$_2$H$_2$ to form aziridine (or other C$_2$H$_5$N isomers), which can also be photolyzed to form HCN and other interesting compounds. In the first scenario, the hot hydrogen atoms can be quenched by H$_2$, effectively cutting off production of CH$_3$ and nitrogen-bearing organics (see also Raulin et al. 1979; Ferris and Morimoto 1981).

The second, more promising, of these scenarios has been studied in more detail by Ferris and Ishikawa (1987, 1988) and Keane et al. (1996), who have used laboratory simulations to study the detailed mechanisms and product quantum yields of coupled ammonia-acetylene photochemistry. They favor somewhat different pathways and products for the coupled photochemistry, but the reaction sequence still starts with the NH$_2$ + C$_2$H$_2$ reaction. The relevance both of these experiments and of the models Kaye and Strobel (1983a, b) to the real situation on Saturn is not completely clear because the tropospheric C$_2$H$_2$ abundance is likely much smaller than was assumed in those experiments and models (e.g., Moses et al. 2000a, 2005). Similarly, coupled PH$_3$-C$_2$H$_2$ photochemistry (e.g., Guillemin et al. 1995a), or coupled chemistry of NH$_3$ and/or PH$_3$ with other unsaturated hydrocarbons (e.g., Ferris et al. 1992; Guillemin et al. 1997) may be inhibited on Saturn due to the likely low tropospheric abundance of C$_2$H$_2$ and other unsaturated hydrocarbons. However, if the tropospheric haze opacity is large enough to allow PH$_3$ to reach the tropopause (cf. the CIRS observations of Fletcher et al. 2007b), PH$_3$-hydrocarbon coupling is more likely to occur. Observations that detect or put upper limits on the HCN and HCP abundance on Saturn (e.g., Weisstein and Serabyn 1996) could help constrain the coupled NH$_3$-C$_2$H$_2$ and PH$_3$-C$_2$H$_2$ photochemistry.

Because differences in the abundances of NH$_3$, PH$_3$, and (in particular) aerosols lead to differences in the shielding of the photochemically active molecules on Saturn as compared with Jupiter and because NH$_3$ condenses deeper in Saturn’s colder atmosphere, some differences in tropospheric photochemistry are expected to exist between the two planets. PH$_3$ photochemistry may be more important, PH$_3$-hydrocarbon coupling is more likely, and NH$_3$-PH$_3$ coupling may be suppressed on Saturn. The extent and consequence of these differences remain to be quantified in up-to-date photochemical models that include accurate aerosol extinction.

Some H$_2$S could be present in and below the putative NH$_4$SH cloud on Saturn. Because H$_2$S has a substantial photoabsorption cross section out to $\sim 260$ nm (and a weak H-S bond), some sulfur photochemistry could possibly occur on Saturn, but the deep levels to which the UV radiation must penetrate suggest that sulfur photochemistry is not very important on Saturn, except perhaps in localized areas with reduced cloud cover. The details of the possible H$_2$S photochemistry are highly uncertain (e.g., Lewis and Prinn 1984; Prinn and Owen 1976). Similarly, GeH$_4$ and AsH$_3$ photochemistry is poorly understood (e.g., Fegley and Prinn 1985; Nava et al. 1993; Guillemin et al. 1995b; Morton and Kaiser 2003), but more likely to be occurring. In all, tropospheric photochemistry on Saturn is less well understood than stratospheric photochemistry, due to a critical lack of reaction rate coefficients for the appropriate reactions. It is hoped that new Cassini and Earth-based observations that
have helped derive the altitude profiles of some of the key tropospheric species (NH$_3$, PH$_3$, GeH$_4$, AsH$_3$, see Section 5.2) will help generate a resurgence in interest in tropospheric photochemistry on Saturn.

5.3.2 Stratospheric Hydrocarbon Chemistry

Stratospheric hydrocarbon photochemistry on Saturn and the other giant planets has been reviewed recently by Moses et al. (2005, 2004, 2000a), Strobel (2005), and Yung and DeMore (1999), and the interested reader is referred to those works for more details. Because most of the major equilibrium hydride species condense in the cold upper troposphere of Saturn, stratospheric photochemistry is dominated by photolysis of the relatively volatile molecule methane. Methane is transported up from the deep interior past the tropopause cold trap to the top of the middle atmosphere (the mesopause region), where its abundance eventually falls off due to molecular diffusion of the relatively heavy CH$_4$ molecules in the lighter background H$_2$ gas. A common misconception is that photolysis limits the CH$_4$ abundance at high altitudes—it is actually molecular diffusion, rather than photochemistry, that is responsible for the sharp drop off in CH$_4$ abundance with altitude that is observed in spacecraft ultraviolet occultation data (e.g., Festou and Atreya 1982; Smith et al. 1983; Vervack and Moses 2009; Shemansky and Liu 2009; see also Chapter 12). Methane can be photolyzed in the upper atmosphere by ultraviolet radiation, and the photolysis products react to form the plethora of complex hydrocarbons that have been observed in Saturn’s stratosphere (see Section 5.2). These complex hydrocarbons diffuse down into the troposphere, where they eventually encounter high temperatures and can be thermochemically converted back to CH$_4$, thus completing a “methane cycle”. Strobel (1969) was the first to work out the concept of this methane cycle for the giant planets.

5.3.2.1 Chemical Reactions

Hydrocarbon photochemistry on Saturn is initiated by methane photolysis in the upper atmosphere. Because the photoabsorption cross section of methane is negligible at wavelengths longer than $\sim$145 nm, and because the solar Lyman alpha line (121.6 nm) provides the largest flux source at wavelengths less than 145 nm, Lyman $\alpha$ photodissociation of CH$_4$ controls much of the subsequent hydrocarbon photochemistry in Saturn’s stratosphere. Although the methane photolysis branching ratios (i.e., the likelihood of forming a particular set of reaction products during photolysis) at 121.6 nm are not completely understood, the major photolysis products are CH$_3$, excited CH$_2$(a $^1$A$_1$), and CH (e.g., Cook et al. 2001; Wang et al. 2000; Smith and Raulin 1999; Brownword et al. 1997; Heck et al. 1996; Mordaunt et al. 1993). The CH$_3$ radicals can recombine with another CH$_3$ radical to form C$_2$H$_6$, or can combine with H to recycle methane. The CH$_2$(a $^1$A$_1$) radicals can react with H$_2$ to form CH$_3$ ($\geq$90% of the time) or be quenched to ground-state CH$_2$ ($\geq$10% of the time) and eventually react with H to form CH. The CH radicals can insert into CH$_4$ to form C$_2$H$_4$. Photolysis of both C$_2$H$_6$ and C$_2$H$_4$ produces C$_2$H$_2$. Atomic hydrogen is a major product of hydrocarbon chemistry on Saturn, and reaction of atomic H with hydrocarbons helps define the relative abundance of the observable species. More complex hydrocarbons are produced through radical-radical combination reactions (e.g., CH$_3$ + C$_2$H$_3$ + M $\rightarrow$ C$_3$H$_6$ + M, where M represents any third molecule or atom, CH$_3$ + C$_3$H$_5$ + M $\rightarrow$ C$_4$H$_8$ + M, CH$_3$ + C$_2$H$_5$ + M $\rightarrow$ C$_3$H$_8$ + M, 2 C$_2$H$_3$ + M $\rightarrow$ C$_4$H$_6$ + M), through CH insertion reactions (e.g., CH + C$_2$H$_6$ $\rightarrow$ C$_3$H$_6$ + H, CH + C$_2$H$_2$ $\rightarrow$ C$_3$H$_4$ + H, CH + C$_2$H$_4$ $\rightarrow$ C$_3$H$_5$ + H), and through other radical insertion reactions (e.g., C$_2$H + C$_2$H$_2$ $\rightarrow$ C$_4$H$_2$ + H, CH$_3$ + C$_2$H$_3$ $\rightarrow$ C$_3$H$_4$ + H, C$_3$H + C$_2$H$_4$ $\rightarrow$ C$_4$H$_4$ + H). Hydrocarbons are destroyed through photolysis, reaction with hydrogen atoms, and various other radical addition, insertion, and disproportionation reactions (e.g., C$_2$H$_2$ + C$_2$H$_3$ $\rightarrow$ C$_4$H$_2$ + C$_2$H$_3$). Stratospheric hydrocarbon photochemistry on Saturn is rich and complex. Rather than going through the major production and loss mechanisms for each of the observed stratospheric constituents, we will direct interested readers to the reviews of Moses et al. (2000a, 2004, 2005), for which the hydrocarbon reactions and pathways thought to be most important on Jupiter and Saturn are discussed in gory detail. Note that the dominant reactions are expected to be the same on both Jupiter and Saturn, with quantitative differences caused by different stratospheric temperatures, heliocentric distances, atmospheric transport, auroral processes, condensation, and influx of external material.

Although the production and loss mechanisms for the major hydrocarbons are qualitatively understood, a full quantitative understanding has been hindered by a lack of relevant chemical kinetics data at low temperatures and low pressures. Moses et al. (2005) provide a table (their Table 6) that lists some critical data needed to improve our current understanding of hydrocarbon photochemistry. Of particular importance is information on the photochemistry of benzene and C$_3$H$_4$ molecules under conditions relevant to giant-planet stratospheres, details of the photolysis branching ratios for CH$_4$ at Lyman alpha wavelengths (especially the quantum yield of CH formation), and information on the low-pressure limit and falloff behavior of the rate coefficients for relevant hydrocarbon termolecular reactions at temperatures of 80–170 K (e.g., Huestis et al. 2008).
5.3.2.2 One-Dimensional Models

Several one-dimensional (1-D; in the vertical direction) models for hydrocarbon photochemistry in Saturn’s stratosphere have been developed in the past several decades (e.g., Strobel 1975, 1978, 1983; Atreya 1982; Festou and Atreya 1982; Lee et al. 2000; Ollivier et al. 2000; Moses et al. 2000a, b, 2005; Dobrijevic et al. 2003; Cody et al. 2003; Sada et al. 2005). In these models, the continuity equation is typically solved to predict the concentration of atmospheric species as a function of pressure. Photochemical production and loss rates for the hydrocarbons as a function of pressure are calculated after providing such inputs as a chemical reaction list, photoabsorption and photolysis cross sections, photolysis branching ratios, and temperature-dependent reaction rate coefficients. Transport of the atmospheric constituents is usually achieved by eddy and molecular diffusion. Molecular diffusion coefficients for various hydrocarbons in H₂, He, and other hydrocarbon gases have been studied theoretically and in the laboratory (e.g., Marrero and Mason 1972), and empirical formulas that depend on atmospheric temperature and gas densities are typically adopted.

Eddy diffusion, on the other hand, is a parameterization in these 1-D models that is introduced to account for macroscopic transport processes that act to keep the atmosphere well mixed (i.e., dissipative waves, small-scale and large-scale eddies, diabatic circulation, and other macroscopic mass motions). Eddy diffusion coefficients cannot be calculated from first principles without knowing the full three-dimensional wind fields from diabatic circulation, waves, etc., which are certainly not known for Saturn. The eddy diffusion coefficient $K_{zz}$ is therefore an important free parameter in the photochemical models. Most modelers assume that the same $K_{zz}$ profile can be used to determine the vertical transport rates for all constituents in the atmosphere, despite the warning of Strobel (1981, 2005) and West et al. (1986) that the chemical loss rate of a constituent can affect its inferred eddy diffusion coefficient $K_{zz}$. Constituents like C₂H₆ and CO that are long-lived chemically are typically used as tracers to help constrain $K_{zz}$ in the lower stratosphere of the giant planets. Spacecraft ultraviolet occultations of hydrocarbons in the mesopause region of Saturn (e.g., Festou and Atreya 1982; Smith et al. 1983; Vervack and Moses 2009; Shemansky and Liu 2009) or ultraviolet emission from He 58.4 nm or H Lyman $\alpha$ airglow (e.g., Sandel et al. 1982; Atreya 1982; Ben-Jaffel et al. 1995; Parkinson et al. 1998) are used to help constrain the location of the methane homopause—the altitude level at which $K_{zz}$ equals the methane molecular diffusion coefficient—and the magnitude of $K_{zz}$ in the homopause region.

Accurate constraints on the location of the methane homopause on Saturn are important for the photochemical models because methane is photolyzed just below its homopause region, and the pressure at which methane is photolyzed affects the subsequent chemistry through molecular and other pressure-dependent reactions. One interesting result that has arisen from the analysis of the few Cassini/UVIS stellar occultations that have been analyzed to date (Shemansky and Liu 2009), the recent analysis of all the Voyager/UVS solar and stellar occultations (Vervack and Moses 2009), the analysis of the Cassini/VIMS $\alpha$ CMi stellar occultation at 55° N latitude (Nicholson et al. 2006), and analysis of auroral images and spectra from Cassini/UVIS (e.g., Gérard et al. 2009; Gustin et al. 2009) is that the homopause pressure level on Saturn appears to vary significantly with latitude and/or time, a fact that was not realized during the Voyager era. If so, the appropriateness of 1-D models in representing the entire Saturnian atmosphere is called into question. Chapter 8 in this volume has more details about the ultraviolet occultations from Cassini.

The Cassini/UVIS stellar occultation at ~43° latitude described by Shemansky and Liu (2009) implies a homopause pressure level that is nearly two orders of magnitude greater (i.e., at a lower altitude) than the Voyager 2 solar ingress occultation at 29.5° latitude analyzed by Vervack and Moses (2009). Figure 5.7 illustrates these differences. The Voyager 2 stellar egress occultation (3.8° latitude) analyzed by Smith et al. (1983) and Festou and Atreya (1982) suggests a homopause at very low pressures (high altitudes), similar to the results of the Voyager 2 solar ingress profile, whereas the Voyager 1 solar egress profile (~27° latitude) (Vervack and Moses 2009) suggests a high-pressure homopause more similar to the Shemansky and Liu (2009) Cassini/UVIS ~43° latitude results (see Fig. 5.7). Although differences in analysis techniques and assumptions can play a role in these results, studies that use a consistent technique to analyze multiple occultations (i.e., Shemansky and Liu 2009; Vervack and Moses 2009) derive different homopause levels for different occultation latitudes, suggesting real variation with location and/or time. As suggested by Vervack and Moses (2009), the likely cause of the variable homopause levels is small vertical winds that vary with latitude and time. Existing and future Cassini/UVIS solar and stellar occultations, as well as Cassini/VIMS occultations, may help map out the latitude dependence of the homopause level and perhaps allow winds and circulation in the mesopause region to be derived.

Note that we try to put all quantities on a pressure scale on the giant planets because the altitude or radius scale varies significantly with latitude on these rapidly rotating, oblate planets, due to variations in the gravitational acceleration with latitude. However, occultation data are inherently a function of planetary radius, and converting to a pressure scale introduces a model dependency in the results (the greatest assumption being the temperature profile), and the reader should keep that fact in mind with the above discussion. The simultaneous or near-simultaneous measurement
of atmospheric temperatures from 1 bar on up to ~0.01 mbar from Cassini/CIRS limb or other measurements at the UVIS occultation latitudes would greatly aid the occultation analyses, as would more accurate determinations of the planetary shape (i.e., determinations of the radius levels of isobaric surfaces, which are not well represented by oblate spheroids). Cassini/VIMS occultations (e.g., Nicholson et al. 2006) may be particularly useful in helping place the homopause location in pressure space.

Photochemical models for Saturn that have been published since the Voyager encounters all assume a high-altitude methane homopause most relevant to 3.8° latitude or 29° N latitude during the Voyager flybys. Figure 5.5 shows the results from one such 1-D photochemical model for Saturn (Moses et al. 2005). The eddy diffusion coefficient in the lower stratosphere for this model is constrained from the global-average ISO/SWS observations of C_2H_6 (e.g., Moses et al. 2000a, de Graauw et al. 1997). The model is designed to represent global-average conditions, with an assumed temperature profile that was derived from the globally averaged ISO observations (Lellouch et al. 2001), an assumed solar UV flux that represents low-to-average conditions within the solar cycle, and fixed vernal equinox solar insolation conditions at 30° latitude. An external influx of H_2O, CO, and CO_2 is introduced at high altitudes, and the oxygen photochemistry slightly affects the abundances of the unsaturated hydrocarbons. Diacetylene, benzene, and water are found to condense in the lower stratosphere and contribute to a stratospheric haze layer (C_4H_2 and C_6H_6 condense near ~10 mbar in this model, whereas water condenses closer to 1 mbar, but these values depend on temperature profiles that need to be updated based on the Cassini CIRS results, e.g., Guerlet et al. 2009).

Consistent with the infrared and ultraviolet observations discussed in Section 5.2, the Moses et al. (2005) model—and all other photochemical models—predict that ethane is the second-most abundant hydrocarbon in Saturn’s stratosphere (behind methane), followed by acetylene, and propane. Ethylene is abundant at high altitudes but its mole fraction falls off in the middle and lower stratosphere due to reaction with atomic H (to eventually form C_2H_6) and photolysis (to eventually form C_2H_2). The Moses et al. model accurately predicts the global-average abundances of C_2H_6, C_2H_2, CH_3C_2H, C_4H_2, and CH_3 (not shown), but underpredicts the column abundance of C_2H_4 and C_3H_8, and greatly overpredicts the column abundance of C_6H_6. Moreover, when the same reaction list is applied to Jupiter, Uranus, and Neptune, the model has difficulty in reproducing the observed C_2H_2/C_2H_4/C_2H_6 ratio on all the giant planets, suggesting systematic problems with the adopted chemical inputs.

Although some of the model-data mismatch may be caused by the attempt to represent a three-dimensional
atmosphere with a one-dimensional, steady-state model, the chemical reaction list used by Moses et al. (2005) clearly needs improvement. Models developed by other groups also fail to reproduce all available observations (see below), indicating that we do not have a complete quantitative understanding of hydrocarbon photochemistry under Saturnian stratospheric conditions. Sensitivity and “uncertainty” studies (e.g., Dobrijevic et al. 2003; Smith and Nash 2006) can help identify the key reactions that affect species abundances at different pressures and can help evaluate the overall robustness of the models. Laboratory measurements and theoretical calculations are needed to help fill in current uncertainties in the critical reaction schemes (e.g., see Table 6 of Moses et al. 2005), and further observations that constrain the vertical profiles of the observed constituents will provide important model constraints.

Other recent 1-D photochemical models that have proven useful in defining the hydrocarbon photochemistry on Saturn include those presented by Ollivier et al. (2000), Dobrijevic et al. (2003), Cody et al. (2003), and Sada et al. (2005). The model of Ollivier et al. (2000), like those of Moses et al. (2000a 2005), considers the chemistry of a long list of hydrocarbon and oxygen species and examines the sensitivity of the results to variations in several key input parameters. The model succeeds in reproducing the observed CH₄ and C₂H₂ abundances but greatly underestimates the C₂H₆ abundance and overestimates the CH₃C₂H, C₂H₂, and CH₃ abundances. The CH₃ problem may partly be remedied by the updated line strengths provided by Stancu et al. (2005). The C₂H₆ underestimation appears to have been caused by the adoption of a rapid reaction between C₂H₂ and C₂H₆ to form C₃H₃ and C₂H₅. This reaction between acetylene and ethane would be exceedingly slow at Saturnian temperatures; Ollivier et al. (2000) have apparently mistaken the reaction of vinylidene (H₂CC) radicals plus ethane with the acetylene plus ethane reaction in their model. Despite this reaction-rate problem, Ollivier et al. (2000) have provided sensitivity studies for such parameters as solar irradiance, latitude, H influx from the thermosphere, external oxygen influx, and absorption only vs. multiple scattering that are useful in understanding model sensitivities and limitations.

The Ollivier et al. (2000) C₂H₂ + C₂H₆ reaction-rate problem has been corrected in a follow-up model by Dobrijevic et al. (2003). The updated Dobrijevic et al. (2003) results compare well with the C₂H₂ and C₂H₆ observations from the ISO satellite (Moses et al. 2000a), but the model tends to underestimate CH₃C₂H and overestimates the abundance of C₂H₂, although Dobrijevic et al. (2003) emphasize that the model results are acceptable given the uncertainties in the rate coefficients and other model parameters. In fact, the main advance of the Dobrijevic et al. (2003) study is a quantification of uncertainties in product abundances in photochemical models based on uncertainties in reaction rate coefficients and other model inputs.

The model of Cody et al. (2003) is designed to specifically study the influence of new experimentally derived rate coefficients for the CH₃ + CH₂ self reaction on the predicted abundance of CH₃ on Saturn and Neptune. Cody et al. (2003) emphasize the relative importance of the ratio of low-pressure limiting vs. high-pressure limiting rate coefficient for the termolecular CH₃ + CH₂ recombination reaction in affecting the methyl radical abundance in photochemical models.

Sada et al. (2005) have developed a photochemical model for Saturn in order to better define the vertical profiles of C₂H₆ and C₂H₂ to more accurately retrieve mole fractions from ground-based infrared observations and Voyager IRIS data. The Sada et al. (2005) model simultaneously reproduces the emission in the observed C₂H₂ and C₂H₆ infrared bands, but the model profiles were shifted by some unspecified amount in mole-fraction space to obtain this good fit. Interestingly, their vertical profile for C₂H₆ differs from that of other photochemical models in the upper atmosphere such that their mole fraction continues to increase sharply from ~1 to 0.01 mbar. The C₂H₆ profiles in other models such as Moses et al. (2000a, 2005) and Ollivier et al. (2000) exhibit a more constant C₂H₆ mole fraction in the upper stratosphere. Limb observations acquired with Cassini/CIRS (e.g., Guerlet et al. 2009) and ultraviolet occultations with Cassini/UVIS (Shemansky and Liu 2009) may help constrain the C₂H₆ vertical profiles to help distinguish between models.

### 5.3.2.3 Seasonal Variation in 1-D Models

Most photochemical models to date have been concerned with steady-state conditions for either global-average atmospheres or for single specific latitudes and seasons. The time-variable, multiple-latitude model of Moses and Greathouse (2005) is an exception in that the effects of seasonally varying insolation, ring shadowing, and the solar cycle on stratospheric chemistry are examined in a more realistic manner; however, the model still considers transport in the vertical direction only—horizontal transport is neglected. Moses and Greathouse find that at very high altitudes (i.e., pressures less than ~0.01 mbar), the hydrocarbon abundances responded quickly to insolation changes, and the mixing ratios of the photochemical products are largest at those latitudes and seasons where the solar insolation is the greatest. At lower altitudes, however, the increased vertical diffusion time scales are found to introduce increasing phase lags in the chemical response of the atmosphere to the changing solar insolation. Below the ~1 mbar level, the response times of the relatively long-lived species such as C₂H₂, C₂H₆, and C₂H₆ become larger than a Saturnian year, so that their abundances
reflect annual-average insolation conditions (see Figs. 5.8 and 5.9). Because the annual-average solar insolation decreases toward the poles, Moses and Greathouse (2005) predict that the abundances of these photochemically produced species should decrease with increasing latitude at the few-mbar level (and at lower altitudes) at all seasons.

Figure 5.6 shows how the photochemical model of Moses and Greathouse (2005) compares with the ground-based, thermal-infrared observations of Greathouse et al. (2005), the Cassini/CIRS nadir data of Howett et al. (2007), the Cassini/CIRS limb data of Guerlet et al. (2009), and the HST ultraviolet observations of Prangé et al. (2006). The model roughly reproduces the observed meridional variation of C$_2$H$_2$ (albeit not as steeply in the northern hemisphere, which is likely caused by the constant-temperature-with-latitude assumption of the model) but clearly fails to reproduce the observations for the longer-lived C$_2$H$_6$ (especially in the southern hemisphere); the observations indicate that at the 2-mbar level, the C$_2$H$_6$ mixing ratio increases with increasing latitude in the southern summer hemisphere, whereas the model predicts a strong decrease with increasing latitude. Moses and Greathouse suggest that the long photochemical lifetime of C$_2$H$_6$ (i.e., $\sim$700 years at 2 mbar at mid-latitudes in the summer) is the root cause of this behavior—C$_2$H$_6$ is sensitive to horizontal transport, which is not included in the model (see Nixon et al. 2007 for a similar conclusion for Jupiter). Based on the failure of the model to reproduce the C$_2$H$_6$ but not the C$_2$H$_2$ meridional gradient, Moses and Greathouse suggest that the meridional transport time scale at 2 mbar on Saturn is in the $\sim$100–700 year range (i.e., somewhere between the photochemical lifetimes of C$_2$H$_2$ and C$_2$H$_6$). Although it is possible that $K_{zz}$ profiles that vary with latitude might be developed that could reproduce some of the observed behavior, it is more likely that
meridional transport is occurring in Saturn’s stratosphere, and multi-dimensional photochemical models that include horizontal transport will be needed to make sense of these observations.

### 5.3.2.4 Two-Dimensional Models

The observations and modeling discussed above and shown in Figs. 5.5–5.6 make it clear that the abundances of the photochemically produced species change with altitude, latitude, and time on Saturn. Because ethane and acetylene, along with methane, are the dominant coolants in giant-planet stratospheres (e.g., Yelle et al. 2001; Bézard and Gautier 1985), variations in the abundances of these species affect the radiative properties, thermal structure, and energy balance in the atmosphere, which in turn affect atmospheric dynamics, which in turn redistributes constituents that feed back on the chemistry and temperatures. A general circulation model (GCM) will be required to fully explore this complex coupling between chemical, dynamical, and radiative processes. Unfortunately, GCMs for Saturn’s stratosphere do not yet exist, and little is known about stratospheric circulation on Saturn due to a lack of clouds or other wind tracers. The two-dimensional “diabatic” or “residual mean” circulation can in principle be derived from modeling the momentum and energy budgets from seasonal radiative forcing, but the radiative-dynamical models that have been developed to

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**Fig. 5.9** The column density of acetylene ($C_2H_2$) above different pressure levels as a function of planetocentric latitude and season ($L_s$) from the Moses and Greathouse (2005) model: above 0.001 mbar (top left), above 0.01 mbar (bottom left), above 0.1 mbar (top right), above 1 mbar (bottom right). The contour intervals and overall scale change for each figure. Note the strong seasonal dependence at low pressures; the lack of seasonal dependence in the column abundance above 1 mbar is due to large photochemical and vertical transport time scales at pressures $\gtrsim$ 1 mbar (figure modified from Moses and Greathouse 2005)
date (e.g., Conrath et al. 1990; Barnet et al. 1992; see also the purely radiative seasonal climate model of Bézard and Gautier 1985) do not go high enough in the stratosphere to encompass the photochemical production regions and do not take variable hydrocarbon abundances into account. The latter variation and its effect on temperatures has been studied by Strong et al. (2007), who find that radiative time constants vary significantly with pressure such that high-altitude temperatures respond quickly to changes in insolation.

In the absence of direct information on stratospheric circulation, the observed meridional distribution of the hydrocarbons or other tracers can be used to learn something about the general nature of the stratospheric transport (see the Jupiter modeling of Friedson et al. 1999; Liang et al. 2005; Lellouch et al. 2006). Temperature maps, such as were produced from Cassini CIRS (Flasar et al. 2005; Simon-Miller et al. 2006; Fletcher et al. 2007a; Fouchet et al. 2008; Guerlet et al. 2009), also provide clues. For example, the elevated south polar temperatures (Fletcher et al. 2007a; Flasar et al. 2005) and the observed increase in the C2H6 abundance (Fletcher et al. 2007a; Flasar et al. 2009) provide clues. For example, the elevated south polar temperatures (Fletcher et al. 2007a; Flasar et al. 2005) and the observed increase in the C2H6 abundance toward high southern latitudes (e.g., Howett et al. 2007; Greathouse et al. 2005) led Flasar et al. (2005) to suggest subsidence in the high-latitude southern stratosphere. Complex wave-like structure in the low-latitude regions suggests an effect similar to the Earth’s semi-annual oscillation but on a ~15-year period (Fouchet et al. 2008; Orton et al. 2008; see also Chapter 6). This oscillatory feature seems to be influencing the C2H2, C2H6, and C3H8 vertical distributions in the low-latitude regions (Fouchet et al. 2008; Guerlet et al. 2009). Similarly, fine- and broad-scale features in the meridional profiles of temperatures and abundances have led Guerlet et al. (2009) to suggest vertical winds are influencing behavior at certain latitudes.

Although no 2-D photochemistry-transport models have yet been reported in the refereed literature, some preliminary models have been presented by Moses et al. (2007). In these models, the Caltech/JPL two-dimensional chemistry transport model (2-D GCM, see Morgan et al. 2004; Shia et al. 2006) is used to study the meridional and vertical distribution of stratospheric species. Both advection and/or horizontal and vertical diffusion are considered in the transport terms. Various ad hoc scenarios involving large-scale circulation cells or latitude- and altitude-dependent eddy diffusivities are examined, and the results are compared to the observed meridional distribution of constituents. The key conclusion of this modeling is that the abundances of C2H6 and C2H2 are highly linked by both photochemistry and vertical transport on time scales shorter than the estimated meridional transport time scales of Moses and Greathouse (2005), such that the meridional distribution of C2H2 in the models closely tracks that of C2H6. This model result is in conflict with observations (see Figs. 5.6). Moses et al. (2007) came up with some highly contrived scenarios involving latitude or altitude-dependent diffusivities that could roughly reproduce the observed C2H2 and C2H6 distributions, but the overall conclusion from this modeling is that the cause of the observed uncoupled distributions remains a mystery. Aerosol and gas-constituent shielding, multiple Rayleigh scattering, auroral chemistry, and incorrect model branching ratios for C2H6 have all been tentatively ruled out as possibilities. Further modeling, including the development of GCMs, is needed.

### 5.3.3 Oxygen Chemistry

The detection of CO2 and H2O that is unambiguously in the stratosphere of Saturn points to an external supply of oxygen to the planet (e.g., Feuchtruber et al. 1997, 1999; de Graauw et al. 1997; Bergin et al. 2000; Moses et al. 2000b; Ollivier et al. 2000; Simon-Miller et al. 2005; see also the discussion in the Jupiter papers of Bézard et al. 2002; Lellouch et al. 2002, 2006). Water from the deep interior would condense in the troposphere and would not make it up into the stratosphere. Carbon dioxide from the interior, on the other hand, might not condense and some could diffuse up into the stratosphere; however, the observed stratospheric abundance is much larger than the quenched equilibrium abundance predicted in thermochemical models (e.g., Fegley and Prinn 1985; Fegley and Lodders 1994; Visscher and Fegley 2005), indicating an external source. Possible sources of the exogenic oxygen-bearing material include comets, micrometeoroids, or ring/satellite debris.

The chemistry that is initiated from this exogenic oxygen influx is discussed by Moses et al. (2000b) and Ollivier et al. (2000) and is illustrated in Fig. 5.10. Although water is readily photodissociated at wavelengths less than 185 nm into predominantly OH + H, shielding by hydrocarbons lengthens its photochemical lifetime in Saturn’s stratosphere; moreover, the OH is efficiently recycled back to H2 through the reaction OH + H2 → H2O + H. A small portion of the H2O can be converted to CO through addition reactions of OH with unsaturated hydrocarbons (Moses et al. 2000b):

\[
\begin{align*}
\text{H}_2\text{O} + h\nu & \rightarrow \text{H} + \text{OH} \\
\text{OH} + \text{C}_2\text{H}_2 + \text{M} & \rightarrow \text{C}_2\text{H}_2\text{OH} + \text{M} \\
\text{C}_2\text{H}_2\text{OH} & \rightarrow \text{CH}_3\text{CO} \\
\text{CH}_3\text{CO} + \text{H} & \rightarrow \text{HCO} + \text{CH}_3 \\
\text{HCO} + \text{H} & \rightarrow \text{CO} + \text{H}_2 \\
\text{Net:} & \quad \text{H}_2\text{O} + \text{C}_2\text{H}_2 + \text{H} \rightarrow \text{CO} + \text{CH}_3 + \text{H}_2
\end{align*}
\]
Fig. 5.10 (top) The important reaction pathways for oxygen photochemistry in Saturn's stratosphere. The symbol $h$ corresponds to an ultraviolet photon. Figure is from Moses et al. (2000b). (bottom) H$_2$O, CO, CO$_2$ mole fraction profiles from Ollivier et al. (2000). These profiles were obtained with an external flux of water alone ($10^7$ molecules cm$^{-2}$ s$^{-1}$) and tropospheric CO (with a mole fraction equal to $10^{-9}$). The square and the triangle correspond, respectively, to the water and carbon dioxide mole fraction found by Feuchtgruber et al. (1997), and the diamond-shaped point corresponds to distribution CO inferred by Noll and Larson (1991).

and

\[
\begin{align*}
    \text{H}_2\text{O} + h & \rightarrow \text{H} + \text{OH} \\
    \text{OH} + \text{C}_2\text{H}_2 + \text{M} & \rightarrow \text{C}_2\text{H}_3\text{OH} + \text{M} \\
    \text{C}_2\text{H}_3\text{OH} & \rightarrow \text{CH}_3\text{CO} \\
    \text{CH}_3\text{CO} + \text{H} & \rightarrow \text{H}_2\text{CCO} + \text{H}_2 \\
    \text{H}_2\text{CCO} + h & \rightarrow ^1\text{CH}_2 + \text{CO}
\end{align*}
\]

Net: $\text{H}_2\text{O} + \text{C}_2\text{H}_2 \rightarrow \text{CO} + ^1\text{CH}_2 + \text{H}_2$.

Carbon monoxide can in turn be converted to CO$_2$ through the reaction of CO + OH $\rightarrow$ CO$_2$ + H. The CO$_2$ photolyzes back to CO + O($^1\text{D}$) or CO + O. The O($^1\text{D}$) atoms react with H$_2$ to form OH and eventually water, whereas the O can react with CH$_3$ or unsaturated hydrocarbons to eventually reform CO. Other hydrocarbons like H$_2$CO, CH$_3$OH, and CH$_3$CHO are formed in the models, but not in currently observable quantities. Water can diffuse down through Saturn's stratosphere and eventually condense in the lower stratosphere. The Ollivier et al. (2000) model differs from that of Moses.
et al. (2000b) in that the interesting oxygen photochemistry proceeds through reaction of \( O + CH_3 \) or \( O + \) unsaturated hydrocarbons rather than through addition reactions of \( OH \) with unsaturated hydrocarbons. These differences have some impact on the final product abundances and the inferred influx rates from the two models.

As discussed in Section 5.2.4, most observations of CO to date have not allowed the discrimination between an internal or external source of CO on Saturn. Ollivier et al. (2000) favor an internal source based on the failure of their external-source models to reproduce the CO abundance derived by Noll and Larson (1991). Moses et al. (2000b), on the other hand, were able to produce the observed CO column abundance from external-source models under certain conditions, although they favor a situation in which CO has both and internal and external source. Both Ollivier et al. (2000) and Moses et al. (2000b) show how the models are sensitive to the assumed flux of the external oxygen and use model-data comparisons to constrain the external flux; they also discuss implications regarding the source of the external oxygen (see also Feuchtgruber et al. 1997, 1999). Ollivier et al. (2000) do not weigh in with a favored source, whereas Moses et al. (2000b) favor interplanetary dust or ring-particle diffusion as the source of the external oxygen. However, this conclusion came into effect before active venting on Enceladus was discovered by Cassini (e.g., Porco et al. 2006)—Enceladus may be a major supplier of water and oxygen species to Saturn—and before the recent 345 HZ observations of Cavalié et al. (2009) that suggest an external source of CO from a large cometary impact 200–300 years ago.

### 5.3.4 Auroral Chemistry

As on Jupiter (e.g., Waite et al. 1983; Perry et al. 1999; Wong et al. 2000, 2003; Friedson et al. 2002), auroral ion chemistry and subsequent neutral chemistry has the potential for affecting the global distribution and abundance of stratospheric constituents on Saturn. Models of auroral chemistry have not yet been presented for Saturn, but the Jupiter studies discussed above, as well as the obvious importance of ion chemistry in producing \( C_2H_6 \) on Titan (e.g., Waite et al. 2005, 2007; Vuitton 2007, 2008; Imanaka and Smith 2007), suggest that auroral ion chemistry may be important for forming benzene and polycyclic aromatic hydrocarbons (PAHs) on Saturn. Observations such as those presented by Gérard et al. (1995) demonstrate the possible link between the aurora and polar haze, most likely due to the formation of complex hydrocarbons. The overall effect of auroral chemistry on other molecules like \( C_2H_2 \) and \( C_2H_4 \) is unknown, although the Jupiter models of Wong et al. (2000, 2003) show an increase in the production rate of both molecules, which could affect the observed meridional distribution of \( C_2H_2 \) and \( C_2H_6 \), but which is not likely the culprit in explaining the disparate observed meridional distribution of the two species. Given the potential importance of auroral chemistry on Saturn, this topic deserves more study, especially given the high-quality observational constraints that can likely be supplied by the Cassini/CIRS and UVIS instruments.

### 5.4 Summary and Conclusions

Our understanding of the composition and chemistry of Saturn’s atmosphere has improved widely since the Voyager flybys. The ever-increasing sensitivity and resolution (in the spatial and spectral dimension) of Earth-based observations have provided a wealth of new information on the Kronian atmosphere. The Cassini spacecraft is now participating in this ongoing effort, but its results are still in their infancy.

In terms of global composition, Cassini measured the carbon abundance and the carbon isotopic ratio with a precision that will not be challenged for several years. Saturn’s carbon enrichment relative to the solar composition will vary more certainly in response to changes in the solar composition than in the Kronian composition. In contrast, the abundance of helium is still a subject of continuing analyses. The inversion of the collision-induced hydrogen continuum observed by Cassini in the far infrared yields different \([He]/[H_2] \) ratios depending on whether the inversion is carried out including the radio occultation profiles or whether both the temperature and the composition are inferred from the far-infrared spectrum only. This discrepancy suggests that unknown systematic uncertainties still affect the data analysis. Of particular concern is the sensitivity of the inversion to the wind field. The elemental composition of nitrogen and sulfur has not been constrained from Cassini data yet. Our knowledge of these two elements still relies on ground-based centimeter observations that are difficult to calibrate and to analyse. However, there is some hope that Cassini radio science can provide new estimates in the future. Pre-Cassini observations yielded low D/H ratios in comparison with the Jupiter deuterium abundance or with the early solar abundance. The first Cassini observations have yielded even smaller values, which do not fit easily in the Solar System picture, although the error bars are still large.

Below the ammonia cloud level, at 1–5 bars, several molecular species have been measured to tremendously exceed their thermodynamic equilibrium abundances. These molecules, phosphine, germane and arsine, which are thermodynamically stable in the warm interior of the planet, are transported more rapidly to the shallow atmosphere than they are destroyed by chemical reactions. Their measurement
gives clues to the vertical mixing timescales and to the elemental composition of the deep interior. Cassini/VIMS is in position to measure the meridional variation in the abundance of these elements that would reveal differential vertical mixing, a constraint of great importance for dynamical models of Saturn. However, the kinetics and rate coefficients of the interconversion mechanisms are still preventing reliable estimates of the deep abundance on Saturn, and/or the mixing timescale, from being obtained using this method. Experimental data are greatly needed here. Simultaneous measurements of aerosol opacity at ultraviolet wavelengths and species profiles would also help separate out the effects due to mixing versus the effects due to aerosol shielding.

In the upper troposphere, above the cloud tops, Cassini/CIRS has measured for the first time the meridional variation in phosphine abundance. In this atmospheric region, \( \text{PH}_3 \) is photolyzed along with \( \text{NH}_3 \), and any variation in abundance can trace the intensity of vertical and horizontal mixing. This measurement will hence help to constrain the dynamics above the cloud level. Such variations could also be linked with variations in the visible cloud colors to understand whether \( \text{PH}_3 \) and \( \text{NH}_3 \) photolysis does produce some of the chromophores that determine Saturn’s visible aspect. However, to obtain quantitative constraints on the dynamics, the tropospheric photochemistry on Saturn would need to be better understood than it is presently, due to a critical lack of reaction rate coefficients for the appropriate phosphorus and nitrogen reactions under reducing conditions. It is hoped that new Cassini and Earth-based observations will generate a resurgence in interest in tropospheric photochemistry on Saturn.

In the stratosphere, several hydrocarbons have been detected (\( \text{CH}_3 \), \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_4 \), \( \text{C}_2\text{H}_6 \), \( \text{CH}_3\text{C}_2\text{H} \), \( \text{C}_2\text{H}_6 \), \( \text{C}_3\text{H}_2 \), \( \text{C}_3\text{H}_6 \)) from Earth-based spectroscopy. These species are critical in controlling the stratospheric temperature. One-dimensional photochemical models are able to reproduce the observed abundance of ethane, acetylene, and several of the other observed stratospheric constituents, but have more troubles in predicting the abundance of some of the heavier hydrocarbons. Moreover, models that best reproduce Saturn’s hydrocarbon photochemistry are often unable to reproduce the observed hydrocarbon abundances on the three other Giant Planets. The problem lies partly in a lack of appropriate laboratory data at the conditions (temperature, pressures) relevant to Saturn’s stratosphere. Data on photolysis quantum yields, branching ratios, chemical pathways and kinetics are greatly needed. It must also be understood how dynamics interplays with the photochemistry. Ground-based and Cassini measurements have started revealing the meridional profiles in hydrocarbon abundance, while one-dimensional seasonal models and two-dimensional models are being developed. Currently the models do not succeed in reproducing the observed meridional profiles. These models now need to reproduce more accurately the dynamics, especially the meridional transport and large-scale circulation. The models would be better constrained by the measurements of the vertical and meridional distributions of large variety of hydrocarbon species. Hopefully, the Cassini equinox and solstice missions will provide insights into the seasonal variations of the hydrocarbons abundances. Observations that monitor the location of the methane homopause, and its temporal and spatial variations would also provide critical clues to understanding hydrocarbon photochemistry. Cassini CIRS limb observations and VIMS and VIMS occultations are still expected to deliver much new information on this problem.

In the upper stratosphere, Saturn is receiving an external flux of oxygenated species. A recent study supports a dual source, both from a cometary impact and from a continuous flux, conceivably from the oxygen-rich bodies in Saturn’s system. The magnitude of both sources should be better constrained in the near future by new sub-millimetric observations.

If great results have been already obtained, the Cassini spacecraft still promises to deliver much more. The unprecedented spatial resolution and possible duration over almost half a Kronian year should provide a wealth of useful information to constrain the chemistry and its relation with the dynamics in Saturn’s atmosphere. The supporting ground-based observations, with their unchallenged sensitivity and spectral resolution, will also contribute to our study of Saturn. Cassini, with its spectral, spatial and temporal coverage, is a unique endeavor to study in depth a Giant Planet.

References


