Seasonal Variations of Hydrocarbons in Saturn’s Stratosphere

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1 Introduction

The presence of a rich photochemistry on the outer planets has been predicted for some time. Cadle (1962) first, qualitatively, discussed the production of more complex hydrocarbons, such as acetylene ($C_2H_2$) and ethane ($C_2H_6$) from ultraviolet photolysis of methane in the upper Jovian atmosphere. Further studies provided estimates of the reaction rates and the resulting vertical density profiles of photochemical products (for example, Strobel (1969)). The detection of acetylene and ethane in Jupiter’s upper atmosphere provided conclusive evidence of the presence of such processes (Ridgway, 1974). Detection of these species in Saturn’s atmosphere quickly followed.

Investigation of Saturn’s mid-infrared spectrum revealed a strong emission peak at approximately 12 μm (Gillett & Forrest, 1974). This was suggested to be the result of ethane emission (from the $v_9$ band centred at 12.2 μm, Table 1) above a temperature inversion layer. The observation of brightening at this wavelength in scanning from the equator to the limb confirmed the presence of a temperature inversion (Tokunaga et al., 1975). This and the agreement of features in the highly spectral resolved observations with theoretical line positions confirmed the presence of ethane on Saturn. Detection of acetylene soon followed that of ethane. Initially, acetylene was detected through its absorption bands at 0.18 μm in the ultraviolet using the IUE (International Ultraviolet Explorer, (Lane et al., 1978; Moos & Clarke, 1979). Subsequent infrared observations, using the IRTF (Infrared Telescope Facility), likewise determined the presence of acetylene through emission at its $v_5$ feature (Table 1).

Ethane and acetylene are highly stable and are readily observed due to their strong emission features. Saturn’s photochemistry, however, produces several other, higher order hydrocarbons such as propane ($C_3H_8$), methylacetylene or propyne ($CH_3C_2H$), diacetylene ($C_4H_2$) and even benzene ($C_6H_6$). However, their infrared features are comparably weaker and therefore detection of them in spectra has only been possible recently with greater instrument sensitivity and spectral resolution. Only in 1997 did ISO-SWS observations (the Short Wave Spectrometer aboard the Infrared Space Observatory (de Graauw et al., 1996)) provide detection of $CH_3C_2H$ and $C_4H_2$ using their features at 15.8 μm and 15.9 μm respectively (de Graauw et al., 1997). In particular, propane was only detected in Saturn’s atmosphere in 2006 using NASA-IRTF (Infrared Telescope Facility) observations taken in 2002 (Greathouse et al., 2006). Only with the high spectral resolution ($\lambda/\delta\lambda = 10^6$) provided by IRTF’s TEXES instrument (an echelle spectrometer, Lacy et al. (2002)) was propane’s weak feature at 13.4 μm identified and distinguished from the neighbouring, dominant acetylene feature.

Following their initial detection, hydrocarbons in Saturn’s atmosphere were studied from a variety of infrared instruments, including the ISO (Infrared Space Observatory), CFHT (Canada-France-Hawaii telescope) and IRTF-TEXES (an echelle spectrometer on the Infrared Telescope Facility). From these earlier observations, a brightening of ethane’s 12 μm feature towards Saturn’s summer pole was observed.
Species | Feature | Band centre
<table>
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<tr>
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<tbody>
<tr>
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<tr>
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<td>$\nu_5$</td>
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<td>C$_4$H$_2$</td>
<td>$\nu_8$</td>
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</tr>
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**Table 1:** Summary of the (approximate) positions (in both wavelength ($\mu$m) and wavenumber ($\text{cm}^{-1}$)) of hydrocarbon features in the infrared.

which could not be explained by limb brightening alone. It remained a challenge to determine whether this was a result of an enhanced thermal structure (since a hotter atmosphere is more radiant) and/or an enhancement of the emitting species - ethane. Eventually, Greathouse et al. (2005) disentangled these two contributing factors and determined that as well as the obvious temperature enhancement towards the Summer pole, there was indeed twice as much ethane near the pole than at the equator in the lower stratosphere (2.3 mbar). This behaviour was likewise determined from Cassini-CIRS observations, where the vertical temperature profile was initially retrieved, followed by retrieval of the vertical profile of ethane and acetylene (Howett et al., 2007; Hesman et al., 2009; Guerlet et al., 2009).

This latitudinal enhancement of ethane towards the summer pole is in disagreement with photochemical modelling of Saturn’s stratosphere. Owing to ethane and acetylene’s long photochemical lifetimes compared with the length of one Saturn year, their meridional profiles are expected to match the meridional profile of the annually-averaged solar insolation (Moses et al., 2000a). This deviation is concluded to be a result of a meridional wind system, transporting hydrocarbons from the equator the summer pole (Howett et al., 2007; Hesman et al., 2009; Guerlet et al., 2009). In order to explain only a poleward enhancement of ethane, this must occur on a timescale longer than acetylene’s photochemical lifetime, but shorter than ethane’s photochemical lifetime (~3 years and ~300 years at 1 mbar respectively (Moses & Greathouse, 2005)).

These conclusions are drawn from Cassini-CIRS observations obtained in the prime mission (2004 to 2008), therefore, studying Saturn’s atmosphere shortly after southern summer solstice in 2002. With the vernal equinox in 2009, Saturn’s northern hemisphere is now in ‘spring’ with northern summer solstice in 2017. The seasonal response of Saturn’s photochemistry with the transition to spring in the northern hemisphere and ‘autumn’ in the southern hemisphere remains to be determined. Saturn has an obliquity of ~27° and therefore experiences seasons much in the same way as Earth, though on a longer timescale with 1 Saturn year corresponding to approximately 30 Earth years. The irradiance of ultraviolet photons
at a particular latitude will vary with season and therefore the photochemistry is expected to exhibit a response with season. Photochemical models show a winter-summer contrast in ethane’s abundance at 1 μbar of an order of magnitude at high latitudes (Moses & Greathouse, 2005).

A review of the current understanding of Saturn’s photochemistry forms the first part of this report. The chemical reaction scheme, as included in photochemical models of Saturn, is detailed in Section 2. The development of modelling of Saturn’s photochemistry and the results of the most recent, seasonal models are discussed in Section 3. A review of the observations of Saturnian hydrocarbons is conducted in Section 4 with detail given to the most recent Cassini-CIRS studies. In light of the current understanding of Saturn’s photochemistry, the need for studying its seasonal response is justified in the proposal in Section 5.

The work conducted towards this research goal, thus far, is discussed in the remainder of this report. The retrieval algorithm used to determine the vertical temperature structure and subsequently the vertical hydrocarbon profiles is described in Section 6. This algorithm is then tested in Section 7 to demonstrate its accuracy in retrieving these profiles. The methods used in the extraction of Cassini-CIRS data are discussed in Section 8. This section also analyses the different types of Cassini-CIRS observations to determine which gives the best latitudinal and temporal coverage necessary for this study. The results of a preliminary analysis of Cassini-CIRS MIRMAP observations are highlighted in Section 9. A preliminary study of the practicality of retrieving ethane from its 7 μm feature using new line data is discussed in Section 10. The final section outlines a plan of the work to be undertaken in the remainder of this project.
2 Photochemical and Chemical Reactions

In the atmospheres of the outer planets, methane is produced in a chemical equilibrium reaction by hydrogenation of carbon monoxide, as shown in Equation 1 (Irwin, 2003).

\[
\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \tag{1}
\]

Production of methane in this reaction is favoured at temperatures below 1000 K (Irwin, 2003) therefore corresponding mostly to the deep, unobservable atmosphere of Saturn. Convective overturning and eddy diffusion transport the methane to the stratosphere where the atmosphere is optically thin to ultraviolet radiation (Ollivier et al., 1998). Production of hydrocarbons with more than one carbon atom proceeds by a combination of photodissociative and chemical processes. It is predicted that 42% of methane in the upper atmosphere is eventually recycled while 57% is permanently converted to C\textsubscript{2} compounds with less than 1% converted permanently to C\textsubscript{3} and C\textsubscript{4} compounds (Moses et al., 2000a). As shown in Figure 1, there are several different reaction paths to produce a certain chemical species, in particular for higher order species. The dominant reaction paths of acetylene and ethane, as described in (Moses et al., 2000a), are summarised below.

2.1 Production of the methyl radical

Figure 1 highlights the importance of the photolysis of methane in producing the methyl radical in initiating the hydrocarbon photochemistry production, as outlined below.

\[
\text{CH}_4 + h\nu \rightarrow \text{CH}_3 + \text{H} \tag{2}
\]

Methyl is also produced through recombination of the \text{CH}_2 radical and atomic hydrogen with the aid of a catalyst.

\[
\text{CH}_4 + h\nu \rightarrow \text{CH}_2 + \text{H}_2 \tag{3}
\]
\[
\text{CH}_2 + \text{H} + \text{M} \rightarrow \text{CH}_3 + \text{M} \tag{4}
\]

where ‘\(h\nu\)’ denotes an ultraviolet photon and M denotes a catalyst. Different wavelength ranges activate different photolysis reactions, but are mostly in the range from 0.067 \(\mu\text{m}\) to 0.3 \(\mu\text{m}\) with the most energetic, short wavelength photons initiating photolysis of smaller hydrocarbons (due to their smaller cross sections).
Figure 1: The chemical and photochemical reaction schemes for hydrocarbons (up to C$_4$ compounds) as shown in Figure 3 of Moses et al. (2000a). 'hv' signifies an ultraviolet photon. Radical species are outlined as ovals while stable compounds are outlined as rectangles.

2.2 Production of Ethane

Following the methyl production outlined above, production of ethane proceeds mostly by methyl-methyl recombination, with the aid of a catalyst (Reaction 5).

$$2\text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}$$ (5)

This is shown to have an approximately constant reaction rate with altitude from $\sim$10 mbar to $10^{-3}$ mbar of $\sim$10 cm$^{-3}$ s$^{-1}$ with a distinct maximum of $\sim$100 cm$^{-3}$ s$^{-1}$ at $\sim$10$^{-4}$ mbar (Moses et al., 2000a). A second reaction pathway is also present, as outlined below, but only in the upper stratosphere with reaction 6 restricted to the $10^{-3} \rightarrow 10^{-5}$ mbar levels (Moses et al., 2000a).

$$\text{CH}_4 + \text{hv} \rightarrow \text{CH} + \text{H}_2 + \text{H}$$ (6)

$$\text{CH} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \text{H} + \text{M} \rightarrow \text{C}_2\text{H}_5 + \text{M}$$ (7)

$$\text{C}_2\text{H}_5 + \text{H} + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}$$ (8)

Reactions 5 and 7 account for 85% of the total production of C$_2$ compounds. The remaining 15% arise
from photochemical destruction of C\textsubscript{3} and C\textsubscript{4} compounds (Moses et al., 2000a).

2.3 Production of Acetylene

Both photochemical destruction of ethane (Reaction 9) and its reaction with the C\textsubscript{2}H and CH radicals (Reactions 10 and 11 respectively) are believed to account for most of the production of acetylene. Photolysis of ethene (C\textsubscript{2}H\textsubscript{4}) is also considered a pathway in acetylene production (Reaction 12).

\[
\text{C}_2\text{H}_6 + \text{hv} \rightarrow \text{C}_2\text{H}_2 + 2\text{H}_2 \quad (9)
\]

\[
\text{C}_2\text{H}_6 + \text{C}_2\text{H} \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_5 \quad (10)
\]

\[
\text{C}_2\text{H}_6 + \text{CH} \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3 \quad (11)
\]

\[
\text{C}_2\text{H}_4 + \text{hv} \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 \quad (12)
\]

As discussed by Guerlet et al. (2009) and also Moses et al. (2007), this shows that ethane and acetylene are photochemically coupled since photolysis and reaction of the C\textsubscript{2}H and CH radicals onto ethane describe the efficient pathways to acetylene production. This places the majority of C\textsubscript{2}H\textsubscript{2} production in the upper atmosphere where ethane is the most unstable (Figure 4).

2.4 Vertical Transport

Production of these hydrocarbons via these processes tends to dominate in the upper stratosphere (at pressures less than 0.1 mbar). Eddy and molecular diffusion then transfers the photochemical species to the lower stratosphere on a timescale much shorter than the photochemical lifetime (Ollivier et al., 2000b). Eddy diffusion describes efficient mixing due to planetary waves and the breaking of vertically propagating waves (Sandel et al., 1982). Molecular diffusion describes the response of the atmosphere to maintain a density-altitude profile consistent with the scale height of each gas constituent (H_i = kT/M_i g). The homopause marks the height where the relative importance of these two diffusion processes are equal and varies depending on the gas constituent in question (Moses et al., 2000a). In Saturn’s atmosphere, the homopause of methane is at ~10^-5 mbar (Fouchet et al., 2003; Moses et al., 2000a) therefore describing the dominance of molecular diffusion above this height and the mixing below. The position of the homopause for ethane and acetylene will differ from that of methane, but qualitatively this description is accurate. Vertical transport of photochemical products to deeper in the atmosphere will initially proceed by molecular diffusion with mixing taking over in the lower stratosphere.
3 Photochemical Models of Saturn’s Stratosphere

Following their initial detection on Saturn, hydrocarbons on Saturn were studied from a variety of space-borne and ground-based observations. The availability of quantitative measurements of the abundances of hydrocarbons prompted the need to model the photochemical production in Saturn’s atmosphere so as to try and reproduce such values.

3.1 Early photochemical models

The earliest photochemical models were one dimensional (a function of height only) and steady state. A photochemical model scheme was developed for Jupiter’s upper atmosphere (Gladstone et al., 1996). The model determines production and loss rates of a photochemical species at all altitudes and then solves the vertical continuity equation accounting for a vertical flux due to eddy and molecular diffusion. The solution is steady state and therefore the results represent diurnally averaged values (since sunlight is switched on and off as the planet rotates through a Saturn day).

This photochemical model was adapted for Saturn’s atmosphere at 30°N (Moses et al., 2000a). They combine temperature profiles obtained from the Voyager 2 RSS ingress observation (1000 to 1 mbar) (Lindal et al., 1985) and the 28 Sgr occultation (1 to 10⁻⁵ mbar) (Hubbard et al., 1997). Again, the solar insolation is averaged over the solar cycle. Further additions to this model are inclusions of a downward atomic hydrogen flux from the thermosphere/ionosphere. Atomic hydrogen is highly efficient in breaking of the carbon-carbon bonds and therefore is important in calculating the destruction rates of species high in the stratosphere. Their derived vertical profiles of the abundances of CH₄, C₂H₂, C₂H₄, C₂H₆ and CH₃ reproduce the abundances inferred from UVS observations (29.5°N in 1981) (Smith et al., 1983) and ISO (Infrared Space Observatory) globally-averaged 1996 observations (de Graauw et al., 1997).

3.2 Time-dependent, two-dimensional models

The one-dimensional, steady state nature of the earliest photochemical models were appropriate at the time given the way in which observations to which they were compared were highly spatially-averaged or restricted to an equatorial latitude band. However, with newer spatially-resolved observations (see Section 4) and with the wealth of data the arrival of Cassini at Saturn would provide, there was a need to determine the latitudinal and temporal dependence of the stratospheric photochemistry (Moses & Greathouse, 2005).

As discussed in Moses & Greathouse (2005), the following factors will introduce temporal variations in
Obliquity $\sim 27^\circ$: Saturn experiences seasonal variations in the same way as the Earth does (obliquity of $\sim 24^\circ$) with 1 Saturn year = 30 Earth years. A given latitude will experience a variation of ultraviolet irradiance with season.

Orbital Eccentricity of $\sim 0.055$: Saturn is approximately 1 AU closer to the Sun at perihelion than at aphelion. Perihelion occurs simultaneously with southern summer solstice which induces a hemispheric asymmetry in favour of the southern hemisphere.

Solar cycle: The incident ultraviolet solar flux will vary across the Sun’s 11 year solar cycle. The E10.7 index (the integrated ‘extreme ultraviolet’ solar flux from 1 to 105 nm) historically varies by up to two orders of magnitude between solar maxima and minima (Tobiska et al., 2000).

Ring shadowing: Latitudes from $20^\circ$S to $20^\circ$N will move in and out of the shadow of Saturn’s rings throughout the Saturn year, switching off the sunlight and therefore hydrocarbon photolysis.

Moses & Greathouse (2005) discuss the extension of the photochemical model to two dimensions (altitude and latitude) and the inclusion of the above temporal factors. The results are discussed below.

The predicted response of the hydrocarbon photochemistry to seasonal changes (alone) is most significant at high latitudes, high in the atmosphere. At $\sim 10^{-3}$ mbar, variations in the hydrocarbon abundances at equatorial latitudes are of the order of unity with changing seasons (for example $8^\circ$S) while variations by as much as an order of magnitude are apparent at higher latitudes ($59^\circ$S), as shown in Figure 3.
Figure 3: The predicted temporal variations of the mixing ratios of ethane (thick solid line) and acetylene (thin solid line) at $3 \times 10^{-3}$ mbar for two consecutive Saturn years at $8^\circ$S, $22^\circ$S, $59^\circ$S and $24^\circ$N (Figure 5 of Moses & Greathouse (2005)). Times of aphelion (triangles), perihelion (stars) and periods of solar maxima and ring shadowing are also shown. Dotted lines indicate the season in increments in solar longitude of 90° starting from $L_s = 90^\circ$.

At $59^\circ$S, the maximum in the hydrocarbon abundances is predicted to occur at almost exactly southern summer solstice ($L_s = 270^\circ$). However, minima in the hydrocarbon abundances at the same latitude do not occur at $L_s = 90^\circ$ (southern winter) as symmetry would suggest, but almost 0.2 Saturn years (or 4.5 Earth years) later. Differences in the photochemical loss and production timescales cannot account for this since they are approximately equal at these altitudes (Figure 4). Both southern winters (~1958 and ~1988) were accompanied by a period of a maxima in the solar cycle, a brief period of ring shadowing as well as aphelion of Saturn’s orbit. It is concluded that the solar maxima delays the decay of the photochemistry as the Southern Hemisphere approaches winter and the brief period of ring shadowing together with the occurrence of aphelion extends photochemical winter.

Further response of the photochemistry to variations in the ultraviolet flux due to the solar cycle are observed as perturbations to the general seasonal profile, for example, during the approach to winter at $24^\circ$N in ~1970. Ring shadowing also induces sizeable variations at lower latitudes, for example at $8^\circ$S during Saturn’s southern spring in ~1995 and particularly at latitudes of ~20° in both the southern and
northern hemisphere which spend the longest duration in ring darkness.

At such altitudes ($10^{-3}$ mbar), the photochemistry responds relatively quickly to temporal changes in the ultraviolet insolation. This is due to the relatively short photochemical production and loss timescales. Newly produced hydrocarbons are also rapidly transported downwards to about 0.01 mbar due to shorter diffusion timescales. The strongest seasonal variations are therefore exhibited at such altitudes. Saturn’s atmosphere strongly Rayleigh scatters in the ultraviolet and therefore photochemical production timescales are much longer in the lower stratosphere (Figure 4). Similarly, vertical transport deeper in the atmosphere is much slower - the vertical diffusion timescale is approximately a Saturn year at 1 mbar. This introduces a ‘phase lag’ deeper in the atmosphere where there is a delay in the response of the photochemistry to seasonal changes due to these longer timescales. Moses & Greathouse (2005) derived vertical mixing ratio profiles of acetylene and ethane at mid-latitudes for different seasons. For acetylene and ethane, the vertical profiles for different seasons tend to the same profile below 0.1 mbar - there is no predicted seasonal changes in the ethane and acetylene mixing ratios below this altitude. The meridional profile of both acetylene and ethane at this altitude is expected to match the profile of annually-averaged ultraviolet insolation (Figure 2).

This model does not account for latitudinal or temporal variations in the vertical temperature structure or diffusion coefficients, both of which will affect the vertical profiles of abundances of hydrocarbons.
Reaction rates are temperature dependent and therefore differences in the photochemistry would be expected at warmer or cooler latitudes. The temperature profile determines the scale height which affects the molecular and eddy diffusion. The authors tested the sensitivity of the photochemistry at different latitudes, adopting temperature profiles of 29°S and 81°S measured by IRTF-TEXES during southern summer solstice (Greathouse et al., 2005). These temperature profiles are approximately 10 K and 20 K warmer in the ionosphere than the profile used in their photochemical model. The vertical profiles of both acetylene and ethane remain mostly unchanged. They conclude that variations in the solar flux with latitude impose the largest difference in the photochemistry. The authors have since developed a radiative seasonal climate model to determine the seasonal variations of the stratospheric temperature with latitude (Greathouse et al., 2010). Their photochemical model will likely be extended to include the latitudinal variations in stratospheric temperature in future work.
4 Observations of Hydrocarbons in Saturn’s Atmosphere

4.1 Poleward brightening of Ethane Emission

Following the initial detection of ethane on Saturn, several different studies confirmed the observation of brightening at 12 µm towards Saturn’s Southern Pole (for example, Gillett & Orton (1975); Rieke (1975)). Limb brightening alone could not account for this behaviour since only the southern limb showed brightening. This suggested a south-poleward increase in the temperature (perhaps due to the temperature inversion occurring deeper in the atmosphere) and/or an increase in the concentration of absorbing ethane (which subsequently emits at ~12.2 µm). A stronger temperature inversion was conceivable given this behaviour was observed close to southern summer solstice.

It remained a challenge to differentiate between enhanced emission due to thermal effects and the effect of enhanced ethane abundance. Tokunaga et al. (1978) performed north-south disk scans at 12.2 µm (centred on the ethane ν₉ band) as well as scans at 17.8 µm, 19.7 µm and 22.7 µm. The latter wavelengths cover the pressure-induced absorption spectrum of molecular hydrogen, providing sensitivity deeper in the atmosphere. Assuming that molecular hydrogen is both vertically and meridionally well-mixed, any south-poleward enhancement of emission from hydrogen will suggest thermal enhancement at a given pressure level. Indeed, the north-south disk scans at these three wavelengths yielded: a strong darkening north of the equator; a slight darkening south of the equator; an emission enhancement at all three wavelengths towards the southern limb, most pronounced at 17.8 µm. This concluded the existence of a stronger temperature inversion towards the South Pole. Similar studies were presented in Tokunaga et al. (1979) & Sinton et al. (1980) and conclusion of a thermal enhancement towards the South Pole is made, but none of these studies rule out the possibility of enhancement of ethane’s mole fraction.

Ollivier et al. (2000a) initially attempted to determine the latitudinal variation of hydrocarbon abundances. CFHT (Canada-France-Hawaii Telescope) observations made in 1992 (during Saturn’s Northern Summer Solstice) of northern hemisphere latitudes (17°N, 32°N, 42°N, 52°N & 62°N) were analysed. Observations were modelled by varying the vertical temperature profile or hydrocarbon mole fraction profile to provide the best spectral fit. Assuming a vertically-constant temperature shift in matching the poleward thermal profile change OR varying the vertical abundance profiles of C₂H₂ and C₂H₆ by a scale factor, they find that 6 and 5.5 times as much C₂H₂ and C₂H₆ is needed to match the observations at 62°N. This analysis, however, fails to disentangle the variation of the thermal profile with the hydrocarbon abundances and the author notes that there is a degeneracy of results which would match the observations.

Greathouse et al. (2005) first disentangled the combined effects of temperature and abundance of an emitting molecule on the observed molecular emission. Observations of Saturn, around Southern Summer
Solstice, at several latitudes from 10°N to 80°S were made using the IRTF-TEXES instrument. Initially, they determined the stratospheric temperature profile by fitting synthetic spectra to the \( \nu_4 \) methane band. They assumed a vertical methane profile inferred from stellar ultraviolet occultations (Festou et al., 1981; Smith et al., 1983) which describes a roughly constant abundance with height in the lower stratosphere, decaying above the methane homopause. Acetylene was shown to decay from the equator to the Summer pole at both 1.16 and 0.12 mbar by a factor of 2.7 and 2.3 respectively, matching the shape of the annually-averaged ultraviolet insolation (Figure 2). Ethane, however, is shown to be almost twice as abundant at -80°S compared to the equator at 2.3 mbar. This poleward enhancement was likewise observed by Cassini-CIRS observations.

### 4.2 Hydrocarbon Abundances from Cassini-CIRS

The arrival of Cassini at Saturn in 2004 (shortly after Summer Solstice in the southern hemisphere) provided the opportunity to study Saturn’s atmosphere at an unprecedented spatial resolution and instrument sensitivity. The dedicated orbit of the Cassini spacecraft around Saturn provides highly spatially-resolved observations of Saturn (as well as its satellites) allowing the thermal structure and composition to be determined temporally and spatially (Flasar, 2004). The CIRS (Composite Infrared Spectrometer) instrument (Flasar, 2004) aboard this spacecraft provides observations from infrared to sub-millimetre wavelengths (10 cm\(^{-1}\) to 1400 cm\(^{-1}\) or 1 mm to 7 \(\upmu\)m). This wavelength range is divided into three focal planes - FP1 (far-infrared) from 10cm\(^{-1}\) to 600cm\(^{-1}\) and FP3 from 600cm\(^{-1}\) to 1100cm\(^{-1}\) and FP4 from 1100cm\(^{-1}\) to 1400cm\(^{-1}\) respectively. These wavelengths observe the vibrational and ro-vibrational modes of molecules in Saturn’s atmosphere at temperatures typically in the range from 50 to 220 K. Observations are available at a variety of spectral resolutions - ‘COMPSIT’ (0.5 cm\(^{-1}\)), ‘MIRMAP’ (2.5 cm\(^{-1}\)) and ‘FIRMAP’ (13.5 cm\(^{-1}\)).

Table 2 summarises the studies of hydrocarbons on Saturn using Cassini-CIRS data. The results of these studies are discussed below.

#### 4.2.1 Howett et al. (2007)

Howett et al. (2007) determined the hydrocarbon abundances in the Southern (Summer) hemisphere from the earliest Cassini-CIRS datasets. The highest resolution data (COMPSIT, 0.5 cm\(^{-1}\)) were used in this study. Retrieval of the atmospheric profiles was conducted using the NEMESIS (Non-linear Optimal Estimator for Multivariate Analysis) retrieval tool (Irwin et al., 2008). The retrieval algorithm was conducted as follows.

1. Retrieval of the stratospheric temperature by fitting the \( \nu_4 \) methane band (in FP4 spectra from
Table 2: Summary of previous studies retrieving Saturnian hydrocarbons using Cassini-CIRS observations.

<table>
<thead>
<tr>
<th>Study</th>
<th>Resolution</th>
<th>Geometry</th>
<th>Latitudes</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Howett C. et al. (2007)</td>
<td>COMPSIT</td>
<td>Nadir</td>
<td>~10°S to ~70°S</td>
<td>July 2004 - November 2004</td>
</tr>
<tr>
<td>Hesman B. E. et al. (2009)</td>
<td>MIRMAP</td>
<td>Nadir/Limb</td>
<td>0° to 90°S</td>
<td>2006</td>
</tr>
<tr>
<td>Guerlet S. et al. (2009)</td>
<td>FIRMAP</td>
<td>Limb</td>
<td>~70°N to ~80°S</td>
<td>2005 - 2008</td>
</tr>
</tbody>
</table>

1250 cm\(^{-1}\) to 1350 cm\(^{-1}\)).

2. Retrieval of the tropospheric temperature structure by fitting the H\(_2\)-H\(_2\) and H\(_2\)-He collision-induced spectrum from 600 cm\(^{-1}\) to 680 cm\(^{-1}\) (FP3), using the previous stratospheric retrieval as an *a priori*.

3. Simultaneous retrieval of the vertical profiles of acetylene and ethane volume mixing ratio using their \(v_5\) and \(v_9\) bands. Photochemical models of stratospheric photochemistry were used as *a priori*.

With the nadir viewing geometry of the observations used in this study, the retrieved abundances of C\(_2\)H\(_2\) and C\(_2\)H\(_6\) are studied at 2 mbar where the measurement sensitivity and therefore confidence in the results is greatest.

The retrieved acetylene profile shows an increase in abundance from \(~0.18\) ppm (parts-per-million) at 10°S to \(~0.25\) ppm at 30°S with a subsequent poleward decrease to \(~0.12\) ppm at 65°S. Error bars on the abundances range from 0.01 ppm to 0.02 ppm, therefore, this trend is statistically significant. The trend poleward of 30°S reproduces the trend of the yearly-averaged solar insolation (Figure 2) as expected due to acetylene’s long photochemical lifetime compared to the Saturnian year at this altitude.

Given that ethane has an even longer lifetime than acetylene at this altitude (\(~700\) years (Figure 4), its abundance is likewise expected to follow a profile matching the yearly-averaged insolation with latitude. Yet, there is a general increase of ethane from 9 ppm near the equator to 11 ppm at higher southern latitudes with a sharp increase at approximately 50°S to 20 ppm at 70°S.

The fact that only a poleward enhancement in ethane, and not acetylene, is observed rules out several physical explanations. For instance, an increase in the rate of vertical diffusion from higher in the stratosphere would give an enhancement of both hydrocarbons. The author concludes the presence of a meridional wind system in explaining this behaviour. The transport timescale must therefore be longer than acetylene’s photochemical lifetime but shorter than that of ethane to explain an enhancement of ethane only. This places the transport timescale intermediate of 100 years and 700 years at 2 mbar.
4.2.2 Hesman et al. (2009)

Hesman et al. (2009) conducted a similar analysis of Cassini-CIRS observations from 2005 to 2006 and combined their study with IRTF-Celeste observations made in October 2006. The Celeste instrument is a cryogenic grating spectrometer, observing from 5 μm to 25 μm at a spectral resolution of 0.04 cm$^{-1}$ (Moran et al., 2007).

Nadir observations (emission angles up to 60°) made in 2005 were used to retrieve the vertical temperature profiles using a linear constrained inversional algorithm discussed in Conrath et al. (1998). Higher emission angle (74° to 81°) CIRS observations, made in 2006, as well as Celeste observations with similar emission angles were subsequently analysed to determine the hydrocarbon abundances. The temperature and hydrocarbon mole fraction profiles were retrieved at the same spectral regions as in Howett et al. (2007).

As in Howett et al. (2007), the meridional acetylene mole fraction at 2 mbar obtained from both CIRS and Celeste observations follows the yearly-averaged profile of ultraviolet insolation (Figure 2). A general increase of ethane’s mole fraction towards the South Pole is also observed with approximately twice as much ethane at the south pole than at the equator.

4.2.3 Guerlet et al. (2009)

Low resolution (FIRMAP) limb observations between March 2005 and January 2008 ($L_s$=300° to 340°) were acquired in this study. Their retrieval algorithm differs slightly from that in Howett et al. (2007) and Hesman et al. (2009). In retrieving temperature, they simultaneously retrieved the tangent height correction. In the limb-viewing geometry of Cassini-CIRS, an estimate is made on the altitude within the atmosphere at which the array detector is focused, though with an uncertainty (of typically 50km) due to pointing errors in the instrument. Their retrieval algorithm determined a ‘tangent height correction’ where this altitude is altered to provide the best spectral fit.

Following the retrieval of temperature, ethane and acetylene were retrieved at the same spectral regions as in Howett et al. (2007).

They analysed their retrieved hydrocarbon abundances at 1 mbar as well as 0.1 mbar and 0.01 mbar. At 1 mbar, all chemical species exhibit a sharp maximum at the equator with an overall decay to higher latitudes, though with some hemispheric asymmetries. A maximum abundance of all chemical species
is predicted at the equator where the yearly-averaged ultraviolet insolation is maximum (Figure 2). However, as noted by the authors, the mole fraction maxima in all three species is narrow while the yearly-averaged insolation varies smoothly with latitude. The authors conclude that this trend has a dynamical origin and not simply a photochemical one.

Acetylene follows the predicted trend at non-equatorial latitudes. Although ethane shows a slight enhancement towards the south pole, this is not significant with respect to the uncertainties in the retrieved abundances. Though this trend is constant within the error bars, the authors conclude that the south poleward ethane enhancement is physical and signifies that ethane is more efficiently transported than photochemically destroyed at this altitude. Again, as with previous studies, an equator-to-pole transport timescale intermediate of the acetylene and ethane photochemical lifetimes is concluded.

The meridional acetylene and ethane profiles exhibit a similar trend at 0.1 mbar. As noted by the authors, these hydrocarbons have very similar lifetimes at this altitude (Figure 4) and are photochemically coupled (see Section 2.3), which is supported by these results. A similar equatorial maxima in the hydrocarbon abundances is exhibited at this pressure level and the authors link this to the downwelling of air due to the semi-annual equatorial temperature oscillation. Latitude-altitude temperature maps (also derived from Cassini-CIRS observations) of Saturn’s equatorial temperature oscillation show a temperature maximum at 1 mbar and a temperature minimum at 0.1 mbar (Fouchet et al., 2008). These temperature maps are transformed into zonal wind-altitude maps by means of the vertical thermal wind equations (with an interpolation at the equator where the thermal wind equation is undefined). A strong westerly wind intermediate of 0.1 mbar and 1 mbar with an equally strong easterly wind aloft is determined. The associated wind shear is considered to drive downwelling of hotter air and with it, hydrocarbons leading to this equatorial enhancement.

At 0.01 mbar, the hydrocarbon abundances are predicted to mimic the profile of the instantaneous solar irradiation since vertical mixing and photochemical timescales are much shorter at this altitude (Figure 4). While the subsolar point is at approximately ±30° latitude during each solstice, the length of a Saturn day increases in moving towards the summer pole and therefore the instantaneous solar insolation is roughly constant with latitude in the summer hemisphere. Their derived profiles, however, show almost the opposite trend with a maximum abundance of both acetylene and ethane at mid-northern latitudes and a minimum at mid-southern latitudes, with acetylene exhibiting the greatest difference between southern and northern mid latitudes. Slower vertical eddy diffusion due to lower wave activity is considered a possible explanation of this behaviour.
5 Proposal

All previous studies, using Cassini-CIRS observations agree that there is a southern (summer) poleward enhancement of ethane in the lower stratosphere (~1 mbar). The fact that only an enhancement of ethane is observed rules out several physical explanations. Stronger vertical diffusion at the summer pole, for example, would give rise to an enhancement of both acetylene and ethane. Photochemical processes favouring the production of ethane and/or reducing the destruction of ethane can also be ruled out since these reactions have been modelled (Moses & Greathouse, 2005) and no poleward enhancement of ethane is exhibited. A meridional wind system is concluded as an explanation of this behaviour. This wind system transports hydrocarbons produced at the equator to the south polar regions on a timescale longer than acetylene’s photochemical lifetime, but shorter than ethane’s lifetime. At 2 mbar, this corresponds to a timescale between 100 years and 700 years, as predicted by photochemical models. Assuming transport from Saturn’s equator to south pole, this implies wind speeds of 0.4 to 2 cm s\(^{-1}\) (Howett et al., 2007).

Such long timescales imply that the ethane providing the polar enhancement we observe has taken at least three Saturn years to travel there. This similarly implies a strong hemispheric asymmetry in the hydrocarbon abundances since no enhancement is seen at the winter pole and presumably transport of hydrocarbons to the north pole from previous northern summers would still be in progress, as these timescales suggest. It is inconceivable that such a meridional wind system would only exist in one hemisphere. It is also inconceivable that such a weak flow would survive in the stratosphere given other comparably stronger vertical and horizontal dynamical processes. Either the photochemical lifetimes are very much overestimated or another dynamical or photochemical process is producing the enhancement of ethane at the summer pole.

Cassini arrived at Saturn in 2004 shortly after summer solstice in the southern hemisphere. The ‘prime mission’ (the initial four years of observations) therefore studied Saturn during southern summer. With the occurrence of the vernal equinox in 2009, Saturn’s northern hemisphere is now approaching summer (Figure 5). The extension of Cassini’s mission to 2017 (and possibly beyond) will provide observations of Saturn during its approach to Northern Solstice in approximately 2017. This extended mission offers the opportunity to study the response of Saturn’s photochemistry to seasonal changes.

Even the most recent observations provide evidence of a seasonal shift in both hemispheres. Significant temporal changes in Saturn’s thermal structure and ortho -to-para H\(_2\) fraction have already been determined by comparing observations between 2004 and 2009 (~0.1 Saturn year) (Fletcher et al., 2010). A warming of ~7 K ay 40°N at 1 mbar was determined in Fletcher et al. (2010). However, observational determinations of the seasonal variations of hydrocarbons remain to be conducted.

Seasonal changes could be inferred by comparing the results of (Greathouse et al., 2005) (which uses
Figure 5: The relation of Cassini’s mission to seasonal variations on Saturn. The solid red line indicates Cassini’s operational life with the dashed line indicated the extended ‘Solstice Mission’. The asymmetry in time about the vernal equinox results from Saturn’s slightly eccentric orbit and Kepler’s second law (where Saturn’s orbital speed increases during perihelion).

observations in 2002) and the studies summarised in Table 2, which use Cassini-CIRS observations at different points during Saturn’s approach to vernal equinox. However, the abundances of ethane at 2 mbar estimated by Guerlet et al. (2009) are approximately half the value of those determined by Greathouse et al. (2005). This discrepancy is determined to be the result of the use of different line lists instead of something physical. An accurate line list of ethane’s 12 μm feature was presented by Auwera et al. (2007) and this line list has now been incorporated into the HITRAN 2008 line database (Rothman et al., 2009). In addition, several different improvements have been made to the calibration techniques used in the reduction of Cassini-CIRS data. The newest ‘v3.1’ release now accounts for calibration spikes due to electrical noise and instances where the calibrated spectrum was systemically shifted down in radiance space (see Section 9.1). Previous studies of hydrocarbons using Cassini-CIRS data will have used the earliest releases of v2.0 calibration. There remains the need to determine the seasonal variations of hydrocarbons in Saturn’s stratosphere using a consistent set of observations (and corresponding calibration) and line lists.

Comparison of hydrocarbon retrievals from older and recent observations will determine whether the
photochemistry has responded to seasonal changes. High emission angles will sound the upper stratosphere (at pressures less than 0.1 mbar) where hydrocarbons have a mostly photochemical origin. Near nadir observations will provide sensitivity to the lower stratosphere (~1 mbar) where hydrocarbons have mostly been dynamically transported from the upper stratosphere. Comparison of any observed enhancement at these altitudes will provide constraint on the photochemical production and vertical diffusion timescales.
6 The Retrieval Algorithm

In accordance with previous work, the retrieval of vertical hydrocarbon profiles, in this project, is conducted as follows:

1. Simultaneous retrieval of the tropospheric temperature and stratospheric temperature profiles by fitting the H$_2$-H$_2$ and H$_2$-He collision-induced spectrum from 600 cm$^{-1}$ to 680 cm$^{-1}$ and the $\nu_4$ methane band from 1250 cm$^{-1}$ to 1350 cm$^{-1}$.

2. Setting the temperature retrieval as the vertical temperature profile, retrieving the vertical profiles of acetylene and ethane from 720 cm$^{-1}$ to 740 cm$^{-1}$ and 770 cm$^{-1}$ to 890 cm$^{-1}$, respectively.

A vertically continuous profile of the hydrocarbon abundances will be retrieved instead of a retrieving a scale factor to apply to the reference profile.

6.1 Nemesis

The retrieval will be conducted using the NEMESIS radiative transfer retrieval tool (Irwin et al., 2008) which retrieves the desired atmospheric profile ($x_{n+1}$) by a non-linear iteration of Equation 13 until maximum consistency between the modelled spectrum ($y_n$) and the measured $y_m$ is acheived, subject to a priori and measurement constraint (see Section 6.3). The iteration is initiated by the a priori profile ($x_0$).

$$x_{n+1} = x_0 + \hat{S}_x K_n T (K_n \hat{S}_x K_n T + \gamma S_x)^{-1} (y_m - y_n - K_n (x_0 - x_n)) \quad (13)$$

where $\hat{S}_x$ is the a priori correlation matrix, $S_x$ is the measurement covariance matrix, $K_n$ is the Jacobian or matrix of functional derivatives describing the rate of change of radiance at a particular wavenumber with respect to a height in the atmosphere. $\gamma$ is a parameter adjusted such that $K_n \hat{S}_x K_n T$ and $S_x^{-1}$ are approximately equal in magnitude (see Section 6.3).

NEMESIS uses the correlated-k scheme where the transmission of an atmospheric path is averaged over a frequency interval, summing all the line contributions falling into the interval. The use of correlated-k vastly reduces the computational time and has been shown to yield results negligible in difference from the more accurate, but slower line-by-line method at Cassini-CIRS wavelengths (Irwin et al., 2004).
6.2 Atmospheric Profile

The reference temperature profile is derived from that observed during Voyager radio occultations (Lindal et al., 1985). The atmospheric profile contains the vertical volume mixing ratio profiles of H$_2$, HD, He, NH$_3$, PH$_3$, CH$_4$, CH$_3$D, $^{13}$CH$_4$, C$_2$H$_6$, C$_2$H$_2$ and C$_3$H$_8$ which are major contributors to the infrared spectrum of Saturn. Their vertical profiles are set from a variety of observation and modelling results.

A vertically constant (well-mixed) mole fraction of 0.881 for molecular hydrogen is assumed in accordance with Voyager IRIS measurements (Conrath & Gautier, 2000). The deuterium profile is derived from that of molecular hydrogen by applying a D/H ratio of $1.7 \times 10^{-5}$ (Lellouch et al., 2001). Ammonia’s profile assumes a deep value with a logarithmic interpolation to zero above 1.2 bar due to photodissociation. Phosphine’s profile is qualitatively similar and is adopted from Orton et al. (2000).

The vertical profiles of CH$_4$, C$_2$H$_6$, C$_2$H$_2$ and C$_3$H$_8$ are taken from photochemical models (Moses et al., 2000a). The CH$_4$ profile is scaled to produce the profiles of $^{13}$CH$_4$ and CH$_3$D using a terrestrial value for the $^{13}$C/$^{12}$C ratio and the D/H ratio mentioned earlier, respectively.

6.3 A Priori Profiles & Constraint

A priori profiles of the temperature and the hydrocarbon abundances for the retrievals are adopted from the reference profile and an error associated with each point in the atmosphere.

A priori temperature profiles were produced using the ‘make_temp_apriori.pro’ procedure provided by P. Irwin. In this program, the a priori error is parameterised by assuming a error in the temperature at the top of the atmosphere and extrapolating this error to deeper in the atmosphere by applying an exponential decay with pressure, becoming effectively negligible at the deepest extent of the atmospheric profile. The error at the top of the atmosphere is adjusted to provide a balance of measurement and a priori constraint. The error which provides this balance can vary from as little as 0.2 K to 10 K, depending on the magnitude of the signal in the observation. The procedure ‘imagecovariance’, provided by P. Irwin, plots the diagonal elements of the matrix, $\mathbf{K}_n \mathbf{S}_x \mathbf{K}_n^T$, and the measurement covariance matrix, $\mathbf{S}_x$, (Equation 13). Constraint is considered to have been achieved when their diagonal elements agree within an order of magnitude.

A priori errors in the vertical hydrocarbon profiles are parameterised as a fractional scaling of the profile itself. Constraint of the hydrocarbon retrievals is likewise tested as described above.

In both retrieval of temperature and hydrocarbons, a vertical smoothing is applied to the retrieved
profile by NEMESIS and is controlled by the ‘correlation length scale’ parameter. In accordance with
previous studies (for example, Howett et al. (2007); Guerlet et al. (2009)), this is fixed at a value of 1.5
logarithmic pressure units in this study.

6.4 Aerosol/Haze Profiles

Models of haze or aerosols have not been included in the retrieval of hydrocarbon profiles in previous
work. Saturn is believed to be host to both a tropospheric and stratospheric haze which vary in form
with latitude. Analysis of HST observations of Saturn determined that discrete layers of haze, separated
by clear gas layers, occur at equatorial latitudes while a continuously stratified haze layer is present
at the southern (summer) pole (Muñoz et al., 2004). These layers vary in optical thickness with both
latitude and altitude. Retrievals of the tropospheric haze layers (400 mbar to 100 mbar) showed the
optically thickest layers to exist at \( \pm 50^\circ \) and \(-10^\circ\) \( (\chi_{0.67 \mu m} \sim 30) \) while the optically thinnest layers
were determined to exist at \( \pm 30^\circ \) \( (\chi_{0.67 \mu m} \sim 18) \) (Muñoz et al., 2004). The stratospheric haze layers
(10 mbar to 1 mbar) were determined to be optically thin \( (\chi \sim 0.03) \) at all latitudes. As discussed in
Howett et al. (2007), inclusion of these haze layers in the forward radiative transfer had almost no effect
and in some cases, deteriorated the quality of the spectral fit in the temperature retrieval of Saturn.
Subsequent studies of hydrocarbons from Cassini-CIRS (Hesman et al. (2009), Guerlet et al. (2009))
also assumed no haze or aerosol layers in their retrieval algorithms.

Fletcher et al. (2007) determined an error estimate in assuming an aerosol-free atmosphere in retrieving
the temperature. Synthetic spectra were produced with a standard temperature profile and tropospheric
aerosols of varying sizes and resultant optical depths. In subsequently conducting a temperature (aerosol-
free) retrieval (from 20 \( \mu m \) to 40 \( \mu m \)) of these synthetic spectra, the retrieved values differed from
the original temperature profile by at most 0.4 K at 550 mbar with differences decreasing to \( \sim 10^{-2} \)
K at higher tropospheric altitudes. This supports the aerosol/haze-free assumption in retrieving the
temperature (at least in the troposphere at these wavelengths). Haze particles are small and therefore
their optical depth decreases with wavelength as \( \lambda^{-4} \). With small stratospheric haze opacities in the
visible, opacities are therefore negligible in the mid-infrared and far-infrared.

Therefore, no haze or aerosol models were included in the atmospheric profile for either the temperature
retrieval or the hydrocarbon retrieval.

6.5 Ortho-to-para H\(_2\)

Simultaneous retrieval of the ortho-to-para H\(_2\) fraction \( (f_P) \) was conducted in preliminary temperature
retrievals. However, this was determined to have negligible effect on the temperature retrieval, especially
at stratospheric altitudes where this study will focus. Therefore, the vertical ortho-to-para H$_2$ fraction is set to equilibrium in retrieving the vertical temperature profile.

6.6 Line data

Correlated-k tables of all molecular species listed in Section 6.2 (apart from hydrogen and helium) are included in the radiative transfer forward model.

The k table for $^{12}$CH$_4$ is derived from recent revisions of the HITRAN database (Albert et al., 2009) while the line data for other isotopes is assumed from Brown et al. (2003). Line data for acetylene is likewise derived from the HITRAN 2008 molecular database (Rothman et al., 2009). An older version of the ethane line list was initially used. However, a newer k-table generated from a more recent and accurate line list (Auwera et al., 2007) was subsequently used. This replaced older HITRAN and GEISA line lists which were shown to give rise to integrated band intensities 1.57 larger and 1.44 smaller than observed values, respectively.

As shown in Figure 6, the fit to the $\nu_9$ band in an example Cassini-CIRS spectrum improves greatly when using the newer line list. The positions of band features are much better reproduced and the P and R branches are better matched. This newer line list is used in all subsequent analysis in this report.

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Line data of ethane’s 7 µm feature recently became available (di Lauro et al., 2011). This feature is
analysed in Cassini-CIRS spectra and discussed in Section 10.

6.7 Example Retrieval

Figure 7 displays the results of an example retrieval. In both the temperature retrieval and hydrocarbon retrieval, the NEMESIS spectrum provides a very good fit of the Cassini-CIRS observation. As expected, the vertical temperature profile is enhanced from a priori since the observation used in this example is of a high latitude in the summer pole. The retrieved profile of ethane shows an enhancement in agreement with previous studies which also show an enhancement of ethane towards the summer pole.
Figure 7: An example retrieval of the vertical temperature profile and the vertical profile of hydrocarbon abundances for a high latitude, Cassini-CIRS observation in the southern (summer) pole. In plots showing spectra, the black solid line and shading represent the Cassini-CIRS data with associated noise and the solid red line represents the NEMESIS spectral fit. In plots showing a vertical profile, the black solid line indicates the a priori profile while the solid red line indicates the retrieved profile. Retrieved uncertainties were small due to the low noise in the observed spectra. These uncertainties have been increased by a factor of 4 for ease of viewing and are shown as the dotted red lines.
7 Testing the Retrieval Algorithm

It seemed logical to test the accuracy of the retrieval method before applying it to Cassini-CIRS observations to determine seasonal variations. Many planetary remote sensing studies have conducted a test of their retrieval algorithm using synthetic spectra (for example, see Fletcher et al. (2009); Guerlet et al. (2009)). A synthetic spectrum of the planetary atmosphere is produced using a known vertical profile of temperature or chemical species abundances. A retrieval is then conducted of the simulated spectrum with the aim of recovering the profile used to initially make the spectrum. Such a test was performed and is discussed below.

The ‘Generatespx’ program was used to produce the synthetic spectra for this test. This program runs the NEMESIS forward radiative transfer model using a reference profile to which random perturbations have been applied. Gaussian and random noise are subsequently added to the resultant synthetic spectra to simulate an observed spectrum.

7.1 Retrieval of Temperature

Initially, the retrieval of the vertical temperature structure was tested. 50 near-nadir synthetic spectra, each derived from a different randomised vertical temperature structure, were produced. These were produced at a spectral resolution of 2.5 cm\(^{-1}\). The forward modelling noise, which controls the quantity of gaussian and random noise added to the synthetic spectrum, was set to 0.01 nW cm\(^{-2}\) sr\(^{-1}\) cm. This resulted in a signal-to-noise ratio comparable, if not slightly worse, than a typical, co-added, Cassini-CIRS spectrum.

Retrievals were conducted of each of the spectra, at the wavelength regions discussed in Section 6. In accordance with previous studies, the temperature profile of each spectrum was retrieved twice using a ‘cold’ and ‘warm’ a priori temperature profile where 20 K was subtracted and added from the reference temperature profile of Saturn, respectively. This was done to demonstrate the ability of Nemesis to perform a retrieval at latitudes where the atmosphere is much cooler or warmer than the reference profile. The balance of measurement and a priori constraint was acheived when the error in the a priori temperature at the top of the atmosphere was set to 2 K.

The temperature retrieval is expected only to reproduce the temperature at altitudes in the atmosphere at which the spectral regions are sensitive, as displayed in Figure 8 for a typical near-nadir spectrum of Saturn. At altitudes outside that of sensitivity where there is no information in the signal, the retrieved temperature profile tends back to the a priori profile.
Figure 8: The absolute, normalised kernel matrices describing the sensitivity of the temperature retrieval as a function of height in the atmosphere (mbar) and wavenumber (cm\(^{-1}\)). The left-hand plot shows the sensitivity of the collision-induced spectrum to Saturn’s troposphere while the right-hand plot shows sensitivity of the methane \(\nu_4\) band to the stratosphere. The contribution function has been normalized at each wavenumber and therefore this shows the relative origin in the atmosphere of the radiance at a particular wavenumber.

Figure 9 shows the results of this test for all 50 synthetic spectra. The retrieval of temperature accurately reproduces the temperature at the atmospheric heights shown. In addition, temperatures derived from retrievals using the cold and warm \textit{a priori} (which are 40 K different in temperature) are also shown to agree within their respective error bars.

In conclusion, the temperature retrieval adequately reproduces the atmospheric profile in both the troposphere and the stratosphere.

7.2 Retrieval of Acetylene and Ethane

Similarly, 50 synthetic spectra were produced using randomly perturbed vertical profiles of the abundances of acetylene and ethane but the same standard temperature profile. The vertical temperature profile was initially retrieved and then the vertical profiles of acetylene and ethane retrieved, as described in Section 6. Each spectra was retrieved twice using a ‘gas-rich’ and ‘gas-weak’ \textit{a priori} where the vertical profiles of hydrocarbon abundances were increased and decreased by a factor of two at all altitudes, respectively. This was conducted again to demonstrate the ability of \textsc{nemesis} to retrieve at latitudes where the hydrocarbon abundances are significantly diminished or enhanced compared to the reference profile. A fractional error of \(\sim20\%\) of the hydrocarbon abundances was determined to provide
Figure 9: A comparison of the retrieved temperature with that used to produce the synthetic spectrum at 200 mbar, 63 mbar, 3 mbar and 0.1 mbar. Blue points represent the results when the cold a priori profile was used while red points show the results where the warm temperature profile was used.

Again, the retrieval is expected only to reproduce the hydrocarbon profiles at atmospheric heights sensitive to the spectral regions used, as shown in Figure 10.

Figure 11 demonstrates that hydrocarbon abundances at 1 mbar are also adequately reproduced within the retrieval uncertainties. In addition, there is statistical consistency between values retrieved using the gas-rich and gas-weak a priori profiles.

In conclusion, the retrieval algorithm described in Section 6 accurately derives the vertical atmospheric profiles of temperature and abundances of ethane and acetylene at the altitudes at which measurement sensitivity is maximum.
Figure 10: The absolute, normalised kernel matrices describing the measurement sensitivity as a function of height in the atmosphere (mbar) and wavenumber (cm$^{-1}$) for a near-nadir Cassini-CIRS spectrum. The left-hand plot shows the sensitivity of the $\nu_5$ acetylene band while the right-hand plot shows that of the $\nu_9$ ethane band. The contribution function has been normalized at each wavenumber and therefore this shows the relative origin in the atmosphere of the radiance at a particular wavenumber.

Figure 11: A comparison of the retrieved hydrocarbon abundances with the true values used to produce the spectra at 1 mbar. Abundances are shown in parts-per-million. Orange points represent the results where a gas-rich a priori has been used while green points show the case of the gas-weak a priori.
8 Extraction of Cassini-CIRS data

All data discussed in this report have been produced using the ‘v2.5’ calibration and the spectra have been apodised. Data were extracted from the ‘/oxpln0/plan/CIRS_data/tables/saturn/calib_v2.5/apod_spectra/’ using the ‘vanilla_extract’ program prepared by L. Fletcher and N. Teanby. This program searches the CIRS database for all spectra observed during a chosen timeframe, a chosen latitude range, a chosen range in emission angle and a given spectral resolution. All appropriate data are then written to a binary formatted ‘.out’ file. The ‘load_in_vanilla_outfile’ procedure then produces a file containing all the spectra acquired from the extraction.

There are several different types of Cassini-CIRS observations which differ mostly in the way observations are sampled spatially and in the spectral resolution. This report will focus on COMPSIT, MIRMAP, FIRMAP and LIMBMAP observations.

COMPSIT observations are the highest in spectral resolution (0.5 cm\(^{-1}\)) and ‘sit-and-stare’ at a given latitude for the long integration times needed for such higher resolutions (Nixon, 2004). MIRMAP observations have a spectral resolution of 3 cm\(^{-1}\). The long axis of the detector array is aligned poleward such that planet’s rotation allows the instrument to map out and observe a latitude band (Nixon, 2004). FIRMAP observations are the lowest in spectral resolution (15 cm\(^{-1}\)) and are performed by a repeated, equatorward slewing over a hemisphere and repeating so that the entire hemisphere is sampled. Their lowest spectral resolution allows for short integration times which serves to produce a comparably larger set of spectra in one observing run. LIMBMAP observations are identical in resolution to FIRMAP observations though the spacecraft orbits much closer to Saturn so that limb viewing geometries are obtained.

8.1 Raw data

Spectra from the raw data are individually too noisy for retrieval of atmospheric variables. It is therefore necessary to co-add (average) many spectra together so as to increase the signal-to-noise. Averaging an ensemble of N measurements together serves to reduce the typical variance by a factor of N (Equation 14).

\[ \sigma_{av}^2 = \frac{\sigma^2}{N} \]  

(14)

where \( \sigma_{av}^2 \) is the variance associated with the average of the measurements, \( \sigma^2 \) is typical variance of each individual measurement and N is the number of averaged measurements. Therefore, the signal-to-noise
Figure 12: The latitudinal and temporal distribution of Cassini-CIRS ‘compsit’ (0.5 cm\(^{-1}\)) observations. The left-hand plot shows a high-resolution binning which most represents the raw data while the right-hand plot shows the data binned into 4 time bins and 18 latitude bins such that the number of spectra in almost all bins is adequate for co-adding. The number of spectra falling into each bin is represented on a colour grid scaled logarithmically from 1 to \(10^4\). Previous studies have typically co-added \(~10^3\) spectra together before conducting atmospheric retrievals.

of a spectrum is expected to improve by a factor of \(\sqrt{N}\) in averaging \(N\) spectra together. The highest spectral resolution observations suffer the worst from instrument noise, as demonstrated by Equation 15 which shows a proportionality of the signal-to-noise to the bandwidth, \(\Delta \tilde{\nu}\).

\[
\text{Signal-to-Noise} = L A \Omega \left( \frac{\Delta t}{a} \right)^{1/2} D^* \Delta \tilde{\nu} \propto \Delta \tilde{\nu} \tag{15}
\]

where \(L\) is the incident radiance on the aperture, \(A\) is the area of the entrance aperture, \(a\) is the area of the detector, \(\Omega\) is the solid angle of the scene, \(\Delta t\) is the integration time and \(D^*\) is the detectivity of the instrument. Though higher resolution observations tend to have longer integration times, this only marginally improves the signal-to-noise, due to the \(\Delta t^{1/2}\) dependence. In using Compsit observations which represent the highest spectral resolution provided by Cassini-CIRS, co-adding of several thousands of spectra, sometimes spanning several years of observations, is required to provide confidence in atmospheric retrievals as shown in Howett et al. (2007) and Hurley et al. (2011 (submitted)). Far fewer Firmap observations need to be co-added so as to produce the same signal-to-noise - only as many as 50 Firmap spectra were coadded in Guerlet et al. (2009) which analysed Firmap observations. In these studies and several others which analyse Cassini-CIRS observations, spectra of a common latitude bin (normally 2°) are averaged and therefore co-adds represent zonal averages.

This project aims to determine whether hydrocarbons exhibit a seasonal variation. Given the need for co-adding spectra and in some cases, representing three years worth of data within a 2° latitude bin as one averaged spectrum, it was necessary to determine whether temporal variations could be resolved from
Figure 13: The latitudinal and temporal distribution of Cassini-CIRS ‘MIRMAP’ (2.5 cm⁻¹) observations. The data has been binned into 90 latitude bins and 45 bins in solar longitude. The representation of colours is the same as with Figure 12.

analysis of Cassini-CIRS observations. Can a balance be struck between co-adding a sufficient number of spectra to provide the high signal-to-noise needed for retrieval of atmospheric profiles but maintaining a sufficient spatial and temporal resolution? In particular, an adequate sampling at high latitudes is required since photochemical models show the greatest seasonal variations at these latitudes.

The latitudinal and temporal distribution of raw spectra from COMPSIT, MIRMAP and FIRMAP and limb FIRMAP observations are studied below.

8.2 Latitudinal and Temporal Distribution of Cassini-CIRS observations

COMPSIT, MIRMAP and FIRMAP observations with emission angles between 0° and 60° were extracted from the Oxford Cassini-CIRS database, as described earlier. Limb observations (defined in this study as spectra with emission angles in excess of 70°) were also extracted.

8.2.1 Determining the Solar Longitude

The extraction procedure provides a value of the spacecraft ‘scet’ time - the number of seconds elapsed since noon on Jan 1st 1970. These values were readily converted into a standard time format - year,
Figure 14: The latitudinal and temporal distribution of Cassini-CIRS ‘FIRMAP’ (15 cm$^{-1}$) observations. The data has been binned into 90 latitude bins and 45 bins in solar longitude. The representation of colours is the same as with Figure 12.

month, day, hour, minute and second - by the ‘fscet2date’ function provided by L. Fletcher. For the ease of data analysis and for the allowance of quickly determining the season in which an observation was made, a routine was developed which would convert either a scet or standard time into the solar longitude. The solar longitude describes the phase of Saturn on its approximately 30 year orbit around the Sun and therefore quantitatively describes the current season. 0° corresponds to the vernal equinox (spring in the northern hemisphere), 90° corresponds to summer in the Northern Hemisphere and 270° corresponding to summer in the Southern Hemisphere.

The HORIZONS Ephemeris generator, provided by the Jet Propulsion Laboratory\textsuperscript{3} was used to determine the solar longitude. The ephemeris provides a wealth of various orbital quantities at a high temporal resolution but, as far as can be seen, does not simply output the solar longitude, as defined above. It was therefore necessary to derive the solar longitude from the sub-solar latitude provided in the ephemeris table. If one were to sit at the centre of the Sun and observe Saturn, the latitude observed at the centre of the Saturnian disk is the sub-solar latitude. This value is sensitive to the season on Saturn. At summer solstice in the northern hemisphere, the sub-solar latitude will be at maximum and similarly will be at a minimum during southern summer solstice, passing through 0° at each equinox. The vernal equinox (0° in the solar longitude) occurs when the sub-solar latitude is zero and increasing. An accurate value for Saturn’s orbital period was calculated as the time between two adjacent vernal equinoxes. The solar longitude was then determined by simply calculating the fraction of the Saturn year elapsed since the last vernal equinox at the time of an observation and multiplying by 360° (Equation 16).

\textsuperscript{3}http://ssd.jpl.nasa.gov/horizons.html
Figure 15: The latitudinal and temporal distribution of Cassini-CIRS (15 cm\(^{-1}\)) observations with emission angles in excess of 70°. The representation of colours is the same as with Figure 12.

\[
L_s = 360 \left( \frac{t_{\text{obs}} - t_{\text{ve}}}{P_{\text{saturn}}} \right) \circ
\]

where \(L_s\) is the solar longitude, \(t_{\text{obs}} - t_{\text{ve}}\) is the time elapsed since the last vernal equinox and \(P_{\text{saturn}}\) is Saturn’s orbital period. It should be noted that this will provide only an approximate value of the solar longitude. Saturn’s orbit is slightly eccentric. Due to Kepler’s 2nd law, its orbital velocity therefore changes throughout its orbit and is maximum at perihelion and minimum at aphelion. With southern summer solstice occurring during perihelion and northern solstice at aphelion by symmetry, the relationship of the sub-solar latitude with time is therefore not a simple sinusoid but one with troughs which are slightly narrower than the peaks. However, only an approximate value of the solar longitude is required and this method was therefore deemed sufficient.

8.2.2 COMPSIT

Figure 12a shows a highly resolved latitudinal and temporal distribution which most represents the distribution of the raw spectra from COMPSIT observations. As shown, COMPSIT observations focused mostly on equatorial and mid latitudes with less data sampling at polar latitudes. Although there are several clusters of data where the number of spectra falling within a latitude-time bin exceeds 1000, much of the planet’s surface in space and time is undersampled. Only in significantly binning the data into 18 latitude bins and 4 time bins (Figure 12b) does an adequate number of spectra (for co-adding)
fall into each latitude-time bin. High latitudes however remain undersampled at \( L_s \approx 320^\circ \) and \( L_s \approx 360^\circ \). This is not ideal given the aim of this project and the fact that photochemical models show the greatest seasonal variations at high latitudes.

COMPSIT observations were therefore deemed unsuitable for the preliminary aim of this project.

### 8.2.3 MIRMAP & FIRMAP

MIRMAP observations are far more discretised in time and exhibit a greater latitudinal coverage (Figure 13). FIRMAP observations are similarly discretised in time and exhibit an extensive latitudinal coverage (Figure 14).

LIMBMAP observations are more randomly spaced in latitude and time than their nadir counterparts. There however exist several high latitudes which are sufficiently sampled at different seasons - for example 80°S at solar longitudes of approximately 310°, 345° and 15°.

Both MIRMAP and FIRMAP observations will therefore provide highly accurate spectra representing only a small spatial and temporal extent, in particular with FIRMAP observations. Similarly, LIMBMAP observations will provide measurement sensitivity to the upper stratosphere to polar latitudes as well as equatorial and mid-latitudes at several points in time. Nadir MIRMAP and FIRMAP observations and LIMBMAP observations are therefore concluded to be highly ideal in determining the seasonal variations of hydrocarbons at different latitudes on Saturn.

### 8.3 Co-adding spectra

Spectra were co-added using the ‘diet_rv_latbin_time’ procedure provided by L. Fletcher and N. Teanby. This procedure extracts all individual spectra from the ‘.out’ files and bins the spectra by latitude, time (as above) and also emission angle and proceeds to co-add the selected. In this study, only spectra within a common 30° emission angle band were co-added and represented as one spectrum.

The co-adding of the spectra is conducted by a weighted average where the contribution to the radiance at a particular wavenumber is weighted inversely by the corresponding noise (Equation 17).

\[
R_\nu = \frac{\sum_{i=1}^{N} \frac{R_{\nu,i}}{\sigma_{\nu,i}^2}}{\sum_{i=1}^{N} \sigma_{\nu,i}^2}
\]  (17)
where $R_\tilde{\nu}$ is the co-added variance at wavenumber, $\tilde{\nu}$, $R_{\tilde{\nu}}, i$ is the radiance at wavenumber, $\tilde{\nu}$ of the $i^{th}$ spectrum used in the co-add, $\sigma^2_{\tilde{\nu}, i}$ is the corresponding variance and $N$ is the number of spectra co-added. In co-adding spectra several spectra together, average values of the emission angle, solar angle, zenith angle are determined. The resultant latitude and longitude are determined by averaging in cartesian co-ordinates and subsequently converting back to spherical coordinates to avoid wrap-around problems and biasing at polar latitudes.

A number of ‘dark’ or deep-space spectra are used in the calibration of each individual spectrum. Cassini-CIRS observation runs couple on-target observations with off-target observations of deep-space which are used to account for unphysical signal produced by the instrument itself (for example, due to electronic noise). Such unphysical sources of signal can then be removed from the on-target observation. Owing to the random nature of this noise, it is more accurately characterised by combining several deep-space spectra together and therefore, the on-target spectra are more accurate. It was therefore ensured that co-added spectra were produced from individual spectra calibrated with a sufficient number of different deep-space spectra. MIRMAP co-adds produced from an average of less than 20 different deep-space spectra were deemed unsuitable.
9 Stratospheric Hydrocarbons from MIRMAP observations

MIRMAP observations were extracted and co-added as described in Section 8 and the retrieval algorithm, described in Section 6, applied to the resulting ~500 pairs of FP3 and FP4 spectra of varying latitudes and solar longitudes.

A balance of the a priori and measurement constraint was achieved when setting the temperature at the top of the atmosphere to 1.2 K in the temperature retrieval. Similarly, assuming a fractional error of 25% at all heights in the a priori profiles of acetylene and ethane provided constraint in the hydrocarbon retrievals.

9.1 Calibration Issues

Preliminary retrievals revealed calibration faults in certain spectra. These initially presented as unusually high $\chi^2$ values in the hydrocarbon retrieval or abnormalities in the retrieved temperature profile in comparison to adjacent latitudes. Only on a case-by-case inspection of these problematic retrievals did the calibration issues become apparent.

Spikes due to electrical noise appeared consistently at ~800 cm$^{-1}$ in several spectra (for example, Figure 16), in particular those at southern mid-latitudes observed at solar longitudes of ~15$^\circ$. Such spikes are in the P branch of the ethane $v_9$ band and therefore significantly induce unphysical trends in the retrieved ethane abundance profiles.

Regions of negative radiance in the P branch of methane’s $v_4$ band were also apparent in several FP4 spectra (for example, Figure 16), in particular at northern mid-latitudes in 2005. Initially, the problematic region was removed from the temperature retrieval, however, the anomalies in the retrieved profile in comparison to adjacent latitudes remained. Such a calibration issue had already been known of these particular observations. Although the majority of the $v_4$ band in these observations have a positive radiance, the negative radiance in the P branch is in fact evidence of over-calibration where the entire spectrum has been shifted down in radiance space (L. Fletcher, private communication). Retrievals of such spectra will therefore significantly underestimate the temperature, hence why this issue was first discovered in this study.

Subroutines which would test FP3 and FP4 spectra for these respective calibration issues were developed and used to omit such problematic spectra from analysis.
Figure 16: Example calibration problems in mirmap observations. The left-hand plot shows an example calibration spike due to electrical noise present in some FP3 spectra at $\sim 800 \text{ cm}^{-1}$ in the ethane $v_9$ band. The right-hand plot shows an example of an FP4 spectrum which becomes negative towards 1200 cm$^{-1}$ which is evidence of a systematic underestimation of the radiance.

9.2 Temperature Results

Figure 17 displays the results of all temperature retrievals at $\sim 1 \text{ mbar}$. After omitting problematic observations with calibration issues, the majority of $\chi^2$ values are approximately 1 and no more than three which signifies consistently good fits of the retrievals to the observations. At a first glance, these results reproduce those determined from previous studies.

Although equatorial latitudes are poorly sampled in these observations, a localised maximum in the temperature is apparent at such latitudes. This signifies the presence of the temperature oscillation at the equator. Fouchet et al. (2008) used Cassini-CIRS limb observations to map the temperature oscillation using observations from 2005 to 2006 and showed a peak at $\sim 150 \text{ K}$ at 1 mbar which is in agreement with these results.

Northern mid latitudes ($20^\circ \text{N}$) show a localised warming which is concluded to be a result of the end of ring shadowing at such latitudes. As expected, southern mid-latitudes have exhibited a strong cooling of approximately 15 K in moving from summer to late autumn. Likewise, similar northern latitudes show a warming of approximately 10 K in moving from late winter to late spring. In fact, the majority of the spring hemisphere exhibits a warming only 1.4 Saturnian week after the vernal equinox. Cooling of approximately 6 K between solar longitudes of $\sim 310^\circ$ (2005) and $\sim 340^\circ$ (2008) at 70$^\circ$S is consistent with the cooling observed in Fletcher et al. (2010) where temperature maps in these two years were compared. The lack of seasonal constrast at $\sim 30^\circ$S and $\sim 10^\circ$S between these two years is similarly consistent with Fletcher et al. (2010).
Figure 17: The top plot shows the retrieved temperatures at ~1 mbar against latitude for all MIRMAP observations, discounting those with calibration issues discussed in Section 9.1. Each temperature result is coloured according to the solar longitude at which it was observed, as shown in the colour bar. The $\chi^2$ values of each retrieval are shown in the bottom plot for comparison. The vertical dashed lines mark the known latitudinal position of jets.

9.3 Hydrocarbon Results

Figure 18 displays all the results of hydrocarbon retrievals at approximately 2 mbar, again omitting spectra with the calibration issues discussed in Section 9.1. Again, the majority of the values of $\chi^2$ are approximately unity with retrievals in high southern latitudes tending to be higher than 1. These retrievals however exhibit a visually good fit. Typical, small discrepancies between observation and retrieval appear as larger $\chi^2$ values due to the larger signal at such high latitudes. Retrievals at all latitudes and solar longitudes are considered to exhibit a good fit.
Figure 18: The retrieved abundances of acetylene (top) and ethane (middle) at 2.1 mbar respectively with latitude for all MIRMAP observations, again discounting those with calibration issues discussed in Section 9.1. The colour representation is the same as with Figure 17. $\chi^2$ values of each retrieval are shown in the third plot and the position of jets are likewise shown.

9.3.1 Acetylene

The profile of acetylene’s mole fraction latitude exhibits a similarity to the trend of the annually-averaged solar insolation (Figure 2), as concluded of previous studies (Howett et al., 2007; Hesman et al., 2009). The poleward trend south of 30°S for solar longitudes of approximately 300° to 310° is consistent in shape with that of Howett et al. (2007) though the abundances in this study are approximately a factor of two smaller. Such a discrepancy has already been noted by Guerlet et al. (2009) as a result of the use of different line data. Abundances are consistent with those in Guerlet et al. (2009).

There appears to be a diminishment of acetylene at approximately 20°S which seems to deviate from the overall trend and this is true during southern summer, late southern summer and southern autumn.
This can’t be the result of ring shadowing in the summer hemisphere observations since Saturn’s rings shadow the winter hemisphere. This might signify localised upwelling from the deeper hydrocarbon-depleted atmosphere, though ethane’s latitudinal profile exhibits no such dip.

An enhancement of acetylene is apparent in the most recent observations at high northern latitudes. This and the fact that no enhancement of ethane is observed are both consistent with photochemical models which predict acetylene’s production timescale at this altitude (~3 years) to be shorter than that of ethane (~300 years), as shown in Figure 4.

9.3.2 Ethane

The meridional profile of ethane appears mostly flat in the northern hemisphere and for equatorial to mid latitudes in the southern hemisphere with a general increase from 50°S to the south pole, in agreement with previous studies (Howett et al., 2007; Hesman et al., 2009; Guerlet et al., 2009). Again, mole fractions in this study appear to be about a factor of two smaller than those presented in Howett et al. (2007) which again is concluded to be the result of the use of newer line lists for ethane in this study. Studies since that of Howett et al. (2007) have used the newer line data presented in Auwera et al. (2007).

There does appear to be a diminishment of ethane at approximately 60°S at solar longitudes of ~20° in comparison to those retrieved at solar longitudes of ~300°. This can be explained by the decreasing ultraviolet insolation at these latitudes resulting in a slower photolysis rate. The occurrence of this behaviour almost two years after the vernal equinox suggests a delay in the response of the photochemistry of a similar timescale.

A slight enhancement of ethane at Ls ~7° in comparison to those at Ls ~340° is likewise observed from 10°N to 30°N. This behaviour at latitudes from 10°N to 20°N can be explained by these latitudes moving out of ring shadow as the sub-solar point moves north of the equator. This therefore describes a relatively quick response of the photochemistry (of approximately 3 years) to moving out of ring shadow.

A slight seasonal enhancement of ethane is observed also at high northern latitudes, though this enhancement is not statistically significant in the error bars. If this enhancement is physical, then this suggests that ethane’s photochemical production timescale at 1 mbar is much shorter than the ~300 years predicted by photochemical models (Figure 4). These observations were taken only ~1.5 years after the vernal equinox and therefore the photochemistry is likely yet to respond to the increasing insolation as northern solstice approaches.

In conclusion, seasonal variations of the abundances of acetylene and ethane are observed only 1.5
Saturn weeks after the vernal equinox. A depletion of both ethane and acetylene is observed at high southern latitudes in comparing southern summer and southern autumn observations. An enhancement of acetylene is observed at higher northern latitudes as northern solstice approaches. Ethane at similar latitudes and time shows no enhancement significant in comparison to the error bars. The fact that only acetylene is enhanced at this time is in disagreement with the prediction that acetylene and ethane are photochemically coupled since the former is thought to be produced mostly by photolysis of the latter (Section 2.3). Acetylene in this case must therefore have been mostly produced by photolysis of \( \text{C}_2\text{H}_4 \) (Reaction 12). Photochemical models predict a longer photochemical production timescale for ethane in comparison to that of acetylene. The lack of enhancement in ethane thus far describes a phase lag in the response of ethane’s production. An enhancement of ethane in the northern hemisphere is expected in future observations as the northern summer solstice approaches.
10 Preliminary Investigation of Ethane’s 7 micron band

High resolution laboratory data of ethane’s 7μm (~1430 cm⁻¹) ν₀ band was recently published (di Lauro et al., 2011). This presents line data providing a further infrared region of the spectrum at which ethane can be studied. This band might offer sensitivity to another altitude in the atmosphere. Simultaneous retrieval of this band with the 12 μm band might therefore provide sensitivity to a larger altitudinal extent in the atmosphere.

The line data published in this study was converted into a correlated-k table at 2.5 cm⁻¹ resolution by L. Fletcher. A Cassini-CIRS spectrum of the same resolution and of a high southern latitude (83°S at Lₚ ≈300°) was chosen as a case study since an enhanced abundance of ethane is expected at such a latitude and time, as demonstrated in Figure 18. A strong ethane signal should therefore be present.

The vertical abundance of ethane was initially retrieved as before, using the 12 μm band, as described in Section 6. The abundance from the 7 μm band was subsequently retrieved and Figure 19 compares the retrieval in these two different regions.

The retrieved spectrum at the 7 μm band appears consistent with the observed spectrum, at least within the observed noise. The peaks at approximately 1378 cm⁻¹, 1398 cm⁻¹ and 1427 cm⁻¹ are especially well matched in wavenumber position and strength. The 7 μm data is at the edge of the FP4 focal plane and is therefore comparably noisier than the 12 μm data. The retrieved uncertainties of the 7 μm data are therefore comparably larger as the a priori error had to be increased such that measurement and a priori constraint were matched.

As demonstrated by the contribution functions in Figure 20, the two ethane bands exhibit sensitivity to very similar altitudes. The 7 μm retrieval is the most deviant from a priori at 2 mbar while the 12 μm retrieval provides sensitivity 1 mbar higher. Despite the similar altitudinal sensitivity, retrieval of the 7 μm band yields approximately 30 % more ethane at 2 mbar than the 12 μm band at the same altitude. This disagreement is significant with respect to the uncertainties in each retrieved profile.

Forward modelling of the 7 μm region, setting the 12 μm retrieval as the ethane profile, was conducted and the results shown in Figure 21. As shown, the radiance of the forward model is consistently less than that of the 7 μm retrieval owing to the lower abundance of ethane at the altitude of sensitivity. The forward model does tend to agree with the observations, at least within the observed noise. The peak at 1378 cm⁻¹ is however poorly reproduced by the forward model and does outly the observations by greater than the noise.

In conclusion, this preliminary study of an example Cassini-CIRS spectrum reveals that the new 7 μm data (di Lauro et al., 2011) tends to underestimate the strength of the 7 μm features. Retrieval of
Figure 19: A comparison of the retrieval of ethane’s profile from the ν9 12 µm band (top left) with that of the 7 µm band (top right) using new line data from (di Lauro et al., 2011). Cassini-CIRS data is shown as solid black lines with shaded regions indicating the associated noise and red lines indicate the Nemesis fits. In the bottom plot, the solid black line indicates the a priori ethane profile while the red solid lines indicates the 12 µm retrieval with dotted red lines showing the upper and lower bounds of the retrieval uncertainty. The blue solid and dotted lines show the same of the 7 µm retrieval.

ethane at this wavelength region therefore overestimates the abundance in order to provide the most consistency with observation.

The noisier nature of Cassini-CIRS data at the ν9 ∼7 µm band in comparison to the ν9 (∼12 µm) band presents no advantage of retrieving ethane at the former wavelength region over the latter, at least using Cassini-CIRS observations. Earth’s atmosphere exhibits strong water vapour absorption in the ∼7 µm region (Irwin, 2003) which similarly rules out the practicality of studying ethane at this wavelength from ground-based observations. The proposed SOFIA-EXES (Echelon-Cross-Echelle spectrometer aboard the Stratospheric Observatory for Infared Astronomy, (Gehrz et al., 2011)) instrument shows potential for the study of ethane at 7 µm. SOFIA observes in an aircraft at 45000 ft (13.7 km) above the Earth, therefore, above ∼99% of telluric H2O absorption, vastly improving the transmission in normally unobservable wavelength regions (Gehrz et al., 2011). The EXES instrument will provide spectrometry from 5 µm to 28 µm at a resolution of λ/Δλ = 10^4. Such observations will be available in 2013.
Figure 20: The absolute, normalised contribution functions of the retrieval of ethane at 12 µm (left-hand plot) and 7 µm (right-hand plot), as a function of wavenumber (cm$^{-1}$) and height in the atmosphere (mbar). The contribution function has been normalised at each wavenumber and therefore this shows the relative origin in the atmosphere of the radiance at a particular wavenumber.

Figure 21: Results of a forward modelling test at the 7 µm ethane region. The black, solid line indicates the Cassini-CIRS spectrum with shading indicating the associated noise. Retrieval of this region is shown as the solid, red line. A forward model using the ethane profile from the 12 µm retrieval is shown as the dashed, red line.
11 Future Work

This section outlines the work planned for the remainder of this DPhil project.

Further analysis of Cassini-CIRS observations will use the newest ‘v3.1’ calibration release. This newest calibration release is believed to have removed the calibration faults discussed in Section 9.1 (L. Fletcher, private communication). Extraction and co-adding of this new data, as described in Section 8, will initially be necessary.

11.1 2011

11.1.1 Analysis of FIRMAP observations

Initially, the analysis discussed in Section 9 will be repeated for firmap (15 cm\(^{-1}\)) observations. As shown in Figure 14, firmap observations exhibit a better latitudinal and temporal coverage than mirmap observations (Figure 13) and in hindsight, firmap observations would have been a better choice for this preliminary study. The newest calibration release will remove the need to omit a significant number of observations due to calibration faults.

The retrievability of ethane and acetylene at such low spectral resolution will be tested. A repeat of Section 7 at this lower spectral resolution will be conducted. 15 cm\(^{-1}\) observations have been used in previous studies to retrieve the abundances of ethane, acetylene as well as propane, methylacetylene and diacetylene (Guerlet et al., 2009; Guerlet et al., 2010). This analysis will serve to sample an extensive latitude range at several different seasons.

11.1.2 Haze & Aerosol Models

The inclusion of haze or aerosol models in the retrieval algorithm will also be considered. The error estimate analysis by Fletcher et al. (2007) as discussed in Section 6.4 will be repeated in the context of retrieval of hydrocarbons. Synthetic spectra will be produced using a forward model including haze layers of different particle sizes and varying optical depths both in the troposphere and stratosphere. The retrieval algorithm discussed in Section 6 (assuming no haze or aerosols) will be applied to such synthetic spectra. The retrieved stratospheric hydrocarbons will be compared to the hydrocarbon profile used to produce the synthetic spectra to determine whether the assumption of no haze or aerosols introduces significant errors. The current retrieval algorithm already exhibits good spectral fit to the observations and it is inconceivable that inclusion of haze models would provide an even better fit. This analysis will
most likely serve as formal proof that such an assumption is valid.

11.2 2012

11.2.1 LIMBMAP analysis

An analysis of LIMBMAP observations will also be conducted. Limb observations will provide sensitivity to higher in the stratosphere (above 0.1 mbar) where photochemical models show the greatest seasonal variation. Temperature retrievals of limb observations will involve a simultaneous retrieval of the tangent height correction. A repeat of Section 7 will be conducted in accordance with this analysis to test the accuracy of the retrieval algorithm with this added step.

Limb observations will also offer the opportunity to study other trace hydrocarbon species (such as C$_3$H$_8$, CH$_3$C$_2$H and C$_4$H$_2$) whose contribution is increased at such viewing geometries and therefore are more observable.

11.2.2 Hydrocarbons in Saturn’s Recent Storm Outbreak

Hydrocarbons in Saturn’s recent outbreak of storms at mid-northern latitudes (Fletcher et al., 2011) will be analysed. The zonal profile of acetylene from retrievals of MIRMAP observations of the storm reveal a significant depletion of acetylene in comparison with retrievals of observations before the storm’s outbreak (Fletcher et al., 2011). This is considered evidence of significant upwelling from deeper in the atmosphere where acetylene is depleted. Further temporal analysis of ethane and acetylene at such latitudes will provide interesting insight into the dynamical evolution of the storm. In addition, the storm is host to temperature enhancements of up to 50 K which have allowed normally weak features of other trace, hydrocarbon species (such as C$_2$H$_4$ etc.) to become readily observable (L. Fletcher, private communication). Such hydrocarbons are normally only observable in limb spectra where the contribution of trace species is increased (Guerlet et al., 2010). The storm will offer the opportunity to study these hydrocarbons and their vertical profiles from near-nadir observations. An analysis of hydrocarbons of this storm will therefore not be restricted to only ethane and acetylene.

11.3 2013

The response of Saturn’s photochemistry to the Sun’s 11 year solar cycle will also be analysed from Cassini-CIRS observations. Forecasts of the current solar cycle ‘24’ predict solar maximum to occur
in June 2013\textsuperscript{1} with the largest increase in solar ultraviolet output occurring before the end of 2012. Cassini-CIRS observations will allow the response of the photochemistry from solar minimum in 2008 to solar maximum in 2012 to be analysed. Photochemical models (Moses & Greathouse, 2005) do show a response of the photochemistry to solar maximum which is most observable at equatorial to mid latitudes where the seasonal variations are significantly smaller. It remains to be seen whether the response of the photochemistry to the solar cycle can be disentangled from the seasonal variations.

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\footnote{http://solarscience.msfc.nasa.gov/predict.shtml}
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