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Hydrogen Sensing in Titan's Atmosphere : Motivations and Techniques

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Abstract

We summarize the observations and context for molecular hydrogen (H_2) in Titan's atmosphere where it is the third most abundant gas. Hydrogen escapes to space but is replenished by methane photochemistry. An open question is whether there are sources and/or sinks in the surface and subsurface : sources might include serpentinization reactions in the deep interior while sinks might involve reactions with acetylene mediated by chemical or even biological catalysts. Cassini data provide weak evidence of a surface sink, and also point to variations with latitude of the tropospheric hydrogen abundance, so further measurements would be of value. We demonstrate that a simple solid-state sensor can provide the required measurement precision in an oxygen-free atmosphere, and consider how measurements on a mobile platform may inform the question of sources and sinks. We underscore the importance of simultaneous methane and hydrogen measurements: whereas the stratosphere is a hydrogen source and methane sink, serpentinization could be a subsurface source of both gasses.

Introduction

Hydrogen is the third-most abundant (~0.1%) gas in Titan's atmosphere, after nitrogen (~95%) and methane (~5%). Although some early detections were reported (e.g. Trafton (1972)) which seem to have been spurious, the abundance was well-determined as 0.002 +/- 0.001 in Voyager infrared spectra by Samuelson et al. (1982). Analysis of the same data was refined by Courtin et al. (1995) to 0.001 +/- 0.0004.

This abundance reflects the balance between production and escape. Methane photolysis by ultraviolet light leads to the production of heavier organic compounds, and hydrogen. Simplistically, the light hydrogen molecules can 'easily' escape Titan's gravity (e.g. Hunten, 1973), making the photolysis process largely irreversible, although the details of the transport and loss processes are complex (e.g. Lebonnois et al., 2003; Strobel, 2010).

Even though its abundance is small, Titan's hydrogen plays a meaningful role in Titan's climate, in that N_2-H_2 absorption fills what would otherwise be a thermal window in the atmosphere (Mckay et al., 1990, 1991). Hydrogen is therefore a significant greenhouse gas that is produced by photochemistry of the main greenhouse gas (in this respect, hydrogen on Titan is analogous to ozone on Earth).

The Cassini mission yielded estimates of the hydrogen abundance at high altitudes (~1000km) via direct in-situ measurements with the Ion and Neutral Mass Spectrometer (INMS, e.g. Cui et al. (2008)). Additional measurements were made by the Huygens probe throughout its descent (~140km down to the surface at 10^{o}S) with the Gas Chromatograph Mass Spectrometer (GCMS, Niemann et al., 2010). The molecular hydrogen mole fraction was $(1.01 \pm 0.16) \times 10^{-3}$ in the atmosphere and $(9.90 \pm 0.17) \times 10^{-3}$ on the surface.

More recently, Courtin et al. (2012) found in spectra from the Cassini Composite Infrared Spectrometer (CIRS) that the latitudinal distribution of H_2 in Titan's troposphere appears to be non-uniform, with a mole fraction above 50°N larger than the globally-averaged value. This is unexpected since the lifetime of hydrogen is expected to be long, and Courtin et al. (2012) speculate that the northern hemisphere was enriched due to downwelling of hydrogen-rich stratospheric air in that winter season (the observations were acquired in 2006-2007). Courtin et al. (2012) note that the implied gradients are "not consistent with the present understanding of dynamics and chemistry in Titan's atmosphere". It seems likely that further insights may accrue from analysis of later Cassini observations.

The vertical profile of hydrogen has attracted some interest : Strobel (2010) noted that a model of photochemical production and escape could not simultaneously match the thermospheric (INMS) abundance and the stratospheric/tropospheric abundance (CIRS/GCMS) without also invoking a surface sink. Although this may be a model-dependent result , such a surface sink is at least superficially consistent with the small decline in the GCMS H_2 abundance towards the surface, and in the following section we consider possible surface sources and sinks. The measurements and processes pertaining to hydrogen are summarized in schematic form in figure 1.

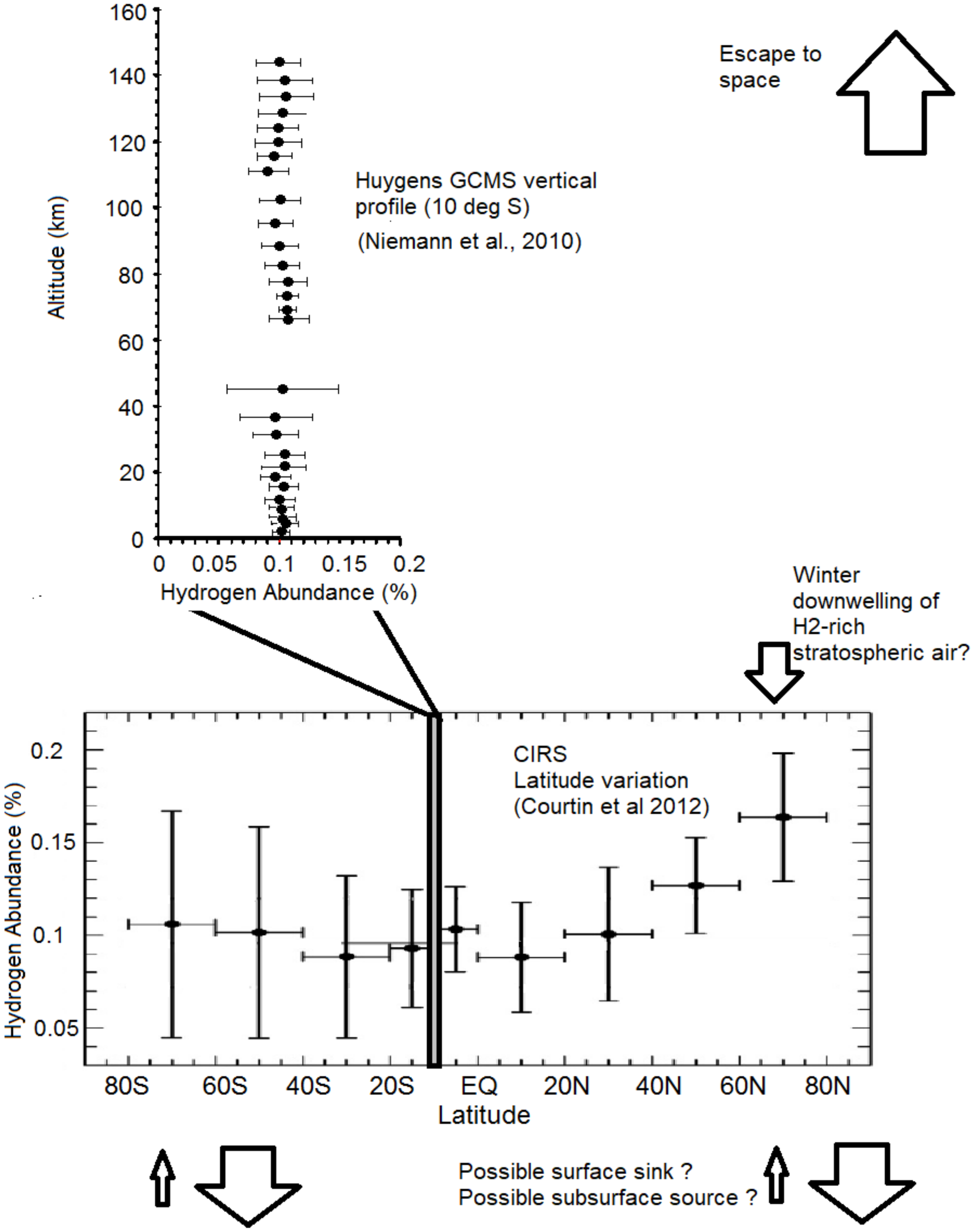

Figure 1. Summary of the observations of hydrogen abundance and the processes influencing it on Titan.

Surface Sources and Sinks for Hydrogen

The photochemical source for molecular hydrogen in the atmosphere is generally established overall as methane photolysis (although both production of H_2 molecules and removal of atomic hydrogen may occur in the process of stratospheric haze formation – e.g. Sekine et al., 2008). There is no need for a subsurface source to explain the observed hydrogen abundance (and indeed, it seems any such source must be overpowered by a stronger sink) but the observation of molecular hydrogen in the plume of Enceladus (Waite et al., 2017) suggests by analogy that Titan might nonetheless have a similar such source. Hydrogen was observed in the Enceladus plume at somewhat higher abundances (0.4-1.4%) than in Titan's atmosphere, and is presumed to have been formed by hydrothermal reactions in Enceladus' warm interior. The serpentinization reaction specifically can yield hydrogen and methane from the reaction of silicates with water and carbon dioxide, and seems consistent (Waite et al., 2017) with the methane abundance in the Enceladus plume (0.1-0.3, a H_2:CH_4 ratio of 1-14). Should such similar reactions occur on Titan – and the presumed long-term geological source of methane on Titan has not been identified – a surface hydrogen vent might be expected to also be a methane source. Serpentinization has been suggested as a possibly important process in providing available free energy for biological systems on the early Earth or Mars (e.g. Schulte et al., 2006).

As for sinks, note that the solubility of hydrogen in liquid methane and ethane is very low, and thus Titan's seas do not make an appreciable reservoir. Dobouloz et al. (1989) calculated saturation mixing ratios of hydrogen in Titan's seas as of the order of 1 ppm : roughly speaking, then, there is about 10 times less hydrogen in a cubic meter of sea liquid as there is in a cubic meter of air above it. A physical absorption onto solids (notably the haze) seems similarly to be unviable as a long-term sink.

Chemical removal of hydrogen is the most plausible sink possibility. Among a number of possible reactions, perhaps the most likely is the hydrogenation of acetylene. This reaction has the advantage that acetylene is an abundant product of photochemistry, and the reaction is exothermic, as pointed out by McKay and Smith (2006). However, the reaction is kinetically inhibited at Titan's low temperatures.

In fact, the hydrogenation of acetylene is a well-studied reaction on Earth in industrial settings (e.g. Bos and Westerterp, 1993). Specifically, the production of the plastic polyethylene from ethylene relies on catalysts for polymerization, and these catalysts are poisoned by acetylene. Unfortunately, typical ethylene feedstocks in petrochemical production are contaminated by a few per cent of acetylene, and so a means is necessary to remove this contamination prior to the polymerization step. This is typically accomplished by hydrogenation with a metal catalyst at temperatures of 400K and pressures of a few bar.

The effective removal of hydrogen at low temperatures on Titan therefore requires an efficient and unknown catalyst. If such a catalyst is nonbiological, its discovery would be of both industrial as well as planetological interest.

Another possibility, not excluded by present data, is that living processes may perform such catalysis. Indeed, kinetic inhibition of exothermic reactions is an ideal setting for life – albeit of necessity for Titan, not the water-mediated 'Life as we know it' (LAWKI). In a seminal paper that considered the range of possible chemistries for life, Benner et al. (2004) - see also Bains (2004) - speculated that hydrocarbons that are naturally liquid on Titan could be a solvent for life. Benner et al. (2004) noted that the organic reactivity in hydrocarbon solvents is no less versatile than in water, and indeed the ability to exclude water is an important aspect of many catalytic sites. Schulze-Makuch and Grinspoon (2005) and McKay and Smith (2005) noted that the photochemically produced organics in Titan’s atmosphere would produce energy if reacted with atmospheric H_2, and that this could be a source of biological energy. McKay and Smith (2005) quantified the energy released from such reactions. Hydrogenation of C_2H_2 provided a particularly energetic reaction, with 334 kJ per mole of C_2H_2 consumed. This can be compared to the minimum energy required to power methanogen growth on Earth of ~40 kJ mole^{-1}, determined by Kral et al. (1998), or the energy from the reaction of O_2 with CH_4, which produces ~900 kJ mole^{-1}. Photosynthesis has even been considered in hydrogen-rich atmospheres (Bains et al., 2014).

In addition to H_2, McKay and Smith (2005) suggested that methane-based life on Titan would also consume acetylene and ethane. There seems to be evidence for depletion of acetylene and ethane on Titan. The data that suggest that there is less ethane on Titan than expected is well established. (Lorenz et al. 2008). Photochemical models have predicted that Titan should have a layer of ethane sufficient to cover the entire surface to a thickness of many meters but Cassini has found no such layer. Clark et al. (2010) find a lack of acetylene on the surface despite its expected production in the atmosphere and subsequent deposition on the ground. There was also no evidence of acetylene in the gases released from the surface after the Huygens Probe landed (Niemann et al. 2005, Lorenz et al. 2006). Thus, the evidence for less ethane and less acetylene that expected seems clear.

Cornet et al. (2015) review photochemical models for Titan and list production rates for C_2H_2, from 0.32 to 1.2 x 10^9 cm^{-2} s^{-1} (e.g., Toublanc et al. 1995, Krasnopolsky 2009) and C_2H_6, from 1.2 to 15 x 10^9 cm^{-2} s^{-1}; thus if ~20% of the available C_2H_2 and C_2H_6 is consumed by methanogens, the corresponding H_2 consumption (10^9 cm^{-2} s^{-1}) should significantly deplete the H_2 profile in the lowest few kilometers of the atmosphere (e.g. McKay, 2016).

There is of course a rich history of considering atmospheric composition as an indicator of life (e.g. Lovelock, 1965). Whether the processes controlling the vertical profile and horizontal distribution of hydrogen on Titan are biological or only physico-chemical, the interest in exploring this compound's distribution is evident. We now consider how hydrogen variations might be determined in future missions.

Measurement Techniques - Review

A future orbiter to Titan (e.g. that studied in the 2007 Titan Flagship study, Leary et al., 2007) could carry an infrared spectrometer able to measure hydrogen abundance in the troposphere in the same way as Cassini and Voyager. An orbiter (at an altitude of e.g. 1500km) would be able to make measurements with better horizontal resolution than typical during Cassini encounters, and of course could obtain much more complete coverage in time and space. However, such remote measurements have very limited ability to discriminate vertical variations, since the weighting functions of the N_2-H_2 dimer transitions are rather broad (e.g. Courtin et al., 2012 figure 4), spanning ~half the troposphere.

In-situ missions, such as landers, aircraft and balloons have considerable appeal at Titan (e.g. Lorenz, 2000) and could provide information on much smaller scales than orbiter data. It is of course possible also to measure the hydrogen abundance on Titan with a mass spectrometer, as done on Huygens. A general challenge with mass spectrometry to measure hydrogen abundance is that hydrogen is obviously a fragmentation product of many hydrocarbons (notably methane) requiring instrument corrections (e.g. Niemann et al., 2010). A further point, related to at least some instrument designs, is that there may exist a limited dynamic range (e.g. a factor of 100) in masses that can be practicably analyzed. Hydrogen is the only molecular species (M=2) of interest below the mass of methane (M=16), yet there are likely hundreds or thousands of potential compounds of interest on Titan with masses in the hundreds or thousands. Thus designing a mass spectrometer to handle hydrogen may mean compromising its ability to study high-molecular-weight compounds. A mass spectrometer in a dense atmosphere like Titan's also requires pumping to maintain an internal vacuum, and thus it is a somewhat elaborate and resource-hungry instrument for making 'routine' monitoring measurements of hydrogen deep in the atmosphre.

The natural choice to measure hydrogen abundance in-situ on Titan is with a hydrogen sensor. Solid-state sensors that respond to the abundance of a single gas (or a limited range of species) have been used since the earliest days of solar system exploration, e.g. on the Venera probes. More recently, an amperometric oxygen sensor was flown on the Thermal and Evolved Gas Analyzer (TEGA) on Mars Polar Lander (e.g. Boynton et al., 2001) and a capacitive water vapor (i.e. humidity) probe was flown on the Phoenix Mars lander (e.g. Zent et al., 2009).

A wide range of hydrogen sensor types exist (e.g. see the review by Hubert et al., 2011). While some familiar types (e.g. the "pellistor", which relies on the catalytic combustion of gas in an oxygen-bearing atmosphere, or thermal conductivity based devices which are insufficiently sensitive to the small [sub-1%] concentrations on Titan) are unsuitable in this application, significant progress in the last couple of decades has been made in Palladium- and Platinum-based sensors. In these, hydrogen diffuses into and is accommodated in the metal lattice (effectively, hydrogen is 'soluble' in the metal – in fact, the accommodation is a two-step process, with dissociation on the palladium into hydrogen atoms being the rate-limiting step : the atomic hydrogen then diffuses into the palladium lattice, causing an expansion.) The lattice expansion manifests as changes in resistivity or work function which can be rather easily sensed by building resistors or Shottky diodes around the relevant metals. Because the absorption of hydrogen into and out of the metal is a purely physical process, it is reversible and does not rely on an oxidizing atmosphere. Indeed, such hydrogen sensors have been used to measure the purging of rocket propellant feed lines by nitrogen or helium (e.g. Hunter et al., 1998), and in equipment on the Space Station (M'Sadoques and Makel, 2005). In the following section, we describe tests of an example sensor suitable for Titan application.

Hydrogen Sensor Tests

Before contemplating use of hydrogen sensor at Titan, it is important to establish the conditions under which it may operate. It is further important to understand the specificity of the sensor, to determine in particular that the sensor does not respond significantly to variations in methane. To that end, we have conducted tests at NASA's Ames Research Center of a palladium sensor in a Titan simulation chamber. These Titan simulation facilities have been used in prior studies of Titan photochemistry, and slightly modified to test the H_2 sensor either under flow conditions using mass flow controllers or under an isolated static condition of a gas mixture. The whole chamber can be cooled down to 77 K with immersing into liquid nitrogen.

The sensor incorporates both resistive and Shottky diode elements to span a wide range of hydrogen abundance measurements (from a few ppm to 100%), but with the relatively large abundances in the present work, only the resistor output is reported here. The sensor is also equipped with a resistance temperature detector on the die itself, to permit precise closed-loop thermal control. Since the hydrogen sensor signal is a strong function of the temperature, this temperature regulation is essential. The sensor die is mounted on a PEEK (Polyether ether ketone) standoff to minimise heat leak and thus heater power, and is installed in a TO-5 can (a ~9mm diameter metal housing) with an aperture to allow gas exchange (figure 2).

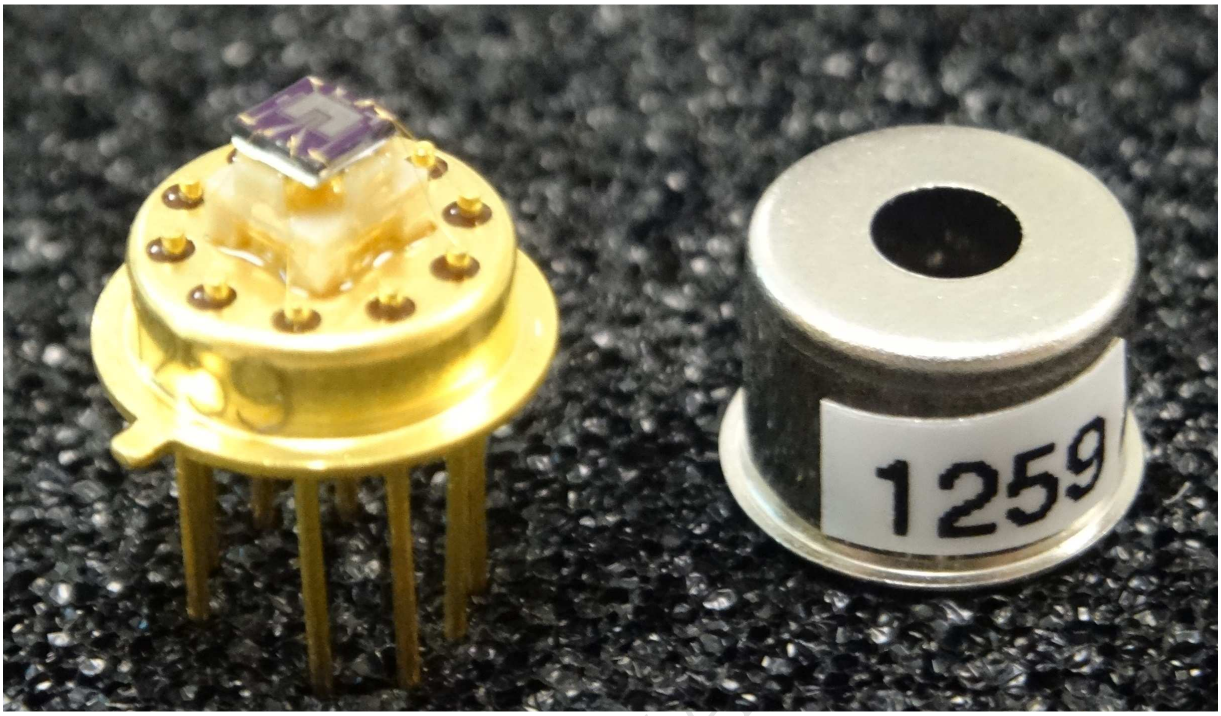

Figure 2. The sensor fabricated by Makel Engineering, Inc. for this test : the die can be seen at left on the PEEK standoff. The TO-5 housing at right is ~9mm in diameter.

Since the transducer response is based on the absorption of elemental hydrogen into the metal, it responds to the partial pressure of hydrogen, rather than the mixing ratio per se. Since total pressure is easy to measure (and varies little on Titan, for a given altitude), the partial pressure inferred from the sensor reading is readily converted into a mixing ratio. The sensor was installed in the Titan chamber (a cylindrical vessel which could be chilled) and gas mixtures delivered by a flow controller. Four different gas mixtures with various H_2 contents in nitrogen were used. Step changes in gas mixture result in corresponding changes in the sensor output (figure 3).

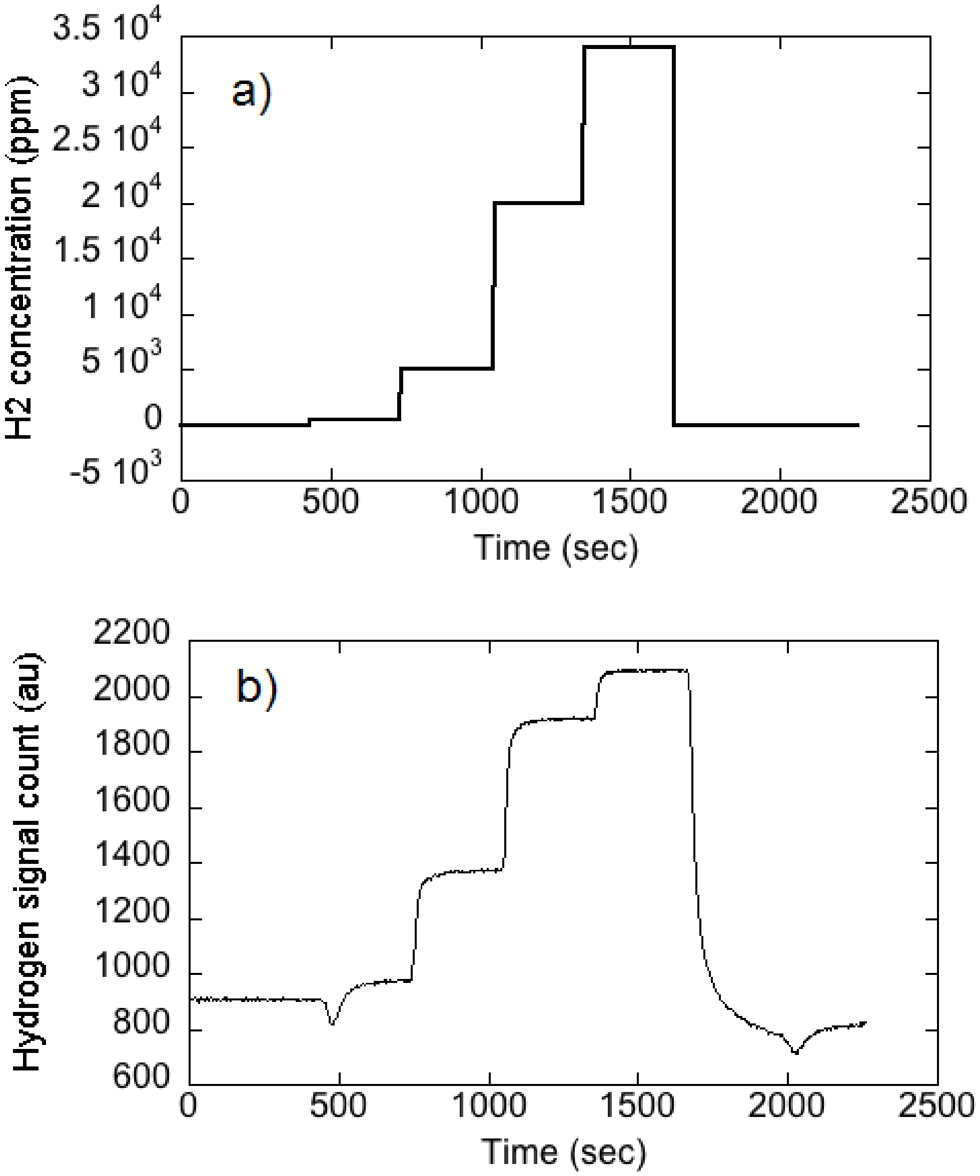

Figure 3. Sensor response (a) to step changes in hydrogen concentration (sensor at 50°C) up to a few per cent (b). In this instance the sensor reading is in counts from a 12-bit analog-to-digital converter reading a voltage formed by the Palladium resistor in a potential divider circuit, with higher counts corresponding to higher resistance and hydrogen abundance. The brief negative-going transients are test

artifacts associated with the adjustment of the nitrogen-hydrogen flow controller to maintain a constant pressure condition. The response time is approximately 40s.

As expected, the response time of the sensor is strongly temperature-dependent. The physical limitation on the process is the finite size of the transducer material, the dissociation of H_2 molecules on the surface , and the diffusion coefficient of hydrogen in the material. Manufacture as a thinner structure might improve matters, as can higher temperature operation. Measurements performed in pure H_2 flow revealed response times of ~ 40 secs at 50 °C (323 K) ~ 80 sec at 22.5 °C (295 K), and some ~250 sec at 5 °C (278 K). Clearly, operation at Titan surface temperature would be impractical, although the sensor is not adversely affected by exposure to such conditions.

The quantitative output of the device, like many solid state gas sensors, is roughly logarithmic (see figure 4). It is evident in figure 3 that the sensor responds well to 1-3% concentrations of hydrogen at 1 bar (thus an order of magnitude higher partial pressure than expected at Titan’s surface, ~ 1500 ubar, or 150 Pa). Figure 4 demonstrates that the output variation is quite measureable with 1000 ppm abundance even at 10 mbar (1 kPa) total pressure, thus 100x lower partial pressure than Titan’s surface (10 mbar corresponds to ~100km altitude on Titan). Thus this type of sensor would be useful for operation in at least the lower stratosphere of Titan during parachute descent, as well as for surface and tropospheric measurements.

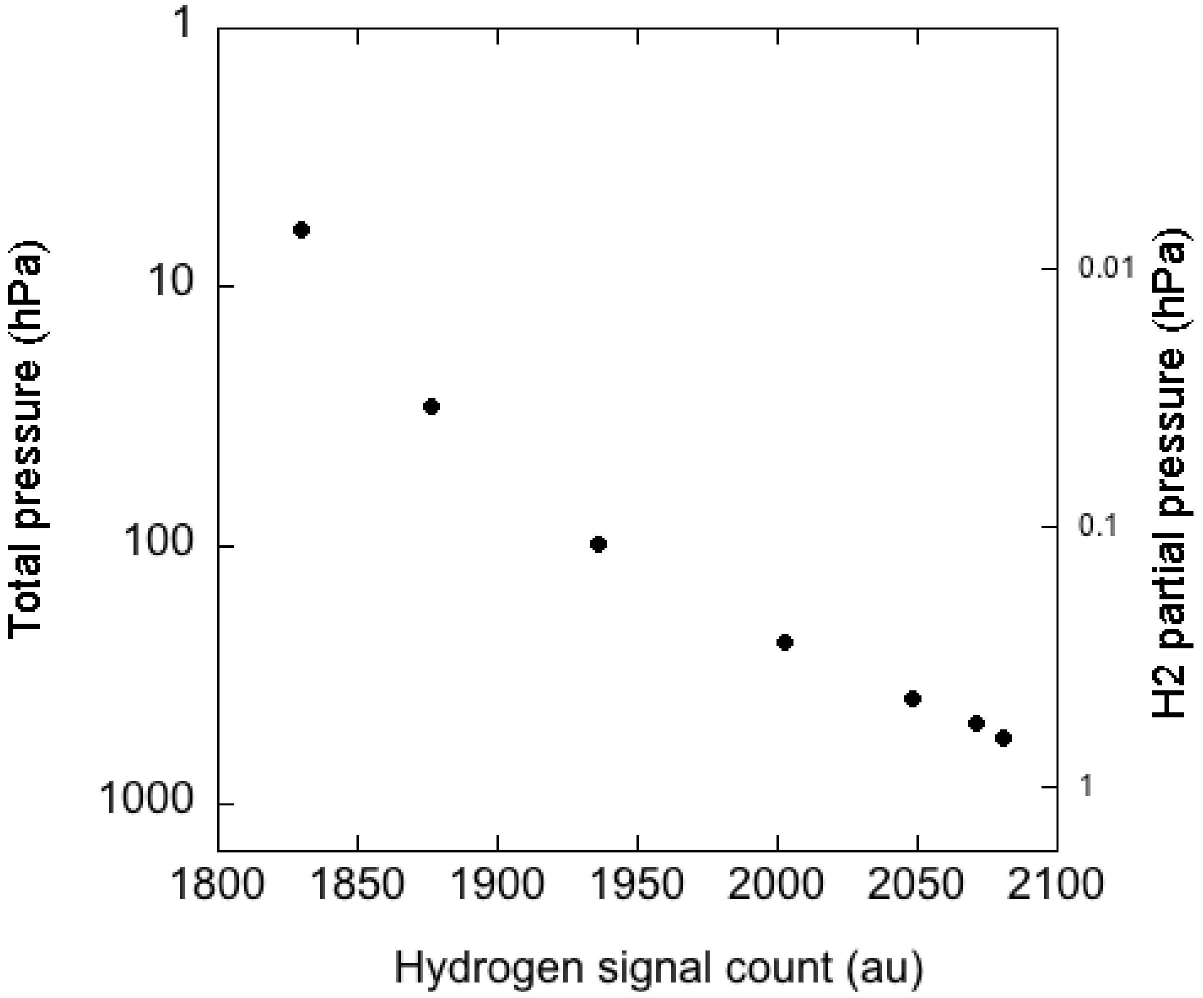

Figure 4. Output as a function of (total) pressure for a simulated Titan atmosphere (97.4% N_2, 2.7% CH_4, 1180 ppm H_2). The gas was at 77K but the sensor itself was heated to 323 K. As expected, the output is roughly logarithmic in partial pressure.

The heater power required to maintain the sensor at 323 K at 1 bar of the Titan gas mixture was 210 mW when the gas was at 77K. Reducing the operating temperature to 278 K (with a 6x penalty in response time, as indicated above) lowers the heater power requirement only to 160 mW, a rather modest saving. Thus operation at 323 K or higher is recommended. For comparison for terrestrial applications, with the gas at 278 K, sensor operation at 323 K requires only 34 mW. In steady flow conditions, the heater maintained the sensor to within about 0.1K of the set point.

Accommodation on a vehicle at Titan should shield the sensor from draughts, to prevent wind (typically 0-0.5 m/s at Titan's surface, e.g. Folkner et al., 2006; Lorenz et al., 2012) from causing fluctuations in the sensor temperature via forced convective cooling. A simple wind shield a couple of cm across (perhaps a wire mesh screen) will suffice, it being straightforward to permit an exchange time of air rapid enough not to slow the sensor response (~50s) without requiring large internal flowspeeds. Note that in the absence of wind, at least, heater power for a given pressure/temperature condition on Titan should be slightly lower than at Earth, since Titan's lower gravity will make free convective heat transfer slightly less effective (e.g. Lorenz, 2016).

Finally, we verified that the sensor (as would be expected from the sensing modality, which is specific to the small size of the hydrogen atom) had negligible sensitivity to methane variations. Note that there can be in principle (Soundarrajan and Schweighardt, 2009) some sensitivity to acetylene if the sensor is hot enough to cause dissociation at its surface, but the concentration of gaseous acetylene in Titan's lower atmosphere is only a few parts per million (e.g. Hörst, 2017). It should be noted that for this Titan application, the relative response of the sensor to hydrogen variations is in any case more important than the absolute value, in that the purpose as described in the next section is to look for gradients in abundance. A test was run wherein about 40 standard cc of nitrogen per minute (sccm) was flowed past the sensor (here at 298K) while the hydrogen flow was flipped between 1 and 2 sccm. The 'square wave' response was essentially unaffected when 2, 4 or 6 sccm of CH_4 flow was added.

As figure 5 shows, the sensor output barely changed in response to CH_4 injections, while the H_2 response was strong. Sequential hydrogen on-off readings were consistent [2016.5, 2015.8, 2013.3] and [2058.9, 2055.2, 2056.2] respectively, with standard deviations within each sample of ~3 points. The change in output driven by the large shift in CH_4 abundance is, then only ~3 points at most, comparable with the sample deviation of individual readings. This may be compared with the consistent variation in output of ~40 points associated with the hydrogen abundance variation (of a factor of ~2) – the sensitivity is at least an order of magnitude less for methane than hydrogen. Note that, as for other effects like pressure, local measurements of the methane abundance could be used to correct the sensor output in any case, although we have only been able to set an upper bound on this cross-sensitivity.

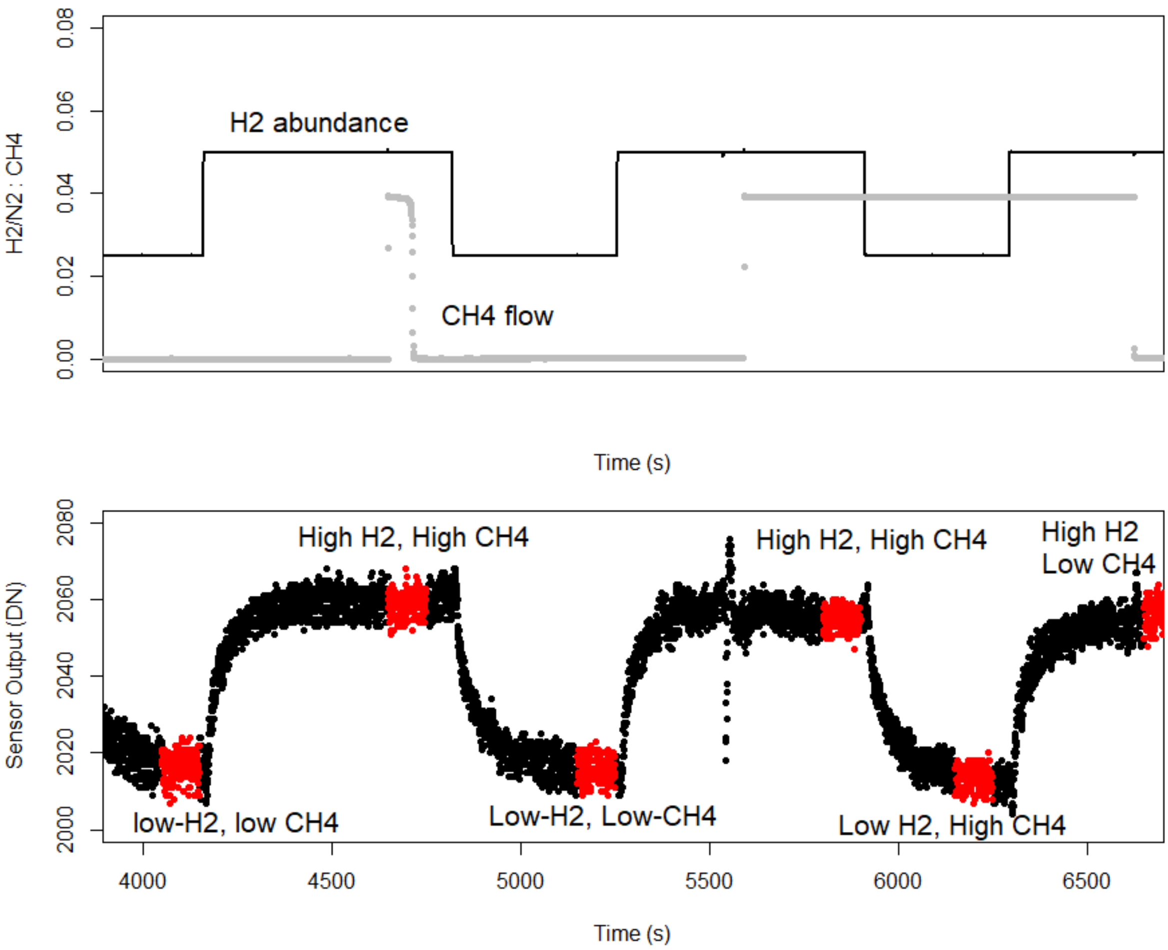

Figure 5. Sensor response to H_2 abundance, and lack of response to CH_4. Apart from a brief transient at 5550s (again, a chamber pressure artifact caused by the adjustment of the flow controller) the response to

methane is barely detectable. The red sections denote where averages and standard deviations were calculated (see text).

In-Situ Observational Strategies at Titan

The instrument at hand is a point sensor, measuring the hydrogen abundance at a single location and time. In order to determine the question of interest, whether there are sources or sinks of hydrogen in the surface, the sensor can be used in a number of ways. These modalities parallel the exploration of terrestrial gas exchanges (such as volcanic gases, or methane, radon etc.) or possible methane sources on Mars.

First, following the initial speculation of Mckay and Smith (2007), the vertical gradient in hydrogen abundance can be measured by transporting the sensor vertically. This occurs naturally during the descent of a lander or a probe, often under a parachute, but could also be accomplished repeatedly by a Montgolfiere (hot air balloon) using the 'waste' heat from a radioisotope power source and with a controlled vent to modulate its buoyancy. Heavier-than-air flight is also possible, as in the AVIATR fixed-wing concept (Barnes et al., 2012: like all long-lived in-situ exploration concepts at Titan, this would also use radioisotope power, in this instance a proposed Stirling generator).

The proposed Dragonfly relocatable rotorcraft lander (Lorenz et al., 2018; Turtle et al., 2018), currently undergoing a Phase A study for possible implementation in NASA's New Frontiers Program, is another platform that could perform hydrogen profiling. This vehicle could make repeated ascents and descents through the planetary boundary layer and thereby constrain the magnitude of surface sources or sinks of hydrogen from the same type of models explored by Strobel et al. (2010) and McKay (2016).

The relocation capability of Dragonfly allows long-term measurements on the surface at different locations. The combination of wind speed and direction knowledge from DraGMet (the Dragonfly Geophysics and Meteorology package) with hydrogen abundance would allow the identification of possible hydrogen plume sources. For example, if a feature such as an impact crater or cryovolcano were considered a possible plume source, then enhanced hydrogen abundance when the lander was downwind of the source might support that hypothesis. Relocating the lander in combination with wind direction variations would allow the structure of the plume to be understood.

A final method, used in many studies of surface-atmosphere exchange on Earth, is the eddy-covariance technique e.g. Fairall (2000). Specifically, if a vertical gradient in a mixing ratio exists, then turbulent eddies will advect parcels of air from lower and higher elevations past the sensor, whose output will therefore have short-term fluctuations. The amplitude of these fluctuations relates to the surface flux in ways that can be modelled and/or measured (specifically, a cross-correlated high resolution time series of vertical wind velocity and the hydrogen abundance would yield the flux directly : in practice vertical winds are often estimated from horizontal winds and there are limitations on the method from the finite height and finite time response of the sensor). Since the preferred sample rate for eddy flux measurements is ~10 u/z, where u is the horizontal windspeed and z the measurement height, a landed instrument should be sampled at ~10Hz, so the sensor tested here is too slow. These limitations aside, it is obvious that if there are no horizontal or vertical gradients in hydrogen abundance, the output of a fixed sensor should not exhibit fluctuations, so even low-resolution time series data provide a simple qualitative test of the possible existence of sources or sinks which can be quantified with the aid of models (e.g. as done for water vapor in the Martian surface, Savijärvi et al., 2015)

Conclusions

Our analysis of the Cassini data and theoretical models indicate that hydrogen in the lower atmosphere of Titan could be variable due atmospheric transport mechanisms, losses due to surface reactions, and subsurface sources and sinks. We conclude that detection and quantification of these hydrogen variations over spatial and temporal scales could point to new atmospheric processes, catalytic surface chemistries, and possibly biological consumption. We have identified Palladium-based hydrogen sensors as capable of making these measurement in situ. In laboratory tests with Titan-like gas mixtures we have shown specificity to hydrogen independent of nitrogen and methane and a rapid response time if heated to 50ºC. We conclude that these low mass sensors could provide a proven and robust method for in-situ determination of variation of hydrogen in Titan's lower atmosphere on future missions.

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