Detecting trace species in the Martian atmosphere with a gas correlation filter radiometer J.A. Sinclair[1], E. Wilson[2], P. G. J. Irwin[1], S. Calcutt[1], [1]Atmospheric, Oceanic & Planetary Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, United Kingdon, [2]NASA Goddard Space Flight Center, 8800 Greenbelt Rd, Greenbelt, MD, 20771

Introduction: The atmosphere of Mars may contain a number of trace gases, which currently remain undetected. Outgassing from the surface in active regions, evaporation of ices and perhaps subsurface microbial activity are thought to produce a range of trace compounds such as methane (CH_4), formaldehyde (H_2CO), and nitrous oxide (N_2O) [1,2]. Only tentative detections (or simply an upper limit estimate on concentration) have been made of these compounds previously. This is due to the challenge of detecting very minor species with a limited signal-to-noise ratio, limited spectral resolving power and/or poor discrimination between telluric and Martian features when observing from the Earth [3,4,5]. In this paper, we present the results of radiative transfer simulations in order to demonstrate the effectiveness of an alternative method for detecting trace gas species – *the gas correlation radiometer method*.

The search for methane on Mars: The search for CH_4 is highly topical since the molecule could have a biogenic origin and therefore serve as a tracer of *life* on Mars [6]. Previous detections of CH_4 on Mars estimate the concentration to be on the order of 10 ppbv with a potential latitudinal and seasonal variation of up to 50 ppbv [3,4,7,8]. However, these detections have used either ground-based measurements, where discrimation between telluric and martian feautures is a challenge, or used instruments with a limited spectral resolving power [5]. In addition, the presence of CH_4 at concentrations of this order of magnitude would have significant implications on the redox budget of the Martian atmosphere [5].

If methane is indeed present in the atmosphere of Mars, the measurement and/or detection of other trace gases would provide insight into the sources and sinks of this gas. For example, if the source of CH_4 is subsurface, water vapour would be expected to accompany plumes of CH_4 and other trace gases due to the sublimation of H_2O in the permafrost. The D/H ratio in H_2O on Mars is several factors higher than on Earth [9], varies with latitude and season [10], and is considered to be a metric of the age and depth of Martian water due to the preferential vapouratisation and escape of H_2O over HDO [11]. Measurement of the D/H ratio in H_2O in active regions may provide insight into the physical location of CH_4 production. Sulphur

dioxide (SO_2) would be expected to accompany CH_4 if the latter has a volcanic source. Subsurface bacteria in anoxic environments can produce up to four times more nitrous oxide (N_2O) compared to the same bacteria in oxygen-rich environments [12]. Thus, a detection of N_2O in addition to CH_4 would point instead towards a biogenic source of methane. Further organic compounds such as H_2CO, CH_3OH and C_2H_2 are largely produced by photodissociation and oxidation of CH_4 [2] and, therefore, would serve as secondary detections of CH_4. However, their photochemical lifetimes (on the order of 100 days) are much shorter than that of CH_4 (predicted to be on the order of 100 years) [1]. Thus, whether or not these species were detected would indicate whether the source of CH_4 is a current or past one. At present, only upper limits on the concentration of these species have been determined from previous studies [3,13]. Thus, there is significant scope to confirm the presence of methane on Mars and measure the concentrations of H_2O, HDO and other trace gases to gain clues of its source.

Gas correlation filter radiometry: A gas correlation filter radiometer could be mounted on an orbiting spacecraft to perform nadir/limb sounding or on a lander on the surface to perform solar occultation measurements. In the gas correlation filter radiometry
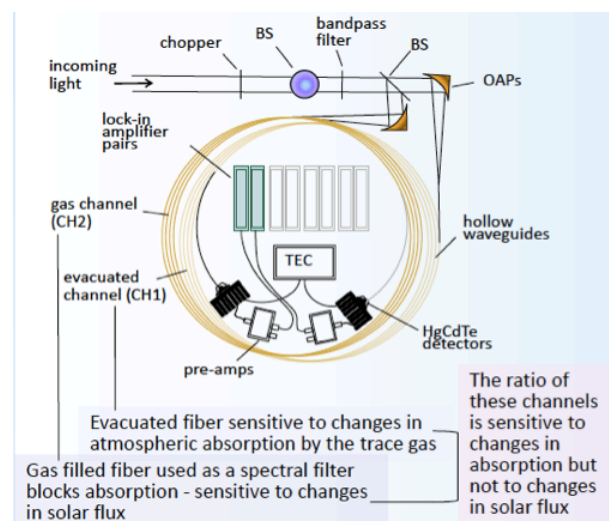

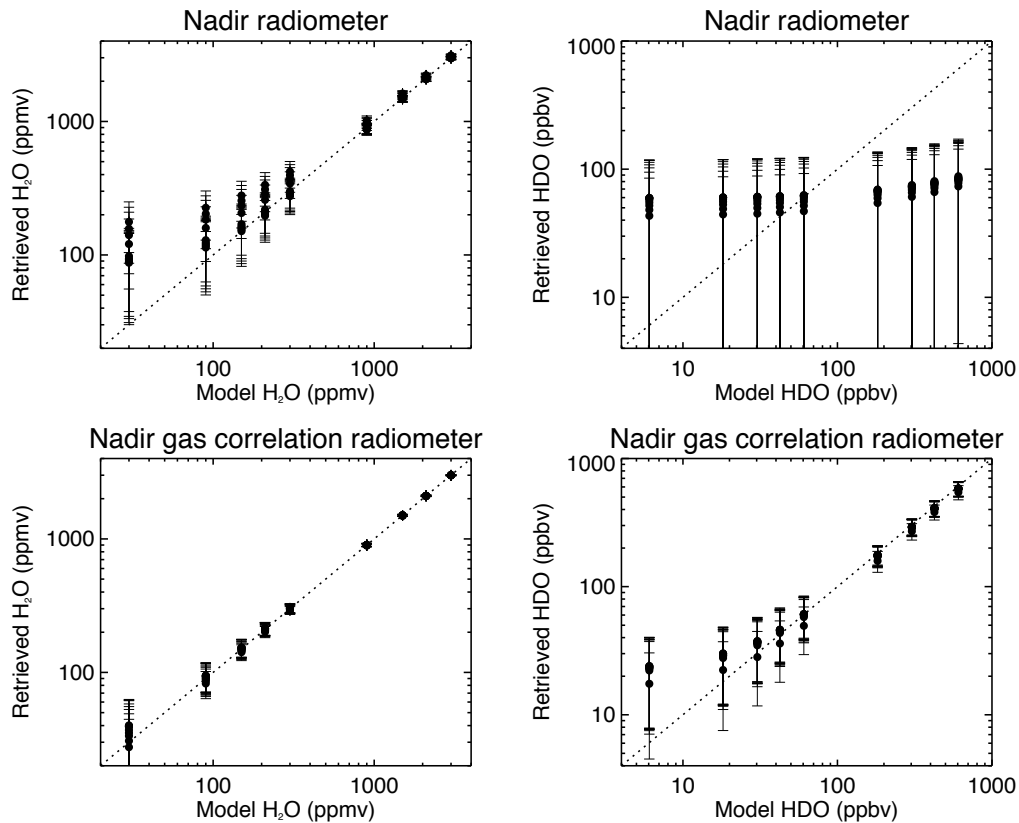**Figure 1:** The layout of a prototype gas correlation radiometer module.

Figure 2: Retrieval tests of H_2O in ppmv (left) and HDO in ppbv (right) using a nadir filter radiometer (top) and a gas correlation filter radiometer (bottom) with $\Delta v = 40$ cm^{-1} channels centred on 220 cm^{-1} and 240 cm^{-1}. In the gas correlation radiometer, a 1.5m gas cell of H_2O vapour (with a terrestrial D/H ratio) at p = 10 mbar, T = 260 K was used. The horizontal red lines indicate the *a priori* concentration used in the retrieval.

method, the planetary atmosphere is viewed through a narrow band filter covering the absorption lines of the candidate trace gas. The incident signal is then split into two optical paths – one containing an evacuated gas cell and the second containing a gas cell filled with the candidate gas – and the difference in signal (or *sideband* signal) and the average signal (*wideband* signal) between the two optical paths is measured by a detector. The first optical path measures the total signal incident from the source. In the second path, signal within the absorption lines of the candidate gas is blocked by the gas cell. Thus, the two optical paths allow a discrimination such that the magnitude of signal being absorbed by the candidate gas in the atmosphere of the planet can be calculated. Radiative transfer inversion can therefore determine the concentration of the trace gas.

This method has been proposed for measuring the concentrations of CO, O_2 and CO_2 column abundances in Earth's atmosphere [14,15]. E. L. Wilson and collaborators first suggested the application of this method to measuring trace species on Mars [16]. Figure 1

shows a prototype design of the instrument, which has been shown in laboratory testing to provide a strong sensitivity to CH_4 and H_2CO in the 3-3.5 μm range using a SiC gas lamp to simulate sunlight viewed through the Martian atmosphere [17,18]. However, the success of this method in detecting and measuring the abundances of trace gas species in the Martian atmosphere is yet to be tested.

Retrieval Tests: A radiative transfer model of the Martian atmosphere has been developed using NEMESIS [19], a forward model and inverse radiative transfer program. Radiative transfer simulations of a simple filter radiometer and a gas correlation filter radiometer were performed in order to demonstrate the performance of the latter compared to the former.

The concentrations of H_2O, HDO, CH_4, N_2O, SO_2 and H_2CO were varied and the channel-integrated radiances, using either a filter radiometer or a gas correlation radiometer, were forward-modelled under different observational geometries: 1) nadir/limb sounding from an orbiting spacecraft; or 2) solar occultation

measuments as viewed from an instrument on the surface. Noise was added to these forward models to simulate a synthetic observation. A retrieval of the concentration of a gas species was then conducted from these synthetic observations. The abundance assumed in the forward model and the retrieved abundance were then compared to demonstrate the effectiveness of each observing geometry/mode in retrieving the gas abundance.

Figure 2 compares the results of retrieval results of H_2O and HDO using a nadir radiometer and a nadir gas correlation radiometer. As shown, a radiometer alone does not offer sensitivity to H_2O below concentrations of 100 ppmv and there is very little sensitivity to HDO. However, a gas correlation radiometer, using a gas cell containing a terrestrial mixture of H_2O and HDO, greatly improves the sensitivity to both species, in particular HDO. We will present a similar analysis for CH_4, N_2O, SO_2, H_2CO, CH_3OH taking into account different Martian seasons, atmospheric dust concentrations and different observing geometries.

References: [1] Wong, A. S et al. (2003), *Journal of Geophysical Research*, 108:5026. [2] Wong, A. S. et al. (2004), *Advances in Space Research*, 33:2236-2239. [3]Villaneuva, G. L. et al. (2013), *Icarus*, 223:11-27. [4] Mumma, M. J. et al. (2009), *Science*, 323:1041- . [5] Zahnle, K. J. et al. (2010), *LPI Contributions* 1538:5570. [6] Atreya, S. K. et al. (2007), *Planetary & Space Science,* 55:358-369. [7] Formarison, V. et al. (2004), *Science*, 306:1758-1761. [8] Krasnopolsky, V. A. et al. (2004), *Icarus*, 172:537-547. [9] Krasnopolsky, V. A. et al. (1998), *Science* 280:1576-. [10] Novak, R. E. et al. (2007) *Planetary Atmospheres* 91-92. [11] Novak, R. E. et al. (2011) *Planetary and Space Science*, 59(2-3):163-168. [12] Goreau, T. J. et al. (1980), *Applied and Environmental Microbiology*, 40(3):526-532. [13] Encrenaz, T. et al. (2011), *Astronomy & Astrophysics,* 530:A37. [14] Tolton, B. T. et al. (2004), *SPIE*, 5543:332-337. [15] Bourne, J. E. et al. (2002), *SPIE,* 4710:657-665. [16] Wilson, E. L. et al. (2007), *AGU Fall Meeting Abstrsacts*, pg. A225. [17] Wilson, E. L. et al. (2011), *Measurement Science and Technology*, 22(8):085902. [18] Wilson, E. L. et al. (2012), *LPSC*, 43:163. [19] Irwin, P. G. J et al. (2008), *JQSRT*, 109:1136-1150