Herschel/HIFI observations of Mars

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LETTER TO THE EDITOR

**Herschel/HIFI observations of Mars: First detection of O_2 at submillimetre wavelengths and upper limits on HCl and H_2O_2**


(Affiliations are available on page 5 of the online edition)

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**ABSTRACT**

We report on an initial analysis of Herschel/HIFI observations of hydrogen chloride (HCl), hydrogen peroxide (H_2O_2), and molecular oxygen (O_2) in the Martian atmosphere performed on 13 and 16 April 2010 (L_σ ~ 75°). We derived a constant volume mixing ratio of 1400 ± 120 ppm for O_2 and determined upper limits of 200 ppt for HCl and 2 ppb for H_2O_2. Radiative transfer model calculations indicate that the vertical profile of O_2 may not be constant. Photochemical models determine the lowest values of H_2O_2 to be around L_σ ~ 75° but overestimate the volume mixing ratio compared to our measurements.

**Key words.** planets and satellites: atmospheres – radiative transfer – submillimeter: general – molecular processes

**1. Introduction**

Hydrogen chloride (HCl) is a reservoir of chlorine species and plays an important role in the atmospheric chemistry of Venus and Earth. Its detection by ground-based infrared spectroscopy (Iwagami et al. 2008) and space borne UV stellar occultation observations by SPICAV/SOIR on Venus Express (Bertaux et al. 2009) provide mid atmospheric mixing ratios between 0.1 and 1 ppm in the Venusian atmosphere. Submillimetre wave observations of HCl in the Earth atmosphere have long been performed from an airplane (Crewell et al. 1994; Wehr et al. 1995). The derived relative abundances are ~2 orders of magnitude smaller than in Venus (~1–3 ppb). In the Martian atmosphere HCl has not been found yet. Its detection would be an indication of present volcanic activity on Mars (Wong et al. 2003; Encrenaz et al. 2004). Krasnopolsky et al. (1997) presented a stringent upper limit of 2 ppb from high-resolution ground-based observations of Mars.

The situation is somewhat different for hydrogen peroxide (H_2O_2). It was detected for the first time in 2003 by Clancy et al. (2004) and Encrenaz et al. (2004) in the Martian atmosphere. The observed abundance varied between 20 and 40 ppb, consistent with photochemical model calculations (e.g.; Krasnopolsky 1993; Atreya & Gu 1994; Nair et al. 1994) for the northern fall season (L_σ = 206°). H_2O_2 may also be produced by electrostatic discharge reactions during dust storms, in dust devils, or during normal saltation (Atreya et al. 2006). Near the surface, the concentration could exceed 200 times that produced by photochemistry alone, enough for condensation and precipitation of H_2O_2 to occur. In its solid phase on the surface, it may be responsible for scavenging organic material from Mars and/or present a sink of methane such that a larger source is required to maintain its steady-state abundance (e.g. Mumma et al. 2009).

Oxygen was claimed to be detected for the first time in the Martian atmosphere (in addition to water) by Very (1909). It took almost 60 years until Belton & Hunten (1968) tentatively confirmed the detection of O_2 in the oxygen A band (around 763 nm) with a mixing ratio of 2600 ppm or less. They claimed that the CO/O_2 ratio was two, consistent with the assumption that both gases were produced by the decomposition of CO_2. By performing observations of the same wavelength range, Barker (1972) and Carleton & Traub (1972) found only 1300 ppm of O_2. Since Kaplan et al. (1969) had in the meanwhile reported a reliable measurement of 800 ppm of CO, they concluded that there was an additional source of O_2 namely most likely water. Molecular oxygen is a non-condensable species in the Martian atmosphere. The pressure of the Martian atmosphere oscillates annually by about a third due to the condensation and sublimation of CO_2, i.e. this variation should also appear in the O_2 volume mixing ratio. England & Hrubes (2004) reanalyzed the Viking lander data and found variations from 2500 to 3300 ppm. They point out that the 1300 ppm published by Owen et al. (1977) are not based on Viking measurements, but on the ground-based data cited above and claim that the amount of 3000 ppm is high enough to directly extract oxygen for use as...
a propellant for sample or crew return as well as for the breathing of astronauts (England & Hrubes 2001).

The observations of the HCl, H$_2$O$_2$, and O$_2$ in the Martian atmosphere are part of the Herschel key programme “Water and related chemistry in the solar system” (Hartogh et al. 2009). This paper describes the observations and data analysis and provides the volume mixing ratios of the gases and their upper limits.

### 2. Herschel/HIFI observations

The set of HIFI observations was carried out between 11 and 16 April 2010 corresponding to $L_p = 75.8^\circ$ to 78, including spectral line surveys of bands 1a – band 6b (band 5b was not available because of technical problems) and dedicated line observations of carbon monoxide and its isotopes, and water and its isotopes. The telescope was used in a dual-beam switch mode with the source placed alternatively in one of the two beams and cold sky in the other beam, a method that yields very flat baselines (de Graauw et al. 2010; Roelfsema et al. 2010). A summary of the observations is presented in Table 1. We note that Mars was not resolved, since its apparent diameter changed from 8.1 to 8.3 $^\circ$

<table>
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<th>OD</th>
<th>Obs. ID</th>
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<th>UT start date</th>
<th>Molecule</th>
<th>Transition</th>
<th>Sideband</th>
<th>Frequency [GHz]</th>
<th>Beam size [&quot;]</th>
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<td>3.4 → 2.4</td>
<td>USB</td>
<td>1876.211</td>
<td>11.3</td>
</tr>
</tbody>
</table>

### 3. Analysis and discussion

Compared to cometary observations of HIFI (Hartogh et al. 2010b; de Val-Borro et al. 2010), the baseline ripple on the Mars observations is rather large, (as frequently experienced by ground-based telescope observations of planets), because of its strong continuum emission. While in the cometary case the baseline ripple has been removed with a polynomial fit, in the case of Mars we determined the baseline frequencies by a normalized periodogram according to Lomb (1976) and subtracted them from the original spectrum. This was applied separately for horizontal and vertical polarization. After removal of the baseline ripple, both polarizations were averaged. In the case of O$_2$ observations, we found that the line strengths in both sidebands were the same, and we therefore averaged the spectra obtained in both sidebands.

The observed spectral lines were modeled using a standard radiative transfer code: Mars was assumed to be a perfect sphere surrounded by a set of a hundred concentric atmospheric layers each of 1 km thickness (compare Rengel et al. 2008). Within each layer, the atmospheric temperature, pressure, and volume mixing ratio of carbon monoxide were assumed to be constant. The surface continuum emission was modeled as black-body emission using a temperature distribution falling off towards the edge of the apparent disk according to $T(\alpha) = T_0 \times (1 - 0.2 \times (1 - \cos(\alpha)))$, with $\alpha$ running from 0–90 $^\circ$ across the apparent disk (see also Cavalié et al. 2008). The disk-averaged emission was obtained by integrating over the apparent disk using sixty four concentric rings distributed unevenly over the disk and the limb region. The variation in the path lengths through the atmosphere were fully taken into account when calculating the radiation transfer of each ring. In our model, the total continuum flux emitted by the surface depends purely on the choice of the temperature $T_0$, which defines the temperature scale for the temperature profile to be retrieved. We adjusted $T_0$ in such a way to match exactly the total flux of about 4230 Jy predicted by the “Mars continuum model” provided by Lellouch & Amri (2008).

The absorption coefficients of the spectral lines were calculated using the JPL spectral line catalog using the terrestrial isotopic ratios. Pressure broadening coefficients for HCl and H$_2$O$_2$ were available only for air, while they have been measured in the laboratory in a CO$_2$ atmosphere for O$_2$. Most lab measurements display greater pressure broadening in a CO$_2$ atmosphere. Its impact on the determination of upper limits is small. A 50%
increase in the pressure broadening coefficient leads to an increase in the upper limit of 10–20%.

For the retrieval of the mean volume mixing ratio of the three molecules, we applied the temperature profile derived from HIFI observations of $^{13}$CO and $^{12}$C$^{18}$O during OD 334 (Hartogh et al. 2010a) shown in Fig. 1.

3.1. HCl

Figure 2 shows the result of the 3746 s integration time on the 1876 GHz $^3$Cl line. We have inserted a modeled spectrum of HCl assuming a constant volume mixing ratio of 300 ppt. HCl was obviously not detected. If we define a line amplitude of $2\sigma$ as the upper limit, we derive 200 ppt for HCl. This is one order of magnitude lower than the upper limit derived by Krasnopolsky et al. (1997) from IR observations. We found no evidence of recent volcanic activity or outgassing from a hot spot on Mars. Nevertheless, the absence of HCl does not preclude extant Martian volcanic activity.

3.2. H$_2$O$_2$

Figure 3 shows the result of the $^2$H$_2$O$_2$ observation on 1847 GHz in the upper sideband. The integration time was 2505 s. The strong absorption feature is CO (16-15) line. Since the line is in the lower sideband centered around 1841 GHz, it does not absorb any features of the $^2$H$_2$O$_2$ line. We did not detect any $^2$H$_2$O$_2$. A modeled $^2$H$_2$O$_2$ spectrum with a constant volume mixing ratio of 4 ppb has been inserted into the measured spectrum. We deduced a $2\sigma$ upper limit of less than 3 ppb of $^3$H$_2$O$_2$. At first glance, this value seems far too low taking into account former observations providing 20–40 ppb (see Introduction). On the other hand $^3$H$_2$O$_2$ is connected to the water cycle and its high variability. Krasnopolsky (2009) compared the annual variability of $^3$H$_2$O$_2$ based on observations and model calculations averaged over $\pm 35^\circ$ around the subsolar latitude. Unfortunately, no other observation for $L_s = 78^\circ$ is available. The model calculations provided predictions for this season (Krasnopolsky 2006, 2009; Moudden & McConnell 2007; Lefèvre et al. 2008), but all overestimated the volume mixing ratio compared to our observation. Lefèvre et al. (2008) found about 10 ppb, Moudden & McConnell (2007) for $L_s = 90^\circ$ about 15 ppm and even the lowest value of $\sim 5$ ppb calculated by Krasnopolsky (2009) is above the upper limit of our observation. Nevertheless, the photochemical models predict lowest $^3$H$_2$O$_2$ values for the season between $L_s = 70^\circ$ and $80^\circ$. Water vapour and its photolysis products are subject to solar cycle variations (Hartogh et al. 2010c). A low Lyman-alpha flux (observations were performed shortly after the solar minimum) may be consistent with less than average production of $^3$H$_2$O$_2$ in the Martian atmosphere and explain a negative deviation from the model values.

3.3. O$_2$

The upper panel of Fig. 4 shows the HIFI observation of the 774 GHz O$_2$ line – the first submm detection of O$_2$ in Mars – and a model fit of a constant volume mixing ratio. The best fit provides a volume mixing ratio of 1400 $\pm$ 120 ppm. This value fits within the error limits to the value of 1300 ppm derived in 1972. We investigated the sensitivity of the pressure broadening coefficient to this value. We initially applied
the data from Golubiatnikov & Krupnov (2003) for O2 in air: 1.62 MHz hPa\(^{-1}\) (half width half maximum, HWHM). Taking into account the higher molecular mass of CO\(_2\) as the main collider compared with air, we multiplied the pressure broadening coefficients in 0.1 hPa steps from 1.1 to 2 and found the best fit of the model to the observation for a factor of 1.2, corresponding to 1.95 MHz hPa\(^{-1}\) (HWHM). We note that the mixing ratio was not found to be very sensitive to these changes, the retrieved value always remaining within the error limits. The pressure broadening factor of 1.2 is smaller than the factor of 1.4 (with CO\(_2\) rather than air being the main collider) for CO that has been found in laboratory measurements (e.g. Dick et al. 2009). The quality of the observation is excellent, the signal-to-noise ratio being higher than 300. Unfortunately, the fit is not optimal. The model underestimates the emission feature and overestimates the depth of the absorption peak. This indicates that the assumption of a constant volume mixing ratio may not be correct. Deviations from the constant profile seem to be positive in the lower and negative in the upper atmosphere. Future work will focus on the vertical profile of O2.

4. Summary

We have presented initial results for HIFI observations of the Martian atmosphere on HCl, H\(_2\)O\(_2\), and O\(_2\). The upper limit of 200 pptv volume mixing ratio determined for HCl is one order of magnitude below the previous value. There is no indication of present volcanic activity. The upper limit to H\(_2\)O\(_2\) of 2 ppbv is remarkably low compared with former detections. However, this observation is the first one around \(L_s = 77^\circ\), a season where photochemical models predict the annual minimum of H\(_2\)O\(_2\). Future HIFI observations of H\(_2\)O\(_2\) during other solar longitudes will provide additional constraints on photochemical models. The O\(_2\) volume mixing ratio of 1400 ± 120 ppm agrees with former ground-based observations. The assumption of a constant vertical profile does not lead to an optimal fit of the model to the observations. The residuals suggest an oxygen fall off with height. Future work will focus on the retrieval of the vertical O\(_2\) profile.

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