Ground-based high-resolution IR spectroscopy of Mars : H_2O and H_2O_2 mapping, search for CH_4, and determination of CO_2 isotopic ratios

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Introduction:

H_2O_2 has been proposed as an oxidizer of the martian regolith, which may have sterilized the soil down to a few meters below the surface (Bullock et al., 1994). In fact, photochemical models have predicted the formation of H_2O_2 in the martian atmosphere, with column densities in the range 10^{15}-10^{16} cm^{-1}. H_2O_2 is formed by the combination of 2 HO_2 radicals resulting from a reaction involving H, O_2 and CO_2 (Krasnopolsky, 1993). Since H is produced from the photolysis of water vapor, to first order, photochemical models expect H_2O and H_2O_2 abundances to be correlated, if all else were equal. Any H_2O-H_2O_2 correlation, however, is expected at a given altitude, and not necessarily in the column integrated sense.

The detection of H_2O_2 requires high-resolution spectroscopy, either in the submillimeter range or in the infrared (Encrenaz et al., 2004a). A good candidate in the IR is the ν_6 fundamental band around 8 μm. For many years, attempts to detect H_2O_2 have been unsuccessful (Krasnopolsky et al., 1997). In particular, a stringent upper limit of $9\ 10^{14}$ cm^{-2} was obtained by Encrenaz et al. (2002), for a Ls value of 112°, when the mean H_2O column density was relatively high (30 pr-μm). During the 2003 opposition, new attempts were performed. They led to the first detection of H_2O_2 by Clancy et al. (2004) in the submillimeter range, and the first mapping of H_2O_2 at 8 μm (Encrenaz et al., 2004b). These latter observations are described below, together with a mapping of H_2O, a search for CH_4 and a determination of the $^{18}O/^{17}O$ and $^{13}C/^{12}C$ in martian CO_2 (Encrenaz et al., 2005).

The 2003 observations:

Observations of Mars were carried out on June 19-20, 2003 (Ls = 209°) using the Texas Echelon Cross Echelle Spectrograph (TEXES) (Lacy et al., 2002) mounted at the 3-m NASA/Infrared Telescope Facility (IRTF). TEXES is a mid-infrared spectrograph covering the 5-25 μm range with high sptial and spectral resolution capabilities (R= 77000, pixel size = 0.3 arcsec). We scanned the northern and southern hemispheres of the planet with a 1.4 x 8 arcsec slit, oriented N-S and shifted from W to E with 0.5 arcsec steps. After binning, our spatial resolution was 1.5 arcsec. Th doppler shift was +0.045 cm^{-1}, corresponding to a martian radial velocity of –11 km /s.

H_2O_2 mapping

Two spectral ranges were covered : 1230-1236 cm^{-1} (8.09-8.13 μm) and 1237-1244 cm^{-1} (8.04-8.08 μm). About 6 transitions of H_2O_2 were identified in each spectral range. Fig. 1 shows the spectrum of Mars in the 1237-1243 cm^{-1} range, averaged over an area where the H_2O_2 line depths (in radiance units) were found to be maximum, in order to maximize the S/N ratio. This area covers the latitude range 10N-35S and the longitude range 20E-30W relative to the subsolar point. Figure 2 shows an enlargement of the 1241.5-1241.7 cm^{-1} range, which shows a doublet of H_2O_2 lines bracketing a central CO_2 martian line.

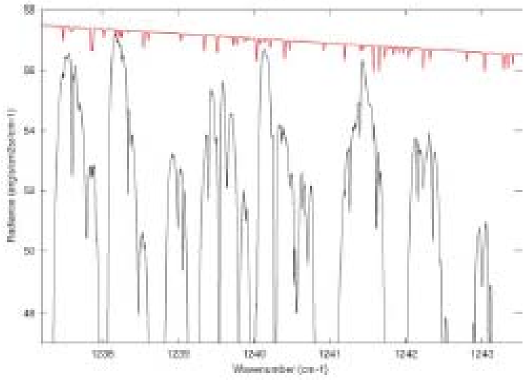

Fig. 1. The TEXES spectrum of Mars in the region of maximum S/N (surrounding the subsolar point) between 1237 and 1244 cm^{-1}. The red curve

corresponds to a synthetic spectrum of H_2O_2 for a mixing ratio of 4 10^{-8}.

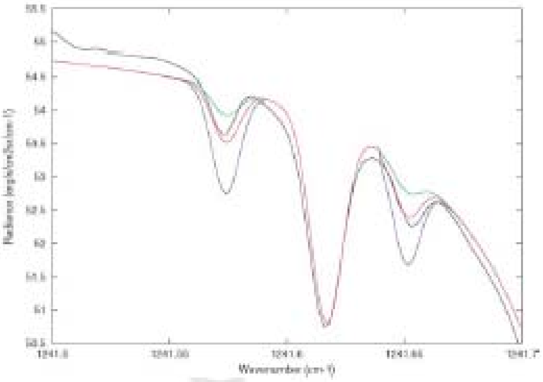

Fig. 2. Same as Fig. 1, in the range 1241.5-1241.7 cm^{-1}. Models correspond to H_2O_2 mixing ratios of 20 ppb (green), 40 ppb (red) and 80 ppb (blue).

It can be seen that the best fit is obtained for a H_2O_2 mixing ratio of 4 10^{-8}, corresponding to a column density of 7.5 10^{15} cm^{-2}. By dividing the averaged depth of the 2 H_2O_2 lines by the depth of the CO_2 line, we have mapped the H_2O_2/CO_2 mixing ratio over the martian disk. The result is shown in Fig. 3, and a comparison with the GCM predictions (Forget et al., 1999) is shown in Fig. 4. It can be seen that the overall agreement is satisfactory in terms of absolute abundances and global distribution ; both observed and computed H_2O_2 mixing ratios behave similarly in the southern hemisphere, with a maximum at the morning limb and around 20S. However, in the northern hemisphere, the model predicts a maximum of the H_2O_2 mixing ratio which does not appear in the observations ; this discrepancy remains to be understood.

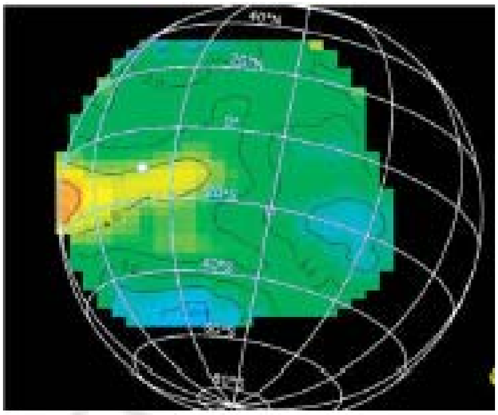

Fig. 3. Map of the H_2O_2/CO_2 mixing ratio, in multiples of 10^{-8}. The subsolar point is indicated with a white dot.

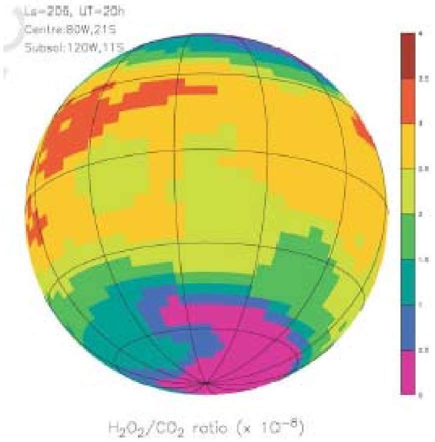

Fig.4. Map of the H_2O_2/CO_2 ratio, as modelled by the GCM for the conditions of our observations.

H_2O mapping

Fig. 5 shows an enlargement of the 1240.02-1240.06 cm^{-1} region, where a martian HDO transition appears in the wing of a stronger H_2O terrestrial absorption, after removal of this continuum with a 2nd-order polynomial. Assuming a D/H martian ratio equal to 5 times the terrestrial value (Krasnopolsky et al., 1997), we find that this line is best fitted with a H_2O mixing ratio of 3 10^{-4}. Dividing again the HDO line depth by the CO_2 line at 1241.6 cm^{-1}, we obtained the H_2O mixing ratio distribution shown in Fig. 6. Comparison with the GCM prediction (Fig. 7) shows a good agreement for both the absolute abundance and the spatial distribution.

Fig. 6

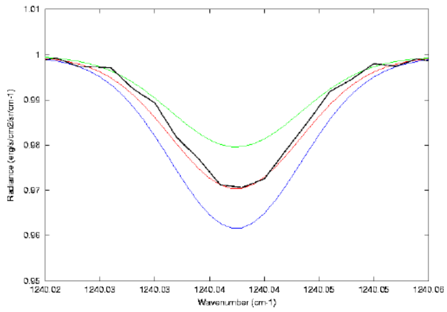

Fig. 5. The HDO martian line observed in the subsolar spectrum of Mars. Models correspond to H_2O mixing ratios of 200 ppm (green), 300 ppm (red) and 400 ppm (blue).

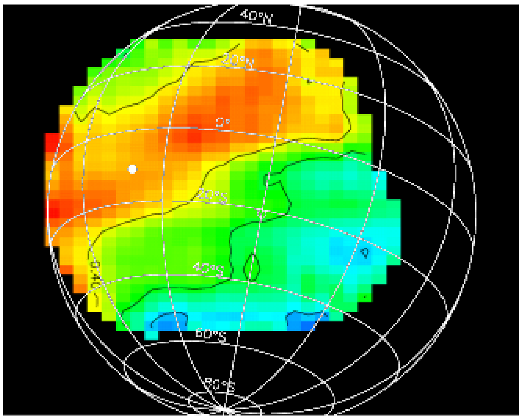

Fig. 6. Map of the H_2O/CO_2 ratio. A line depth ratio of 0.5 corresponds to a H_2O mixing ratio of 30 ppm. The subsolar point is indicated with a white dot.

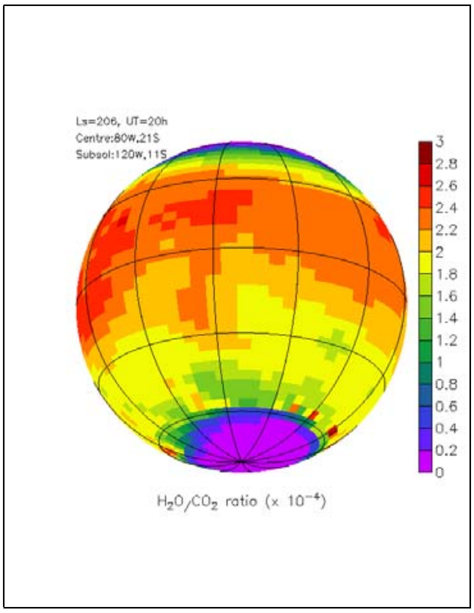

Fig. 7. Map of the H_2O mixing ratio, as modelled by the GCM under the conditions of our observations.

Search for CH4

Several strong terrestrial lines of CH_4 appear in the 1237-1244 cm^{-1} range. We have searched for a possible martian line in the blue wing of 2 of these CH_4 transitions (1242.7 cm^{-1} and 1238.7 cm^{-1}), at the expected doppler-shifted positions (Encrenaz et al., 2005). No absorption was detected over the disk. We derived, for the CH_4 mixing ratio, upper limits of 20 ppb in the morning side and 70 ppb in the evening side (the limit is less stringent in the latter case because the CO_2 lines are less contrasted). This result does not contradict previous results about a possible detection of methane (Krasnopolsky et al., 2004 ; Mumma et al., 2004, Formisano et al., 2004). In particular the region north of Hellas where a high CH_4 abundance (250 ppb) was reported by Mumma et al. (2004) was not in our field of view at the time of our observations.

Oxygen and carbon isotopes in martian CO_2

Several weak transtions of CO_2 isotopic bands appear in the spectral interval recorded by TEXES : (627) and (628) bands are present at 1237-1244 cm^{-1}, while (638) and (628) appear at 1229-1236 cm^{-1}. Using these transitions we have inferred the following results (Encrenaz et al., 2005):

$[^{18}O/^{17}O(Mars)]/[^{18}O/^{17}O(Earth)]=1.03+/-0.09$
$[^{13}C/^{12}C(Mars)]/[^{13}C/^{12}C(Earth)]=1.00+/-0.11$

These determinations are consistent with earlier in-situ measurements by Viking (Nier and McElroy, 1977 ; Owen, 1992) and show no evidence for a departure from a terrestrial value. Our $^{18}O/^{17}O$ ratio is higher than the value inferred by Krasnopolsky (1996) which implied a depletion of the heavier isotope with respect to terrestrial values. Our results are consistent with current models of the martian atmospheric evolution, and do not require any escape nor fractionation mechanism.

The 2005 observations

New measurements of Mars with TEXES have been obtained on Nov. 30 - Dec. 4, 2005 (Ls = 332°). The following spectral intervals have been recorded : 1235-1244 cm^{-1} (HDO, H_2O_2, CH_4), 1348-1354 cm^{-1} (HDO, CH_4) and 937-944 cm^{-1} ($^{18}O/^{16}O$). A preliminary reduction seems to indicate that both H_2O_2 and H_2O are globally les abundant than in 2003 by about 30-50%.

In all spectra, the CO_2 martian lines also show an interesting pecularity : in the dark side of the planet, close to the East limb (morning side), the lines appear in emission. This probably indicates a temperature inversion between the surface and the atmosphere, the surface being colder before dawn. These data wil be used to constrain the diurnal variations of the thermal profile over the martian disk.

In summary, these data illustrate the capability of ground-based high-resolution spectroscopy to detect and monitor minor atmospheric species on Mars. In the case of H_2O, these instantaneous maps provide an important complement to the long-term mapping achieved by the Mars Express instruments, and earlier by MAWD aboard Viking and TES aboard MGS.

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