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Ground-based high-resolution IR spectroscopy of Mars: H₂O and H₂O₂ mapping, search for CH₄, and determination of CO₂ isotopic ratios

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Introduction:

H₂O₂ 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 H₂O₂ in the martian atmosphere, with column densities in the range 10¹⁵-10¹⁶ cm⁻¹. H₂O₂ is formed by the combination of 2 HO₂ radicals resulting from a reaction involving H, O₂ and CO₂ (Krasnopolsky, 1993). Since H is produced from the photolysis of water vapor, to first order, photochemical models expect H₂O and H₂O₂ abundances to be correlated, if all else were equal. Any H₂O-H₂O₂ correlation, however, is expected at a given altitude, and not necessarily in the column integrated sense.

The detection of H₂O₂ 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 ν₆ fundamental band around 8 μm. For many years, attempts to detect H₂O₂ have been unsuccessful (Krasnopolsky et al., 1997). In particular, a stringent upper limit of 9 × 10¹⁴ cm⁻² was obtained by Encrenaz et al. (2002), for a Ls value of 112°, when the mean H₂O column density was relatively high (30 pr-μm). During the 2003 opposition, new attempts were performed. They led to the first detection of H₂O₂ by Clancy et al. (2004) in the submillimeter range, and the first mapping of H₂O₂ at 8 μm (Encrenaz et al., 2004b). These latter observations are described below, together with a mapping of H₂O, a search for CH₄ and a determination of the ¹⁸O/¹⁷O and ¹³C/¹²C in martian CO₂ (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 spatial 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. The doppler shift was +0.045 cm⁻¹, corresponding to a martian radial velocity of -11 km/s.

H₂O₂ 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 H₂O₂ 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 H₂O₂ 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 H₂O₂ lines bracketing a central CO₂ martian line.

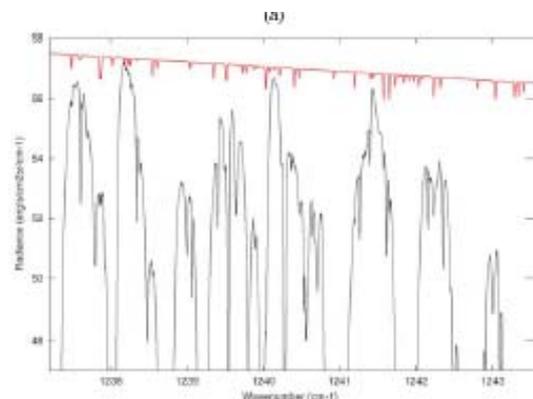


Fig. 1. The TEXES spectrum of Mars in the region of maximum S/N (surrounding the subsolar point) between 1237 and 1244 cm⁻¹. The red curve

corresponds to a synthetic spectrum of H₂O₂ for a mixing ratio of $4 \cdot 10^{-8}$.

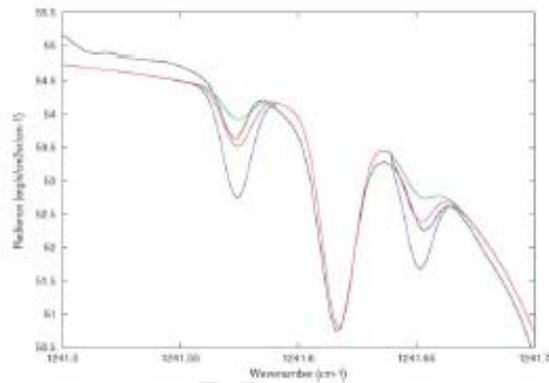


Fig. 2. Same as Fig. 1, in the range 1241.5-1241.7 cm⁻¹. Models correspond to H₂O₂ mixing ratios of 20 ppb (green), 40 ppb (red) and 80 ppb (blue).

It can be seen that the best fit is obtained for a H₂O₂ mixing ratio of $4 \cdot 10^{-8}$, corresponding to a column density of $7.5 \cdot 10^{15}$ cm⁻². By dividing the averaged depth of the 2 H₂O₂ lines by the depth of the CO₂ line, we have mapped the H₂O₂/CO₂ 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 H₂O₂ 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 H₂O₂ mixing ratio which does not appear in the observations; this discrepancy remains to be understood.

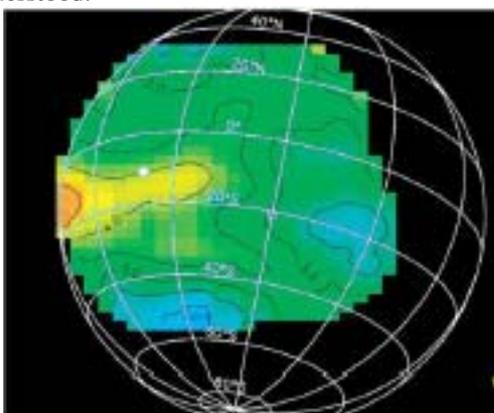


Fig. 3. Map of the H₂O₂/CO₂ mixing ratio, in multiples of 10^{-8} . The subsolar point is indicated with a white dot.

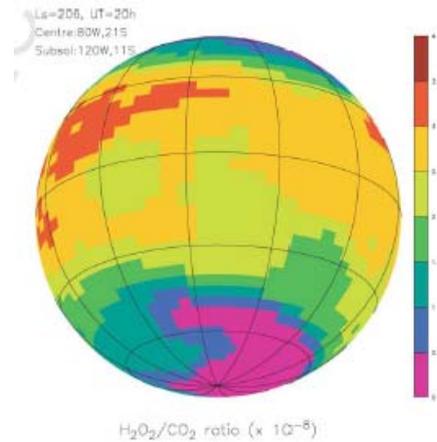


Fig. 4. Map of the H₂O₂/CO₂ ratio, as modelled by the GCM for the conditions of our observations.

H₂O 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 H₂O 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 H₂O mixing ratio of $3 \cdot 10^{-4}$. Dividing again the HDO line depth by the CO₂ line at 1241.6 cm⁻¹, we obtained the H₂O 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

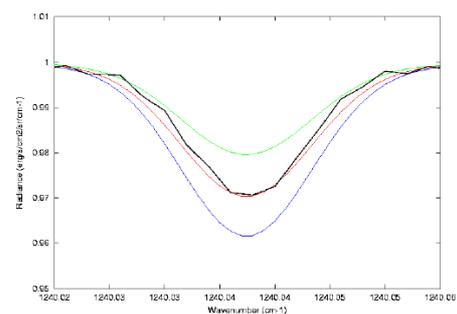


Fig. 5. The HDO martian line observed in the subsolar spectrum of Mars. Models correspond to H₂O mixing ratios of 200 ppm (green), 300 ppm (red) and 400 ppm (blue).

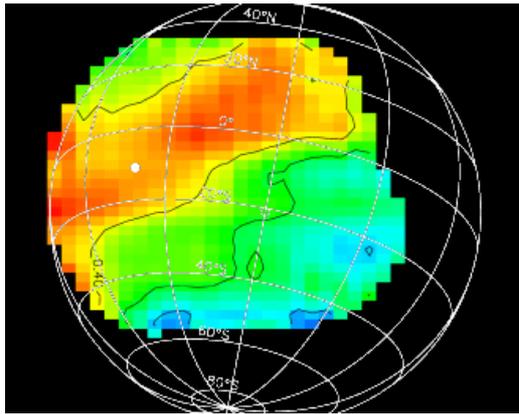


Fig. 6. Map of the H₂O/CO₂ ratio. A line depth ratio of 0.5 corresponds to a H₂O mixing ratio of 30 ppm. The subsolar point is indicated with a white dot.

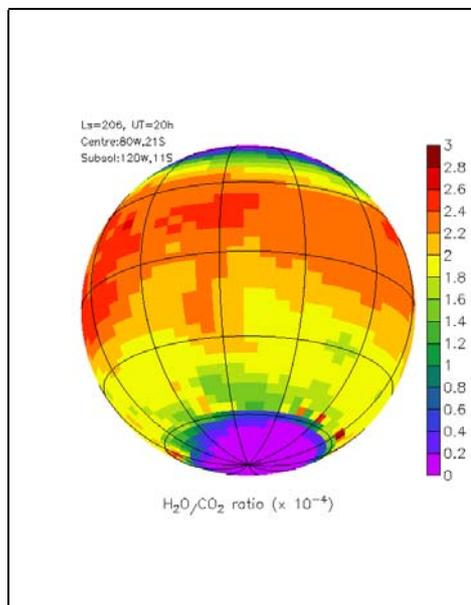


Fig. 7. Map of the H₂O mixing ratio, as modelled by the GCM under the conditions of our observations.

Search for CH₄

Several strong terrestrial lines of CH₄ appear in the 1237-1244 cm⁻¹ range. We have searched for a possible martian line in the blue wing of 2 of these CH₄ 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 CH₄ 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 CO₂ 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 CH₄ 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 CO₂

Several weak transitions of CO₂ 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):

$$[^{18}\text{O}/^{17}\text{O}(\text{Mars})]/[^{18}\text{O}/^{17}\text{O}(\text{Earth})]=1.03\pm 0.09$$

$$[^{13}\text{C}/^{12}\text{C}(\text{Mars})]/[^{13}\text{C}/^{12}\text{C}(\text{Earth})]=1.00\pm 0.11$$

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 ¹⁸O/¹⁷O 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, H₂O₂, CH₄), 1348-1354 cm⁻¹ (HDO, CH₄) and 937-944 cm⁻¹ (¹⁸O/¹⁶O). A preliminary reduction seems to indicate that both H₂O₂ and H₂O are globally less abundant than in 2003 by about 30-50%.

In all spectra, the CO₂ martian lines also show an interesting peculiarity : 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 will 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 H₂O, 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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