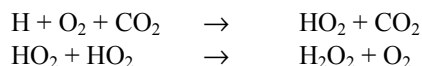


A STRINGENT UPPER LIMIT OF THE H₂O₂ ABUNDANCE IN THE MARTIAN ATMOSPHERE

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INTRODUCTION:

Hydrogen peroxide, H₂O₂, is an important product of odd-hydrogen chemistry in the Martian atmosphere (Parkinson and Hunten, 1972). Its formation is believed to come from the combination of two HO₂ radicals :



As a result, H₂O₂ is expected to be globally correlated with H₂O

The presence of H₂O₂ at the Martian surface has been suggested as a possible interpretation of the positive response of the Viking Labeled Release life science experiment (Levin and Staat, 1988; Hugenin, 1982)

However, H₂O₂ has never been detected so far. An upper limit of $1.5 \cdot 10^{-7}$ was derived by Bjoraker et al. (1987) using infrared high-resolution spectroscopy around 8 μm . This limit was later lowered down to $3 \cdot 10^{-8}$ (or $7.5 \cdot 10^{15} \text{ cm}^{-2}$) for $L_s = 222^\circ$ and $[\text{H}_2\text{O}] = 10 \text{ pr-}\mu\text{m}$ by Krasnopolsky et al.(1997) using the same technique. This value was still compatible with the predictions of current photochemical models, using globally-averaged conditions, and a mean water vapor column density of 10 pr- μm (Krasnopolsky, 1993, 1995 ; Atreya and Gu, 1994 ; Nair et al., 1994).

SEARCH FOR H₂O₂ WITH TEXES/IRTF

On February 2-3, 2001, we used the TEXES high-resolution mid-IR grating spectrograph at the 3m-NASA Infrared Telescope Facility (IRTF) (Lacy et al., 2002) to search for H₂O₂ in the Martian atmosphere. The selected spectral range was 1226-1236 cm^{-1} and the spectral resolution was 0.017 cm^{-1} . The pixel size was 0.3 arcsec.

At the date of observation, the L_s value was 112° . The Sub-Earth-Point latitude was $+12^\circ$, and the Sub-Solar-Point latitude was $+24^\circ$. These conditions were thus optimized to search for H₂O₂, as the water vapor content was expected to be maximum in the northern hemisphere.

The Mars diameter was 6.4 arcsec. We positioned

the slit (of 6 arcsec length and 1.1 arcsec width) toward the northern hemisphere in order to include the northern limb. As the data were obtained in the middle of a Jupiter run, the slit angle (-12°), however, was not optimized, as it corresponded to the Jupiter polar axis direction, while the north polar angle of Mars was 37° .

Two series of data were obtained, the first one of 7 minutes, with the slit in a fixed position (Feb. 2, 2001), and the second one of 8 minutes, with the slit scanning the northern hemisphere (Feb. 3, 2001). No H₂O₂ spectral signature was detected. We made 3 sets of summations according to the latitudinal range: 10N-40N, 40N-60N and 0-90N.

DATA ANALYSIS AND MODELLING

The synthetic spectrum of Mars at 1226-1236 cm^{-1} has been modelled using atmospheric parameters inferred from the fit of CO₂ lines. A mean surface pressure of 7 mbar was used. The thermal profile was described by 3 parameters, the surface pressure T_s , the temperature at $z = 0 \text{ km}(T_0)$ and the temperature at $z=20 \text{ km}(T_{20})$. These parameters are indicated in Table 1. Six H₂O₂ transitions, free from CO₂ absorption, have been selected. The Mars spectra around these frequencies, taken over a bandwidth of 0.07 cm^{-1} , have been co-added and compared to the synthetic model. The H₂O₂ upper limits were derived from a second-order polynomial fit.

Our results ($2\text{-}\sigma$ upper limits) are summarized in Table 1.

Table 1

Data set	1	2	3
Date	Feb. 2, 01	Feb. 3, 01	Feb. 3, 01
Time	16 :32 UT	16 :47 UT	16 :47 UT
Obs. time (s)	2332	1134	648
Latitude range	10N-40N	0-90N	40N-60N
[H ₂ O](pr- μm)	20	30	40
T_s (K)	240	230	230
T_0 (K)	235	225	225
T_{20} (K)	180	170	170
Air mass factor	1.25	1.6	1.6
Mean $q(\text{H}_2\text{O}_2)$	$6 \cdot 10^{-9}$	$4 \cdot 10^{-9}$	$6 \cdot 10^{-9}$
$N(\text{H}_2\text{O}_2)(\text{cm}^{-2})$	$1.2 \cdot 10^{15}$	$9 \cdot 10^{14}$	$1.1 \cdot 10^{15}$

It should be noted that our determination is not sensitive to the vertical distribution of H₂O₂. The column density is the only retrieved parameter.

Our lowest upper limit (0-90N) is 8 times lower than the upper limit of Krasnopolsky et al., 1997 ($[H_2O_2] < 3 \cdot 10^{-8}$ (2- σ) for a mean H₂O abundance of 10 pr- μ m). It is also significantly lower (by a factor of 2.5 to 10) than the predictions derived from current global 1-D photochemical models : Shimazaki, 1989 ($2.2 \cdot 10^{15}$ cm⁻²) ; Krasnopolsky, 1993 ($3.8 \cdot 10^{15}$ cm⁻²) ; Nair et al., 1994 ($2.4 \cdot 10^{15}$ cm⁻²) ; Atreya and Gu, 1994 (10^{16} cm⁻²) ; Krasnopolski, 1995 ($4-6 \cdot 10^{15}$ cm⁻²) ; Clancy and Nair, 1996 (10^{16} cm⁻², i.e. $2 \cdot 10^{-9}$ @ 20 km)

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A NEW PHOTOCHEMICAL MODEL

We have developed a new photochemical model which takes into account the exact geometry, season and insolation of our observations.

-Effect of low dust opacity :

If $\tau_D = 0.2$ (usually 0.4 in global models), then the H₂O₂ abundance is reduced by 20%

-Change in the eddy diffusion coefficient :

If $K = 10^7$ cm²s⁻¹ (usually 10^6), then the H₂O₂ abundance is reduced by a factor 2

-Re-assessment of the rate constant of the HO₂ -> H₂O₂ reaction :

This effect reduces the H₂O₂ abundance by 25%

-Use of the upper bound of the constant for HO₂ + OH reaction (removal mechanism for HO₂): then H₂O₂ is reduced by 25%

With all these changes, our new photochemical model predicts an H₂O₂ abundance of $1.3 - 1.5 \cdot 10^{15}$ cm⁻² (about 1.5 times higher than our upper limits).

CONCLUSIONS

Our upper limit of H₂O₂ is now below all "global" photochemical models (H₂O = 10 pr- μ m), while our measurement corresponds to conditions of maximum H₂O abundance. Adjusting atmospheric parameters (using in particular a high K value) allows to lower the H₂O₂ abundance in the models.

Observational constraints combined with a complete photochemistry-dynamics model would be helpful in a better understanding of the composition, structure and evolution of the Martian atmosphere.

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