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A map of $D/H$ on Mars in the thermal infrared using EXES aboard SOFIA


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ABSTRACT

On a planetary scale, the $D/H$ ratio on Mars is a key diagnostic for understanding the past history of water on the planet; locally, it can help to constrain the sources and sinks of water vapor through the monitoring of condensation and sublimation processes. To obtain simultaneous measurements of $H_2O$ and HDO lines, we have used the Echelle Cross Echelle Spectrograph (EXES) instrument aboard the Stratospheric Observatory for Infrared Astronomy (SOFIA) facility to map the abundances of these two species over the Martian disk. High-resolution spectra ($R=6\times10^4$) were recorded in the 1383–1390 cm$^{-1}$ range (7.2 $\mu$m) on April 08, 2014. Mars was very close to opposition and near northern summer solstice ($L_s=113^\circ$). Maps of the $H_2O$ and HDO mixing ratios were retrieved from the line depth ratios of weak $H_2O$ and HDO transitions divided by a weak CO$_2$ line. As expected for this season, the $H_2O$ and HDO maps show a distinct enhancement toward polar regions, and their mixing ratios are consistent with previous measurements and with predictions by the global climate models, except at the north pole where the EXES values are weaker. We derive a disk-integrated $D/H$ ratio of 6.8 ($^{+1.6}_{-1.0}$) $\times 10^{-4}$. It is higher than the value in Earth’s oceans by a factor 4.4 ($^{+1.0}_{-0.6}$). The $D/H$ map also shows an enhancement from southern to northern latitudes, with values ranging from about 3.5 times to 6.0 times the VSMOW (Vienna standard mean ocean water) value. The $D/H$ distribution shows a depletion over the Tharsis mountains and is consistent with observed latitudinal variations. The variations in $D/H$ with latitude and altitude agree with the models and with the isotope fractionation expected from condensation and sublimation processes.

Key words. planets and satellites: atmospheres – planets and satellites: composition – planets and satellites: terrestrial planets – infrared: planetary systems

1. Introduction

Measuring the $D/H$ ratio in the Martian atmosphere is important for two reasons. On a global scale, the disk-integrated estimate of this ratio, compared with its value in past measurements in the most ancient SNC meteorites and/or in clays at the Martian surface is a tracer of the abundance of the early content of water on Mars (Greenwood et al. 2008; Mahaffy et al. 2015). Indeed, the main mechanism responsible for the deuterium enrichment in the Martian atmosphere is expected to be fractionation through differential escape rates, the HDO molecule being heavier than $H_2O$ and confined at low altitude by condensation (Bertaux & Montmessin 2001).

The HDO molecule was first detected on Mars by Owen et al. (1988) who from near-infrared ground-based observations inferred a disk-averaged ratio for $D/H$ in water enriched by a factor of $6^{+/-3}$ relative to the value in Earth’s oceans (the VSMOW is $1.556 \times 10^{-4}$). The second measurement of $D/H$ in Mars water (from the Kuiper Airborne Observatory) sampled CO$_2$, HDO, and $H_2O$ simultaneously in the 2.7 $\mu$m region and found that $D/H$ was enriched by a factor of $5.2^{+1/-0.2}$ relative to the VSMOW (Bjoraker et al. 1989). Again in the near-infrared range, Krasnopolsky et al. (1997) inferred a $D/H$ enrichment of $5.2^{+1/-0.2}$ times the VSMOW. Encrenaz et al. (1991, 2001) detected HDO in the millimeter range and derived a $D/H$ ratio of six ($^{+6}_{-3}$) times the VSMOW in the northern hemisphere at northern summer solstice.

Attempts to map $D/H$ on Mars as a function of location, altitude, and season were reported by Mumma et al. (2003) using data from 1997 through 2000 and by Novak et al. (2011) using data obtained from 2008 to 2010. They were completed by Villanueva et al. (2015), who mapped $D/H$ over a broad latitude range between the northern spring equinox and the northern summer solstice. From data obtained between 2007 and 2015, Krasnopolsky (2015) also recorded latitudinal variations of $D/H$ for different times around northern spring.

As discussed by Owen et al. (1988) and Owen (1992), a deuteron enrichment of $5 \times$ VSMOW or greater, compared to the terrestrial value, requires the destruction and escape of most of the water originally present on the Martian surface. This process, however, would imply that the early hydrogen escape was much faster than observed today (McElroy et al. 1977). Another open question is related to the very large amount of liquid water apparently required to account for the erosional features observed on...
the surface of Mars. These results have been discussed by several authors (Carr 1986, 1990, 1996; Jakosky 1990; Krasnopolsky et al. 1997; Lasue et al. 2013; Wordsworth et al. 2015).

In their recent analysis, Villanueva et al. (2015) estimate the water amount contained in the initial reservoir $M_B$ using the following equation:

$$M_B/M_C = [l_C/l_P] \exp[1/(1-f)]$$

where $M_C$ is the current water reservoir, $l_P$ and $l_C$ are the initial and current isotopic ratios, respectively, and $f$ is the fractionation escape rate. Using $f = 0.02$ from L1 observations measurements by Krasnopolsky et al. (1998), $l_C = 8$ and $l_P = 1.275$ (using the SNC meteorite analysis of Usui et al. 2012), the authors derive $[l_P/l_C] = 6.4$. Using for $M_C$, a value of 21 m GEL (global equivalent layer) inferred from the polar layered deposits by Zuber et al. (1998) and Plaut et al. (2007), they derive an initial water reservoir of 137 m GEL. This result is consistent with the idea of an ancient northern ocean covering about 20% of the Martian surface, as also suggested by the MARSIS radar observations of Mars Express (Mouginot et al. 2012).

Another estimate of the lost water is derived by Krasnopolsky (2015), who infers a value of 80 m GEL from an update of earlier analyses (Krasnopolsky & Feldman 2001; Krasnopolsky 2002). Krasnopolsky (2015) also suggests that, because the liquid water ocean may be insufficient to drive hydrodynamical escape, another more efficient hydrodynamical mechanism could be the escape of hydrogen released in the reaction of water with iron just after the planet’s accretion. Using a fractionation factor of 0.8 in this case (Zahnle et al. 1990), an initial water abundance of 1200 m is inferred by Krasnopolsky (2015), confirming an earlier analysis by Krasnopolsky & Feldman (2001).

An important result is the measurement by the SAM (sample analysis at Mars) experiment aboard the Curiosity rover on ancient clays, aged about 3 Ga. The inferred D/H value, 3.0+/-0.2 times the VSMOW (Mahaffy et al. 2015), is intermediate between the primordial and present values, which suggests a continuous hydrogen escape over the history of the planet. However, the analysis of ancient SNC meteorites (in particular D/H = 4 VSMOW in ALH84001, aged over 4 Gy; Greenberg et al. 2008) instead suggested an early massive outgassing (Boctor et al. 2003; Greenwood et al. 2008). Thus, the history of water outgassing on Mars is still an open question.

On a local scale, the measurement of D/H on Mars as a function of latitude, location, and season can provide important constraints on the mechanisms responsible for the sources and sinks of water vapor on the Martian surface. The main mechanism is the so-called vapor pressure isotopic effect (VPIE), a fractionation mechanism associated with condensation/sublimation processes. At thermochemical equilibrium, the HDO/H$_2$O ratio in ice, as compared with the gas phase, decreases as temperature increases (Merlivat & Leaf 1967). At condensation, D/H is thus enriched in the ice phase, as compared with the gas phase. The D/H ratio in water vapor is expected to be maximum at the north pole at northern summer solstice, following the massive outgassing of the northern water ice cap. In the same way, this ratio is expected to increase with the water vapor content and with the temperature, as condensation effects are minimized in this case. This behavior has been modeled by Fouche & Lellouch (2000) and introduced in the GCM by Montmessin et al. (2005). The positive correlation of D/H with the temperature and the water vapor content has been confirmed by the observations of Villanueva et al. (2015) and Krasnopolsky (2015).

Ground-based observations of Mars water are limited to times of adequate Doppler shift (generally greater than 10 km s$^{-1}$), but also permit much higher angular resolution and more frequent observations than are feasible with airborne observatories. On the other hand, they cannot be performed near opposition when the size of Mars is maximum, since the Doppler shift is then close to zero. The high-resolution cross-dispersed infrared spectrometers permit simultaneous detections and mapping of multiple species, including CO$_2$, H$_2$O, and HDO. In particular, the Echelon Cross Echelle Spectrograph (EXES) instrument aboard the Stratospheric Observatory for Infrared Astronomy (SOFIA) facility offers this possibility.

We used this instrument during its commissioning flight on April 8, 2014. A short spectral interval at 1383–1390 cm$^{-1}$ (7.2 μm) was recorded over the Martian disk at high spectral resolution ($R = 6 \times 10^4$). The line depths of weak transitions of H$_2$O and HDO were divided by the line depth of a weak CO$_2$ transition in order to retrieve the H$_2$O and HDO mixing ratios over the Martian disk. Such a method was successfully used with the Texas Echelon Cross Echelle Spectrograph (TEXES) instrument, mounted at the InfraRed Telescope Facility (IRTF), to retrieve the H$_2$O and HDO mixing ratios on Mars (Encrenaz et al. 2004, 2012, 2015). The D/H ratio is derived by ratioing the HDO and H$_2$O mixing ratios, taking into account that the D/H ratio is one-half of the HDO/H$_2$O value. In this specific case, the analysis can be done independently of the atmospheric structure retrieval. Indeed it has been shown (Encrenaz et al. 2015) that, for all thermal pro- files expected during daily conditions (which corresponds to the EXES observations), the line depth ratios (or their equivalent widths, which give a similar result) provide a good estimate of the mixing ratio of the two species considered; thus, measuring the line depth ratio (or the equivalent width) HDO/H$_2$O leads to a good estimate of D/H. In our analysis, however, we also get estimates of the H$_2$O/CO$_2$ and HDO/CO$_2$ mixing ratios independently, in order to check the consistency of our results with respect to previous observations and models.

In this paper, we present the analysis of the EXES spectra of Mars. Section 2 describes the observations and the radiative transfer model used in our analysis. Section 3 describes the retrieval of the terrestrial atmospheric transmission associated with our observations, a key parameter in our retrieval of the mixing ratios of H$_2$O and HDO on Mars. The results are presented in Sect. 4. The validity of the linearity method is discussed in Sect. 5, and uncertainties are estimated in Sect. 6. Our results are discussed in Sect. 7 and compared with other observations and models.

2. Observations and modeling

2.1. Observations

EXES is an infrared imaging spectrometer derived from the TEXES instrument in operation at the NASA IRTF (Lacy et al. 2002). EXES operates between 4.5 and 28.3 μm (350–2220 cm$^{-1}$) in three different modes: high resolution ($R = 50 000–100 000$), medium resolution ($R = 5000–20 000$), and low resolution ($R = 1000–3000$). The instrument is equipped with a $1024 \times 1024$ Si:As detector array. The high-resolution mode is provided by a steeply blazed aluminum reflection grating used as an echelon, associated with an echelle grating to cross-disperse the spectrum (Richter et al. 2010).

We selected the 1383–1390 cm$^{-1}$ interval because it contains both weak and strong transitions of H$_2$O, HDO, and CO$_2$. We used the instrument in the high-resolution mode. Observations
of Mars took place on April 8, 2014. SOFIA was flying at an altitude of 11.58 km. Mars was very close to opposition with a diameter of 15.07 arcsec, an illumination factor of 99.98%, and a Doppler velocity of \(-2.70\) km s\(^{-1}\). The season was just after northern summer solstice (Ls = 113\(^\circ\)), corresponding to a maximum amount of water vapor in the northern region. The latitude and longitude of the disk center were 21.6 N and 205.0 E, respectively. The coordinates of the subsolar point were 23.0 N and 204.8 E. It must be noted that, unfortunately, the image quality of the SOFIA telescope is limited to about 3 arcsec. The slit was oriented at a position angle of 332 east of north and had a length of 14.2 arcsec (0.206 arcsec/pix) and a width of 1.44 arcsec. Because of the large size of the planet, we recorded two successive maps of the planetary disk: contributions from CO\(_2\), H\(_2\)O, and HDO mixing ratios.

The retrieval of the H\(_2\)O and HDO mixing ratios on Mars critically depends upon the precise measurement of the terrestrial absorption contribution in the weak transitions used in our analysis. To obtain a precise measurement of the terrestrial contribution in these H\(_2\)O and HDO lines, we model the Earth’s atmosphere and adjust the terrestrial temperature, pressure, and water content to obtain the best fit of the strong terrestrial absorption at 1386–1388 cm\(^{-1}\). This method can be used because (1) H\(_2\)O is the main absorber in the telluric absorption; and (2) in this spectral range, the contribution of the Martian spectrum is very small as compared to the terrestrial absorption. For comparison with the EXES data, we use the integrated spectrum of Mars shown in Figs. 1 and 2 (after removal of the scattered component), in order to optimize its signal-to-noise ratio. The integrated spectrum can be used for this purpose because the terrestrial opacity is not expected to vary over the Martian disk.

### 2.2. Atmospheric modeling

To model the Martian synthetic spectrum, we use the radiative transfer code developed for our analysis of the TEXES data of Mars (Encrenaz et al. 2004, 2012, 2015). Spectroscopic data are extracted from the GEISA molecular database (Jacquinet-Husson et al. 2008). In the case of CO\(_2\), the
self-broadening coefficients of the lines are given in the GEISA table. To account for their variation in temperature, we use the calculations of Rosenmann et al. (1988). In the case of H$_2$O and HDO, we use their broadening coefficients by CO$_2$ and their temperature dependences as described in Delaye et al. (1989).

Table 1 shows the spectroscopic parameters of weak transitions of CO$_2$, H$_2$O and HDO in the 1387.8−1389.2 cm$^{-1}$ range that are used in our calculations to map the species and to fit the spectra. As shown in Fig. 2, there is one available H$_2$O line at 1388.48 cm$^{-1}$, and there are two available HDO lines, at 1387.98 cm$^{-1}$ and 1389.13 cm$^{-1}$. At the positions of the two HDO lines, our inferred transmission function indicates comparable absorptions; however, the standard atmospheric transmission curve indicates a stronger absorption at 1387.98 cm$^{-1}$ than at 1389.13 cm$^{-1}$, which indicates the possible presence of another contribution in the Earth atmosphere. Indeed, the EXES spectra show that the HDO line at 1387.98 cm$^{-1}$ is systematically stronger than the other HDO line. For this reason, we adopt the HDO line at 1389.13 cm$^{-1}$ in the following analysis. For CO$_2$, we use the weak transition at 1388.95 cm$^{-1}$, between the H$_2$O and HDO transitions selected for our analysis.

To correct the terrestrial absorption contribution in our spectra, we first consider the disk-integrated spectrum of Mars. For modeling this spectrum, we use the same temperature profile as Encrenaz et al. (2015) used for modeling the TEXES observations of March 1, 2014 (Ls = 96$^\circ$); indeed, the GCM predictions at the disk center are very similar between March 1 and April 8. In this thermal profile, temperatures are 230 K, 170 K, and 145 K at altitude levels of 0 km, 20 km, and 40 km, respectively, with an isothermal profile above 40 km. We then adjust the surface pressure and temperature on Mars to obtain the best fit in the CO$_2$ lines of the EXES disk-integrated spectrum, because these lines are not affected by telluric contamination (Figs. 1 and 2). The derived disk-averaged surface pressure and surface brightness temperature on the surface of Mars are 6 mb and 255 K, respectively. It must be noted that these parameters, averaged over the Martian disk, are simply used to model the disk-integrated spectrum of Mars. The Martian atmospheric profile used in our modeling is not the only one that fits the CO$_2$ spectral lines but, as discussed in Encrenaz et al. (2015), the exact retrieval of the true Martian profile is not needed for our analysis, because it does not affect the line depth ratios as long as the CO$_2$ Martian lines are properly fitted. We also use the CO$_2$ lines to determine the spectral resolution of our data. Figure 3 shows different profiles (Gaussian and sinc$^2$) with FWHM values of 0.024 cm$^{-1}$ and 0.028 cm$^{-1}$. We note that none of them is fully adapted to the EXES data because the EXES instrumental function exhibits broader wings. As a best fit, we use a FWHM of 0.024 cm$^{-1}$, corresponding to a resolving power of about 60 000 with a Gaussian profile (almost identical to the sinc$^2$ function).

In our nominal model of the disk-integrated spectrum of Mars (Figs. 1 and 2), we use, as a first try, mixing ratios of 300 ppmv for H$_2$O and 467 ppbv for HDO, corresponding to a Martian D/H of 5 (Encrenaz et al. 2015). Then, we divide the observed disk-integrated EXES spectrum by this model, and we adjust the parameters of the terrestrial absorption model to obtain the best fit in the regions of strong terrestrial absorption, where the contribution of Mars is almost negligible (see below, Sect. 3). Then, we multiply the inferred terrestrial transmission function with the Martian synthetic models for comparison with the EXES spectra and determination of the H$_2$O and HDO mixing ratios (see below).

3. Retrieval of the terrestrial atmospheric transmission

Two main factors determine the shape of the terrestrial atmospheric transmission in the H$_2$O and HDO absorptions: the pressure level above which the calculation is made, and the water vertical distribution above this level. We calculated a grid of spectra for different values of these parameters, and we compared the product of these curves with our nominal model of Mars to compare with the disk-integrated EXES spectrum of Mars. Calculations were done at high resolution (with a step of 0.001 cm$^{-1}$), taking the Doppler shift of Mars into account, and were convolved at the EXES spectral resolution for comparison with the EXES disk-integrated spectrum. The best fit transmission curve is shown in Fig. 4, compared with the standard transmission shown in Figs. 1 and 2. This transmission
Standard terrestrial atmospheric transmission (thick black line, also shown in Figs. 1 and 2) compared with our retrieved transmission function applicable for the EXES data of Mars. Our transmission curve was inferred from the best fit between the observed spectrum of Mars (after removal of the offset due to scattered light) and the product of the nominal synthetic model of Mars by the transmission function (see Fig. 5). The terrestrial atmospheric transmission is zero in the core of the strong water line at 1387.5 cm$^{-1}$.

The terrestrial atmospheric transmission function is zero in the core of the strong water line at 1387.5 cm$^{-1}$. The retrieved transmission function for EXES data is shown in Fig. 4. The terrestrial atmospheric transmission is zero in the core of the strong water line at 1387.5 cm$^{-1}$.

Figure 5 shows the disk-integrated EXES spectrum of Mars compared with the product of our Martian model with the retrieved terrestrial atmospheric transmission function. It can be seen that the agreement is quite satisfactory over the whole spectral range, in particular in the 1386.5 cm$^{-1}$ and 1387.5 cm$^{-1}$ water bands where the effect of the Martian spectrum is almost negligible. In what follows, we compare the EXES data with the Martian synthetic spectra multiplied by our retrieved transmission function, taking the Martian Doppler shift into account, and convolved with the EXES spectral resolution.

**4. Mapping Mars**

Figure 6 shows a map of the continuum radiance of Mars at 1388.60 cm$^{-1}$ after removal of the scattered light. In the absence of absolute calibration available on the EXES instrument for our Mars data, we have retrieved a brightness temperature scale using the maximum surface temperature value expected at the disk center, as predicted by the GCM. The absolute radiance scale is derived assuming that the brightness temperature is equal to the surface temperature, i.e.; that the surface emissivity is 1.0. The maps extend over 11 pixels in diameter, and the size of the pixel is 1.4 arcsec. The subsolar point is indicated by a white dot.

Continuum maps of Mars with TEXES. **Top**: continuum radiance map of the Martian disk recorded at 1388.10 cm$^{-1}$ (Ls = 113°) with EXES. **Bottom**: surface temperatures, assuming a maximum surface temperature of 280 K at the disk center, as predicted by the GCM. The brightness temperature is equal to the surface temperature, i.e.; that the surface emissivity is 1.0. The maps extend over 11 pixels in diameter, and the size of the pixel is 1.4 arcsec. The subsolar point is indicated by a white dot.
the vertical distributions of H$_2$O and HDO are expected to be the same, the effect should be weak on the retrieval of the D/H map.

Figure 7 shows the maps of the line depths of CO$_2$ at 1388.95 cm$^{-1}$, H$_2$O at 1388.47 cm$^{-1}$, and HDO at 1389.13 cm$^{-1}$. It can be seen that the CO$_2$ line depth is always equal to 0.20 or higher, which illustrates that the temperature contrast between the surface and the atmosphere is sufficient for the linearity method described above to apply. This behavior is expected near opposition as the full dayside of Mars is observed. As expected, the H$_2$O and HDO line depth maps show similar behavior with a distinct enhancement around the north pole.

We have isolated three areas along the central meridian around the center and in the northern and southern regions, covering latitudes north of 45N and south of 30S, respectively. Each area covers 5 × 5 pixels on the planet, while the entire disk, with a diameter of 12 pixels, is covered by about 112 pixels. As in the case of the disk-integrated spectrum (Fig. 2), some fluctuations are present in the continuum, possibly owing to broad mineralogic features on the Mars surface or may have an instrumental origin. For comparison with the synthetic models, we removed these fluctuations by assuming, for each transition, a straight line between the continuum taken on each side of the transition. The result is shown in Figs. 8–11, which show the best fits obtained for the H$_2$O and HDO mixing ratios for the integrated disk, the disk center, and the northern and southern regions, respectively. It can be seen that, in all cases, the two HDO lines cannot be fitted with a single HDO mixing ratio because the 1387.98 cm$^{-1}$ line is systematically stronger. This suggests, as mentioned above, that some terrestrial contamination might still be present at this frequency, and we use the 1389.13 cm$^{-1}$ transition for deriving the HDO mixing ratio. The following mixing ratios are inferred:

Disk-integrated spectrum: $\text{H}_2\text{O} = 220$ ppmv, HDO = 300 ppbv (D/H = 4.4 VSMOW);
Disk center: \( \text{H}_2\text{O} = 275 \text{ ppmv}, \text{HDO} = 400 \text{ ppbv} \) (D/H = 4.7 VSMOW);
Northern region: \( \text{H}_2\text{O} = 375 \text{ ppmv}, \text{HDO} = 550 \text{ ppbv} \) (D/H = 4.7 VSMOW);
Southern region: \( \text{H}_2\text{O} = 125 \text{ ppmv}, \text{HDO} = 150 \text{ ppbv} \) (D/H = 3.9 VSMOW).

To check the consistency of our results in the northern and southern areas over the whole spectral range, we show the observed EXES spectra in Fig. 12 compared with the best-fit models multiplied by our transmission functions in the spectral range where the terrestrial absorption is maximum (1386–1388 cm\(^{-1}\)). These curves have to be compared with Fig. 5 for the full disk. It can be seen that the agreement is very satisfactory for the southern region, but not as good for the northern region. This may imply that the surface continuum shows variations in the northern hemisphere. Unfortunately, we have no way to account for these minor fluctuations. It can be noted that the HDO line appearing at 1386.55 cm\(^{-1}\) in the wing of the strong H\(_2\)O line centered at 1386.50 cm\(^{-1}\) is well fit in both regions.

Figure 13 shows the maps of the H\(_2\)O and HDO mixing ratios relative to CO\(_2\), inferred from the line depth ratios of the 1388.47 cm\(^{-1}\) H\(_2\)O line and the 1389.13 cm\(^{-1}\) HDO line, divided by the 1388.95 cm\(^{-1}\) CO\(_2\) line. The linearity relationship between the line depth ratios (ldr) and the volume mixing ratios (vmr) are derived from the best-fit model for the disk center and are defined as follows:

\[
\text{vmr(H}_2\text{O)}(\text{ppmv}) = 509.2 \times \text{ldr(H}_2\text{O/CO}_2) \\
\text{vmr(HDO)}(\text{ppbv}) = 723.7 \times \text{ldr(HDO/CO}_2) .
\]
The D/H ratio can be inferred from the line depth ratio of the HDO and H$_2$O lines. This method has the advantage of removing the uncertainties associated with the terrestrial atmospheric transmission. The validity of the linearity method is discussed below. We derive D/H (VSMOW units) = $4.60 \times \text{ldr}$ (HDO/H$_2$O). Figure 14 shows the map of the D/H ratio on Mars in line depth ratio units and in VSMOW units.

5. **Linearity of the mixing ratios with the line depth ratios**

We have shown in our previous analyses (Encrenaz et al. 2008, 2015) that the mixing ratio of two atmospheric species can be directly inferred from the ratio of their line depths provided that the lines are weak with line depths less than about 10% to 15%. This assumption also requires that the two species are homogeneously mixed and that the temperature contrast between the surface and the atmosphere is sufficient. Near terminator, at night, before dawn, or after sunset, these conditions may not be filled (Encrenaz et al. 2015). In the present case, observations are made near opposition, and the full dayside of Mars is observed, so this condition is fulfilled.

However, a departure from linearity is expected to occur because the CO$_2$ line depth is about 0.20–0.25, so larger than in our TEXES analysis. This uncertainty should be reduced on the measurement of the D/H ratio, as D/H is directly retrieved from the ratio of the HDO and H$_2$O line depths, which both have a line depth between 5% and 15%. Still, some error may be introduced because the individual lines are not optically thin. In addition, the quantum numbers of the H$_2$O and HDO lines used for the map retrieval are very different, as shown in Table 1. This difference may introduce systematic uncertainties related to vertical profiles of temperature and abundances. However, as pointed out above, both H$_2$O and HDO are expected to have similar distribution: Near northern summer solstice (Ls = 113°), the atmosphere is cold and the two species are confined in the lower troposphere, so this effect is expected to be minor.

Using the thermal profile and the atmospheric parameters corresponding to the disk center, we determined the HDO/H$_2$O line depth ratio for a D/H ratio of 4.7 VSMOW (corresponding to the best fit at the center) and for different values of the H$_2$O volume mixing ratio. Calculations show that a departure from linearity of 10% is observed for H$_2$O mixing ratios of half and twice the best fit value of 275 ppmv, respectively. The linearity method is thus expected to underestimate the D/H value in the southern hemisphere and to overestimate in the northern hemisphere by a factor of 10%.

6. **Uncertainty analysis**

We first estimate the instrumental noise in the EXES data. Figure 15 shows an enlargement of the disk-integrated spectrum of Mars in the continuum region around 1388.8 cm$^{-1}$. It can be seen that the peak-to-peak (3$\sigma$) noise in the disk-integrated spectrum is less than 1%. Since the full disk is covered by 112 pixels, the 1$\sigma$ noise per pixel is less than 3%. This noise is much lower than the uncertainty induced by (1) the uncertainty in the instrumental function (see Fig. 3) and (2) the uncertainty associated with the telluric atmospheric transmission.
In the first case, the error is maximum in the retrieval of the H₂O line depth at 1388.47 cm⁻¹ because of the limited quality of the fit of the weak neighboring CO₂ line at 1388.44 cm⁻¹. Owing to the uncertainty in the continuum level between the CO₂ and H₂O lines at 1388.455 cm⁻¹, we estimate that the absolute error on the H₂O line depth is about 20% for the disk-integrated spectrum, 15% for the center and the northern region, and 30% for the southern region. The measurement of the HDO line depth at 1389.13 cm⁻¹ is not affected by this effect.

To estimate the uncertainty associated with the retrieval of the terrestrial atmospheric transmission, we took two extreme cases for the terrestrial contribution in the H₂O and HDO line depths. With the retrieved atmospheric transmission curve used in this study, the terrestrial contribution (in depth) is 0.065 for the H₂O line at 1388.47 cm⁻¹ and 0.026 for the HDO line at 1389.13 cm⁻¹, which is 0.4 times its value for H₂O (see Fig. 4). The total depth of the H₂O line (including the terrestrial contribution) in the EXES spectrum of the southern region is 0.10. We estimated that the terrestrial contribution in this line cannot be more than 0.075 in order to avoid negligible (and unreasonably low) values of the Martian H₂O in this region. We scaled the terrestrial contribution HDO accordingly at 0.030. For the lower limits of terrestrial absorption, we assumed 0.055 for the H₂O line and 0.022 for the HDO lines.

The uncertainties on the H₂O and HDO mixing ratios on Mars can be estimated as follows. For the disk-integrated spectrum of Mars, the H₂O nominal line depth (without the terrestrial contribution) is about 0.10 (Figs. 7 and 8). In the case of H₂O, using the two extreme values of the terrestrial contribution leads to extreme line depths ranging from 0.09 to 0.11, corresponding to an uncertainty of 10%. The associated uncertainty is 7% for the northern region and 20% for the southern region. These uncertainties have to be combined quadratically with the error associated with the poor quality of the fit as discussed above. The resulting uncertainties on the H₂O mixing ratio are 22% for the disk-integrated value, 17% for the center and the northern region, and 36% for the southern region.

In the case of HDO, the line depth in the disk-integrated spectrum (without the terrestrial contribution) is about 0.10. It becomes 0.096 if the terrestrial absorption is maximum and 0.104 in the opposite case. The associated uncertainty is then 4%. It becomes 3% at the center and in the northern region and 10% in the southern region.

Because the terrestrial absorption contribution has no effect on the CO₂ line depth, its uncertainty is minor compared with the H₂O and HDO line depths. The final results are thus the following:

- Disk-integrated spectrum: H₂O = 220±/−48 ppbv, HDO = 300±/−12 ppbv;
- Disk center: H₂O = 275±/−47 ppmv, HDO = 400±/−12 ppbv;
- Northern region: H₂O = 375±/−64 ppmv, HDO = 550±/−17 ppbv;
- Southern region: H₂O = 125±/−45 ppmv, HDO = 150±/−15 ppbv.

It should be noted that these error bars are systematic. The relative error bars on the H₂O and HDO maps (Figs. 12) are much lower and only due to the signal-to-noise ratio of the EXES spectrum in one pixel. As discussed above, the 1σ associated uncertainty is 3%.

The absolute uncertainty on the D/H ratio is obtained by associating, on one hand, the maximum values of H₂O and HDO mixing ratios and, on the other, their minimum values. The result is the following:

- Disk-integrated spectrum: D/H = 4.4 (±1.0, −0.6) VSMOW;
- Disk center: D/H = 4.7 (±0.8, −0.6) VSMOW;
- Northern region: D/H = 4.7 (±0.8, −0.6) VSMOW;
- Southern region: D/H = 3.9 (±1.5, −0.8) VSMOW.

The relative uncertainty on the D/H variations shown in the D/H map (Fig. 13) is the quadratic combination of the errors on the H₂O and HDO line depths. The 1σ uncertainty is thus 4.2%.

7. Discussion

Our observation of Mars with EXES leads to a disk-integrated value of 4.4 (±1.0, −0.6) times the VSMOW value. This value tends to be slightly lower than most of the previous disk-integrated determinations, although still consistent with most of them taking the error bars into account (Owen et al. 1988; Krasnopolsky et al. 1997). Part of the difference can be explained by the fact that, at the time of our observations, the Tharsis plateau was in the field of view; indeed, lower D/H values are expected in high-altitude regions where the water vapor content is lower. Figure 16 show a closer comparison of our data with the maps obtained by Villanueva et al. (2015) for Ls = 80 and 83°. The D/H ratio above the Tharsis region is clearly depleted in our map, which is in good agreement with the data of Villanueva et al. (2015). The poor spatial resolution of our map is a consequence of the poor image quality of the SOFIA telescope, which is limited to about 3 arcsec, corresponding to two pixels on our map. We thus confirm the low D/H values for high-altitude regions of Mars. However, at latitudes higher than the Tharsis plateau, our D/H is uniformly close to 5 VSMOW while, in the map shown by Villanueva et al. (2015), it reaches about seven times the VSMOW at 60N north of Olympus Mons, over a region that is larger than our spatial resolution (Fig. 16).

Independently of its limited spatial resolution, the EXES map seems to show less variability than the data of Villanueva et al. (2015).

Our D/H measurement can also be compared with Krasnopolsky’s result for the same season. For Ls = 110°, Krasnopolsky’s value of D/H is about four VSMOW in the northern hemisphere, in agreement with our result. We note that the longitude range for Krasnopolsky’s measurements (Central Meridian at 253 E) was different from the conditions of the...
EXES observations (Central Meridian at 205 E). The mean global D/H reported by Krasnopolsky (2015), integrated over the disk and over time, is $4.6 \pm 0.7$ VSMOW, in good agreement also with the EXES result.

The EXES maps of HDO and H$_2$O can be compared with the GCM predictions and with previous observations. In the case of the HDO map, a comparison can be made with the results recorded by the TEXES imaging spectrometer on the IRTF on March 1, 2014 (Encrenaz et al. 2015) for Ls = 96°. The map of the HDO mixing ratio was obtained from the line depth ratio of a weak HDO transition at 1237.08 cm$^{-1}$ (8.08 μm) divided by a weak nearby CO$_2$ line at 1241.58 cm$^{-1}$ (8.05 μm). Figure 17 shows a comparison of the TEXES and EXES maps, separated in time by five weeks and in areocentric longitude by 17°. The overall agreement is satisfactory, both for the HDO mixing ratio and its global distribution over the disk. Figure 17 also shows a comparison of the two HDO maps with the predictions of the GCM (Montmessin et al. 2005). For both the EXES and TEXES data, the agreement is satisfactory except at the north pole where the GCM prediction is higher than the observed one (by both TEXES and EXES) by a factor of 1.5 to 2 over a region as large as the EXES spatial resolution.

Our H$_2$O map can also be compared with previous observations. The EXES map of H$_2$O is consistent with the map of Villanueva et al. (2015) for Ls = 80–83°. For Ls = 113°, the TES data aboard Mars Global Surveyor (Smith 2004) indicate an H$_2$O column density ranging from 4 pr-μm at 30S latitude to 12 pr-μm at the equator and 40 pr-μm at 60N latitude. In our model, these numbers correspond to 77 ppmv, 204 ppmv, and 680 ppmv at 30S, 0, and 70N latitudes, respectively. At 30S and 0 latitude, these numbers are consistent with our results, taking the error bars into account. At high northern latitudes, the TES value is higher than our result by about 30%. The same comment applies to the comparison of our EXES map with the predictions of the GCM (Forget et al. 1999, Fig. 18). The EXES values are consistent with the GCM values, except in
Fig. 17. Top left: map of the HDO/CO$_2$ volume mixing ratio, retrieved from the EXES data recorded on April 8, 2014 (Ls = 113°). Top right: GCM prediction for the same observing conditions (after Montmessin et al. 2005). Bottom left: map of the HDO/CO$_2$ volume mixing ratio retrieved from the TEXES data on March 1, 2014 (Ls = 96°). Bottom right: GCM prediction for the same observing conditions (Encrenaz et al. 2015).

Fig. 18. Top left: map of the H$_2$O/CO$_2$ volume mixing ratio, retrieved from the EXES data recorded on April 8, 2014 (Ls = 113°). Top right: GCM predictions for the same observing conditions. Bottom left: map of the H$_2$O/CO$_2$ volume mixing ratio retrieved from the TEXES data on March 1, 2014 (Ls = 96°), assuming a uniform D/H ratio of 5 VSMOW. Bottom right: GCM prediction for the same observing conditions (Encrenaz et al. 2015).
the northern region where they are significantly weaker. We note that the TEXES map of H$_2$O was inferred using a D/H mean value of 5 VSMOW, so slightly higher than the EXES value, which explains the lower values of the TEXES H$_2$O map with respect to the EXES map (Fig. 18).

The H$_2$O latitudinal distribution observed by EXES can also be compared with the result reported by Krasnopolsky (2015) for $L_s = 110^\circ$. Krasnopolsky (2015) derives a H$_2$O column density of about 15 pr-$\mu$m and 35 pr-$\mu$m at latitudes of 20 N and 80 N, respectively. Using our model, these numbers translate into 255 ppmv and 600 ppmv, which is consistent with the EXES result. The departure from the GCM in the water vapor map at high northern latitudes is thus observed by the different ground-based observations, which might suggest that some adjustment is required in the GCM to fit the data better around the north pole.

From the water vapor spatial distribution shown in Figs. 13 and 17, it is possible to estimate the D/H map expected if the VPIE is the main mechanism responsible for fractionation. Following Fouchet & Lellouch (2000), we consider an open cloud system, where the solid phase condenses in isotopic equilibrium with the water phase and leaves the cloud by precipitation immediately after its formation (Dansgaard 1964). In this case we expect

\[ 1 + \frac{\delta}{\alpha} = [n_v/n_0] \exp(\alpha - 1), \]

where $\delta$ is the isotopic departure with respect to the reference D/H value, $n_0$ is the reference (maximum) water vapor content, and $\alpha$ the fractionation coefficient, which is the ratio of the D/H ratio in the condensed phase to the ratio in the vapor phase (Merlivat & Nief 1967). Following Fouchet & Lellouch (2000), we adopt $\alpha = 1.24$, corresponding to a temperature of 230 K. We calculate the expected D/H value in the southern region, using $n_v = 125$ ppmv (as derived from the EXES data), and as reference values, the water vapor volume mixing ratio and the D/H value inferred from EXES in the northern region ($n_0 = 375$ ppmv, D/H = 4.7 × VSMOW). Using these parameters, we infer, for the southern region, a D/H ratio of 3.6 × VSMOW, in good agreement with the EXES value. We conclude that the EXES results are fully consistent with the VPIE mechanism being responsible for the deuterium fractionation on Mars. We also note that the above calculation gives an upper limit of the deuterium fractionation expected from the VPIE, considering that the open cloud assumption is an extreme case (because it assumes that the solid phase leaves the cloud immediately after its formation). Thus, assuming the VPIE process, we do not expect stronger D/H variations than observed in our map (Fig. 13).

Our analysis confirms the expected behavior of the D/H ratio as a function of altitude and as a function of the H$_2$O abundance, previously illustrated by Villanueva et al. (2015) and Krasnopolsky (2015). We cannot confirm the high global value of the D/H enrichment over the seasonal cycle inferred by the authors. Indeed, our observations covered a longitude range where low values of D/H were expected. Other observations with EXES aboard SOFIA will be needed for different seasons of the Martian cycle to infer a global value of the D/H ratio, averaged over the whole seasonal cycle.

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