Is there Methane on Mars?

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There have been several reports of methane on Mars at the 10 ppb level [1-3]. Most suggest that the methane is also seasonally and latitudinally variable. Here we review why variable methane on Mars should be seen as an extraordinary claim and why the published reports fall short of providing extraordinary evidence: the strongest signals are from spectral lines where the potential for confusion with other telluric or martian spectral features is most severe, while the observations at more favorable wavelengths are consistent with no methane at all.

An extraordinary claim

The first published reports of methane on Mars [1,2] relied on weak signals that do not rise markedly above the level of noise. By contrast, the 2009 report by Mumma et al [3] shows clear signals coincident with the expected wavelengths of martian methane; we will focus on it. The credibility of the three reports is enhanced by their being independent and mutually consistent in finding methane at the 10 ppb level. Two of the studies [2,3] demand that methane be highly variable at levels between 0 and 30 ppb in both in time and place.

Variation as reported by Formisano et al [2] and Mumma et al [3] requires a methane lifetime in the atmosphere of weeks or months [4], and therefore both a very strong source and a very strong sink. Most discussion on this topic has focused on the source [1-7]. It is relatively easy to posit possible sources and arrogant to argue that such sources could not exist. On the other hand, the sink on atmospheric methane must act in the open, either in the atmosphere or at the surface, and can be addressed in the context of what is now known about Mars.

Conventional Mars photochemistry models predict that methane is an unreactive molecule in the gas phase with a 200-300 year lifetime [4,8-10]. The theory of methane's atmospheric photochemistry is very well established in the context of Earth's atmosphere under conditions that are not greatly different from those to be encountered on Mars. Thus it is very surprising that its lifetime on Mars should be weeks or months and not hundreds of years. Moreover methane destruction on the scale proposed would have major chemical consequences for the martian atmosphere as a whole, because the oxidants that oxidize methane must ultimately come from the atmosphere.

For specificity, consider oxidation of 30 ppb methane to 0 ppb methane in four months. This equates to a methane destruction rate of 6.5×10^8 cm^{-2}s^{-1}, which is in turn equivalent to an O_2 destruction rate of 1.3×10^9 cm^{-2}s^{-1}. At this rate the $\sim$1300 ppm of O_2 in Mars's atmosphere would be destroyed in just 7000 years. This is an order of magnitude faster than H_2O photolysis and subsequent H escape ($2 \times 10^8 - 4 \times 10^8$ H atoms cm^{-2}s^{-1}) can supply new O_2 [10,11]. Hydrogen escape is the biggest source of oxidizing power on Mars identified to date. In other words, oxidizing methane at the rate of 30 ppb methane in four months makes methane oxidation the biggest term in the redox budget of the martian atmosphere by a factor of ten. It would therefore be a second major surprise to learn that the *two* biggest terms affecting the chemistry of the Martian atmosphere—methane oxidation *and* the completely unknown but necessary source of oxidizing power to react with the methane—have *both* been overlooked.

A second possibility is that the methane is not consumed at all, but rather condenses and evaporates seasonally from clathrates [12]. Methane clathrates are known to be unstable at the pressures and temperatures encountered on Mars. It has been shown [4] that if methane does condense, its condensation does not correlate with that of CO_2. Thus the clathrate hypothesis must also posit the existence of a hitherto unknown process.

Extraordinary evidence?

Formisano et al [2] use the PFS instrument on *Mars Express.* Their data do not suffer from telluric contamination, but the spectral resolution is coarse (1.3 cm^{-1}). Methane is inferred indirectly: adding 10 ppb CH_4 to their model appears to improve their model's fit at 3017 and 3018 cm^{-1}. The putative methane varies between 0 and 30 ppb over the two month time span of the observations, and the quantity does not correlate with atmospheric path length—the longest path length discussed in the paper is consistent with zero methane.

Ground-based observations are difficult because Mars must be viewed through Earth's atmosphere. Earth's atmosphere is $\sim$60 times thicker than Mars's and contains $\sim$1.8 ppm methane. If we accept for argument that there are 20 ppb methane on Mars, there are 5400 terrestrial methane molecules to look through to see one martian methane molecule. In practice it is not quite so bad as that (the sunlight passes twice through Mars's atmosphere, and one observes from a mountaintop), but still it is to be expected that the terrestrial $^{12}CH_4$ lines are 2000 times stronger than their putative martian counterparts. Even terrestrial $^{13}CH_4$ lines are 20 times stronger than these martian $^{12}CH_4$ lines. Thus it is necessary to exploit the Doppler shift when Mars is approaching or receding from Earth. The Doppler shift for a relative velocity of 17 km/s is 0.17 cm^{-1} at 3000 cm^{-1}.

Krasnopolsky et al [1] observe one of the ν_3 $^{12}CH_4$ P4 lines in blueshift. The spectral region is rather clean but the retrieved methane signal does not obviously exceed the noise background. If this is methane, it would be consistent with an abundance of 10 ppb. There is no evidence of variability.

Mumma et al [3] report significant latitudinally variable methane on Mars using the R0 and R1 lines of the ν_3 band of $^{12}CH_4$. The apparent methane signature is easy to see in their Figure 1. These observations were made when Mars was in approach at 15-16 km/s in January of 2003, so that the putative martian lines would have been blueshifted by 0.15-0.16 cm^{-1}. They [3] did not detect significant methane using the R0 and R1 lines three years later when Mars was receding at 16-17 km/s from the Earth, for which the martian lines would have been redshifted by 0.16-0.17 cm^{-1}, this despite having made some of the redshifted observations using NIRSPEC on Keck. The upper limit appears to be $\sim$2 ppb.

The redshift/blueshift dichotomy is interesting. It suggests that there might be an explanation other than seasonality. Krasnopolsky [5] notes that the blue wings of the $^{12}CH_4$ R0 and R1 lines are "contaminated" by other terrestrial lines of water and methane, while the red wings of the $^{12}CH_4$ R0 and R1 lines are "rather clean."

Synthetic terrestrial and martian spectra encompassing the frequencies of the published observations reveal clearly that the strong $^{13}CH_4$ R1 and R2 lines are superposed on the blue wings of the $^{12}CH_4$ R0 and R1 lines. The separations between line centers are 0.10 and 0.12 cm^{-1}, respectively. These separations are comparable to the Doppler blueshifts of 0.15-0.16 cm^{-1} in the 2003 observations [3]. The spectral resolution of the instrument is in the best case 0.08 cm^{-1}. Hence the martian $^{12}CH_4$ and the telluric $^{13}CH_4$ can be separated from the telluric $^{12}CH_4$ lines, but they cannot be separated from each other. As noted above the telluric $^{13}CH_4$ lines are $\sim$20 times stronger than the putative martian $^{12}CH_4$ lines; hence the correction for Earth's atmosphere needs to be very close to perfect if the martian lines are to be retrieved. The red wings of the telluric $^{12}CH_4$ R0 and R1 lines are by contrast relatively clean. A simple explanation for why methane was detected on Mars only when Mars was approaching Earth is that the methane detections arose from the imperfect subtraction of telluric $^{13}CH_4$, a problem that is characteristic of the blue wings of the $^{12}CH_4$ R0 and R1 lines.

Martian methane was also reported in the $^{12}CH_4$ P2 line [3]. This line is coincident with a weak water feature and also with a strong martian isotopic CO_2 line. These observations imply strong latitudinal gradients in both methane and CO_2. The unlikelihood of the latter calls the former into question. The latitudinal gradient in CO_2 is not attributable to temperature because the $^{12}C^{16}O^{18}O$ lines all rise from the ground state and are not sensitive to temperature As for the retrieval of methane, the coincidence with telluric water vapor—which is highly variable—raises questions.

Summary

We use the HITRAN database to generate synthetic terrestrial and martian spectra encompassing the frequencies of the published observations. These reveal significant competing telluric and martian spectral features that are most problematic in just those cases where methane's signature seems most clearly seen. The most highly compromised observations are of the $^{12}CH_4$ ν_3 R0 and R1 lines seen in blueshift (obtained when Mars was approaching Earth in 2003), because the Doppler shift moves the two martian lines into near coincidence with strong terrestrial $^{13}CH_4$ ν_3 R1 and R2 lines [4], and the resolving power of the CSHELL instrument is insufficient to resolve the telluric $^{13}CH_4$ lines from blueshifted martian $^{12}CH_4$ lines. The least compromised of the published datasets are also of the $^{12}CH_4$ ν_3 R0 and R1 lines, but taken in redshift when Mars was receding from Earth in 2006. For these the observations are consistent with no methane on Mars at the 2 ppb level [3]. We therefore conclude that there is as yet no compelling evidence for methane on Mars, and that the upper limit may be as small as 2 ppb.

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