

Is there methane on Mars?

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ABSTRACT

There have been several reports of methane on Mars at the 10–60 ppbv level. Most suggest that methane is both seasonally and latitudinally variable. Here we review why variable methane on Mars is physically and chemically implausible, and then we critically review the published reports. There is no known mechanism for destroying methane chemically on Mars. But if there is one, methane oxidation would deplete the O₂ in Mars's atmosphere in less than 10,000 years unless balanced by an equally large unknown source of oxidizing power. Physical sequestration does not raise these questions, but adsorption in the regolith or condensation in clathrates ignore competition for adsorption sites or are inconsistent with clathrate stability, respectively. Furthermore, any mechanism that relies on methane's van der Waals' attraction is inconsistent with the continued presence of Xe in the atmosphere at the 60 ppbv level. We then use the HITRAN database and transmission calculations to identify and characterize the absorption lines that would be present on Earth or Mars at the wavelengths of the published observations. These reveal strong competing telluric absorption that is most problematic at just those wavelengths where methane's signature seems most clearly seen from Earth. The competing telluric lines must be removed with models. The best case for martian methane was made for the ¹²CH₄ ν₃ R0 and R1 lines seen in blueshift when Mars was approaching Earth in early 2003 (Mumma, M.J., Villanueva, G.L., Novak, R.E., Hewagama, T., Bonev, B.P., DiSanti, M.A., Mandell, A.M., Smith, M.D. [2009]. *Science* 323, 1041–1045). For these the Doppler shift moves the two martian lines into near coincidence with telluric ¹³CH₄ ν₃ R1 and R2 lines that are 10–50× stronger than the inferred martian lines. By contrast, the ¹²CH₄ ν₃ R0 and R1 lines when observed in redshift do not contend with telluric ¹³CH₄. For these lines, Mumma et al.'s observations and analyses are consistent with an upper limit on the order of 3 ppbv.

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1. Introduction

The first discovery of methane on Mars was announced in 1969 at a press conference by the Mariner 7 Infrared Spectrometer (IRS) team just two days after the flyby (Sullivan, 1969). The IRS had detected strong absorption centered at 3.3 μm and weaker absorption at 3.0 μm; both absorption features were seen at the edge of the southern polar cap. The 3.3 μm band was briefly attributed to methane's ν₃ vibrational band, and the 3.0 μm band was attributed to ammonia. The press conference created a flurry of excitement before the IRS team discovered soon thereafter that the 3.0 and 3.3 μm absorptions could also be explained by CO₂ ice (Kirkland, 1999; Herr and Pimentel, 1969). The moral of this story is that spectral detection of methane on Mars can trick even experienced researchers and requires extreme care in considering spectral contaminants.

Several recent reports of methane on Mars at the 10–60 ppbv level (Formisano et al., 2004; Krasnopolsky et al., 2004; Geminale

et al., 2008, 2010; Mumma et al., 2009; Fonti and Marzo, 2010) have proved more durable. The credibility of the reports is enhanced by their independence and mutual consistency. More surprising than methane's presence is its apparent variability on short time scales. Both Mars Express (Formisano et al., 2004; Geminale et al., 2008, 2010) and the most comprehensive ground-based study (Mumma et al., 2009) suggest that methane is highly variable both in time and place. Krasnopolsky et al. (2004) do not report variability, but their observations do not span a long period of time. A fourth study (Fonti and Marzo, 2010) subjects archival spacecraft data to extensive statistical analysis to retrieve a weak signal at 1306 cm⁻¹ that can be ascribed to seasonally variable methane, also at the 10 ppbv level. However, identification of the 1306 cm⁻¹ feature with methane is not unique given the low resolution of the spacecraft data and the presence of nearby H₂O and CO₂ lines, and thus the identification with methane depends on spatial and seasonal correlations with results from Geminale et al. (2008) and Mumma et al. (2009).

Reports of methane plumes on Mars have exerted a strong influence on the capabilities of NASA's Mars Science Laboratory (MSL) mission (Webster and Mahaffy, 2010) and on plans for a joint

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ESA-NASA ExoMars Trace Gas Orbiter mission to be launched in 2016 (Zurek et al., 2010). There are robust theoretical reasons to doubt that methane can vary on seasonal time scales (*cf.* Lefèvre and Forget, 2009; Meslin et al., 2010). For methane to vary on short time scales, much else that we thought we knew about atmospheric chemistry and the martian atmosphere would have to be badly wrong. In ordinary science, the burden of proof rests on those who claim the discovery. In principle this maxim should apply to extraordinary claims as well. To quote a friend of Mars science, “extraordinary claims require extraordinary evidence” (Sagan, 1998, pp. 60 and 85).

In Section 2 we review why variable methane on Mars should be regarded as an extraordinary claim. In Section 3 we critically review the published reports. For the latter, we use the HITRAN database (Rothman et al., 2009) to model terrestrial and martian absorption at the wavelengths of the published observations. For Earth we also compute atmospheric transmission in these spectral windows. We find that the three strongest reported signals are from methane lines where the potential for confusion with other telluric or martian spectral features is severe, while the observations at more favorable wavelengths are consistent with no methane above a 3 ppbv noise floor.

2. Variable methane is an extraordinary claim

Variation as reported by Formisano et al. (2004), Geminale et al. (2008, 2010), Mumma et al. (2009), and Fonti and Marzo (2010) requires that methane's lifetime in the atmosphere be weeks or months (Lefèvre and Forget, 2009). Short-lived methane requires both a very strong source and a very strong sink. These two requirements are independent. Most discussion on this topic has focused on the source (Formisano et al., 2004; Krasnopolsky et al., 2004; Oze and Sharma, 2005; Lyons et al., 2005; Krasnopolsky, 2006; Bar-Nun and Dimitrov, 2006, 2007; Atreya et al., 2007; Chastain and Chevrier, 2007; Mumma et al., 2009; Chassefière, 2009; Chassefière and Leblanc, 2010b). It is relatively easy to posit plausible cryptic sources, and difficult to dismiss them. On the other hand, a fast-acting 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 known about Mars and atmospheric chemistry.

Conventional atmospheric photochemistry models predict that methane should be a very slowly reacting molecule in the gas phase with a 300 year lifetime on Mars (Summers et al., 2002; Wong et al., 2003; Krasnopolsky, 2005; Zahnle et al., 2008; Lefèvre and Forget, 2009). The theory of methane's atmospheric photochemistry is well established in the context of Earth's atmosphere, for which high quality, fully documented tabulations of experimentally measured chemical reaction rates are readily available (e.g., Atkinson et al., 1989, 2001, 2004; Sander et al., 2003). Methane—a relatively abundant molecule in air, a major player in ozone chemistry, and an important greenhouse gas—has been very well studied under conditions that are not greatly different from those encountered on Mars. The difference in methane's lifetime between an expectation based on scores of laboratory experiments and uncounted terrestrial atmospheric observations on the one hand and what is required to fit the published detections of methane on Mars on the other is on the order of $\sim 10^3$. Thus it is extraordinary that methane's lifetime on Mars should be weeks or months and not hundreds of years. This is why methane's variations are much more controversial than methane's presence.

In addition to its challenge to conventional atmospheric chemistry, variable methane on the scale proposed would have major consequences for the martian atmosphere as a whole, because the methane has to go somewhere. The possibilities are that meth-

ane is oxidized (in the atmosphere or at the surface), or that methane condenses. Some of these consequences have been discussed elsewhere using a Mars General Circulation Model (GCM) coupled to atmospheric chemistry (Lefèvre and Forget, 2009).

A proposed candidate for a chemical sink is reaction of methane with H_2O_2 in the soil, catalyzed on surfaces by minerals, ultraviolet light, or electric discharge (Atreya et al., 2006, 2007; Delory et al., 2006; Farrell et al., 2006; Geminale et al., 2008; Chassefière, 2009). In considering chemical sinks, it is important to recognize that oxidants in the soil or liberated by electric discharge have their origin in the atmosphere. The primary source of oxidants in the martian atmosphere is hydrogen escape following water vapor photolysis. When an electric discharge creates oxidants, it creates reductants in equal number, which must be channeled into hydrogen escape if electric discharges are to have a net oxidizing effect. Whether methane is oxidized in the atmosphere or on the surface, methane oxidation must ultimately consume oxidants generated in the atmosphere. Reactions in rocks can create H_2 from water by oxidizing ferrous to ferric iron or sulfides to sulfates, but even rocks need hydrogen to escape if they are to be a true net source of oxidizing power.

Here we point out another problem with the atmosphere's chemical budget that has been overlooked: the unknown chemical sink on methane would be by far the biggest term in the atmosphere's redox budget. To illustrate this, consider oxidation of 30 ppbv methane to 0 ppbv methane in four months, a quantity and a time scale consistent with the observations. These equate to a methane destruction rate of $6.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$, which is in turn equivalent to an O_2 destruction rate of $1.3 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$. At this rate the ~ 1300 ppmv of O_2 in Mars's atmosphere would be destroyed in just 7000 years. This loss rate is an order of magnitude faster than H_2O photolysis and subsequent H escape ($2 \times 10^8 - 4 \times 10^8 \text{ H atoms cm}^{-2} \text{ s}^{-1}$, Anderson and Hord, 1971; Nair et al., 1994; Lammer et al., 2003; Zahnle et al., 2008) can supply new O_2 .

Hydrogen escape is the only known source of oxidizing power on Mars. Methane oxidized at the rate of 30 ppbv methane in four months would make methane oxidation $10\times$ bigger than the oxygen source from hydrogen escape. This huge methane sink must therefore be balanced by a source of oxidizing power that is also $10\times$ bigger than anything previously known. In other words, if methane is both persistent (Geminale et al., 2008, 2010) and variable on the reported time scale, the *two* biggest terms affecting the chemistry of the martian atmosphere — methane oxidation *and* the unknown but necessary source of oxidizing power to react with the methane — have *both* been overlooked. This is a surprise given that the conventional models do a good job of accounting for the abundances of known trace species in Mars's atmosphere (Yung et al., 2010). The problem is not limited to discovering an unknown mechanism to oxidize the methane. The problem extends to discovering a new source of oxidants to fuel the unknown mechanism.

A more constructive approach is to ask how much methane can persist at steady state in the atmosphere without overturning the atmosphere's redox budget. The upper limit is set by equating the methane destruction rate to H escape. In such an atmosphere the source of the hydrogen that escapes to space would be methane, not water. Oxidation of one CH_4 molecule generates 8 H atoms. An H escape flux of $4 \times 10^8 \text{ H atoms cm}^{-2} \text{ s}^{-1}$ equates to a CH_4 destruction rate of $5 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$. With conventional atmospheric chemistry a methane flux into the atmosphere of $5 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ would support a *steady state* methane mixing ratio of 1000 ppbv. *Variable* methane requires unknown chemistry that goes $\sim 1000\times$ faster, for which the corresponding upper limit on methane's mean mixing ratio drops to just 1 ppbv, or equivalently 10 ppbv present 10% of the time.

It is of course possible to invoke intermittent methane releases that are rare enough not to overwhelm the redox budget of the atmosphere. These could take the form of relatively rare plumes that are on occasion seen. This point has recently been made by Chassefière and Leblanc (2010a), who argue that methane's mixing ratio is indeed on the order of 1 ppbv, and that the methane flux into the atmosphere is in fact the source of all the hydrogen escaping to space from Mars. But doing so rejects the work of Geminal et al. (2008, 2010), who find that variable methane — on average 14 ppbv — is a persistent feature of Mars. A large part of what makes methane on Mars seem credible to the wider community is that the methane was seen independently from Mars orbit and from Earth. The observations reported by Geminal et al. and Mumma et al. are broadly consistent. They see the same quantity, they see the same rapid variations, they both see correlations with water vapor. The case for methane on Mars is considerably weakened if the space-based observations are rejected as false.

Physical processes that do not consume methane do not introduce problems with atmospheric chemistry (Gough et al., 2010; Yung et al., 2010). For example, it has been suggested that methane can be seasonally adsorbed in the uppermost 3 meters of the regolith (Gough et al., 2010). This hypothesis requires a large available area for adsorption compared to what was measured in Viking soils (Ballou et al., 1978), and it ignores competition for adsorption sites; the latter assumption is problematic because methane is out-competed by polar molecules such as H₂O, H₂O₂ (at ~20 ppbv, it is at least as abundant as methane), and by some nonpolar molecules, such as CO₂ and even xenon. At ~60 ppbv (Pepin, 1991), Xe is more abundant than methane. There is no evidence of any adsorptive concentrations of any gas in the martian meteorite EETA 79001; indeed, it is the tight correlation between the noble gases measured by Viking and those trapped in SNC meteorites that indicates that these meteorites come from Mars (Becker and Pepin, 1984; Bogard et al., 1986; Wiens et al., 1986; Swindle et al., 1986). The continued presence of Xe in the atmosphere suggests that methane adsorption of the required magnitude does not take place on any time scale. The regolith adsorption hypothesis was recently tested in a Global Circulation Model (GCM) where it failed to generate the large seasonal variations required to reproduce the observations (Meslin et al., 2010).

Another speculative possibility is that methane condenses in clathrates. Clathrates have been suggested as the proximate source of methane to the atmosphere (Chastain and Chevrier, 2007; Geminal et al., 2008; Chassefière, 2009). The reported diurnal (Geminal et al., 2008) and latitudinal (Mumma et al., 2009) correlation of methane with water vapor might be consistent with condensation in clathrates. The thermodynamic instability of methane clathrate at or near the martian surface makes clathrates an attractive source, but this same instability makes them implausible as a sink. Methane can enter CO₂ clathrate, but because methane clathrate is less thermodynamically favored than CO₂ clathrate, methane's relative abundance in a CO₂ clathrate should be much lower than its relative abundance in the atmosphere (Miller, 1974). This suggests that quantitative removal of methane in clathrates would be accompanied by quantitative removal of CO₂ into clathrates. Similar arguments apply for Xe clathrate, which is more stable than CO₂ clathrate and much more stable than CH₄ clathrate, yet Xe remains in the atmosphere (*cf.* Swindle et al., 2009). Moreover, laboratory experiments indicate that clathrate formation is severely kinetically inhibited at temperatures cold enough that clathrate is stable (Bar-Nun et al., 1985; Pietrass et al., 1995). Finally, Lefèvre and Forget's (2009) GCM simulations show no correlation between the reported spatial patterns of methane variability and the computed spatial patterns of CO₂ condensation.

Biology is attractive, of course. One could match a biogenic CH₄ source with a biogenic O₂ source, and thus leave the atmosphere in

chemical balance. But biology is hard to reconcile with the high (~800 ppmv) atmospheric abundance of CO on Mars. The reason is that CO at such a high abundance is an excellent food. CO is so energetic that with it organisms can eat water. There are methanogens on Earth that can grow entirely on CO and H₂O, with CO serving both as fuel and as the carbon source (Ragsdale, 2004; Rother and Metcalf, 2004; Lessner et al., 2006). It is energetically advantageous for a generic methanogen to use CO instead of CO₂. On a biologically active planet, abundant atmospheric CO would be used by methanogens in preference to CO₂ until CO became scarce. That CO remains abundant on Mars means that a biological methane source, although not precluded, is deeply puzzling, because if methanogens were in communication with Mars's atmosphere they ought to draw CO down to very low levels while making methane. The same basic arguments apply to hypothetical abiotic (photo)chemical reactions that made CH₄ and O₂ from CO₂ and H₂O (Yung et al., 2010).

A biological methane sink is also contrary to what we know of biological thermodynamics: abundant, energy-rich CO would be eaten first. Moreover, to the best of our knowledge, no organism on Earth can live breathing a low solubility gas such as methane at a dilution of 10 ppbv. Finally, to pull methane out of the atmosphere in four months requires a velocity into the soil of $H/10^7 \text{ s} \approx 0.1 \text{ cm/s}$. For comparison, highly reactive and highly soluble gases such as H₂O₂ have deposition velocities on Earth of ~0.5 cm/s. Because the martian atmosphere is thinner and its surface boundary layer better mixed, the upper limit for Mars would be higher, possibly as high as ~10 cm/s, but even so a biological sink means that one of every one hundred methane molecules to reach the surface is promptly eaten. This requires in turn that a high percentage of Mars's surface be populated by methanotrophs living off of 10 ppbv of methane. This looks like an impossible picture.

3. An absence of extraordinary evidence

The profound theoretical difficulties posed by variable methane on Mars raise an inconvenient question: How robust are the observations?

To improve our understanding of the problem, we prepared HITRAN (Rothman et al., 2009) abundance-weighted absorption spectra for Earth at several altitudes and for Mars at the surface for the spectral intervals for which observations of methane on Mars have been published. These illustrate what lines might be expected and at what relative strengths. We use the Air Force Geophysics Lab (AFGL) standard tropical atmosphere (described by its authors as the annual average for 15 N), which provides pressure, temperature, and abundance profiles of major and minor constituents from sea level to 120 km (Anderson et al., 1986). This atmosphere is illustrated in Fig. 1. We assume line parameters as listed by HITRAN for the major species (CH₄, CO₂, H₂O, O₃, N₂O, CO, O₂). We will find that rare isotopologues are important. For the illustrations, we use the default isotope ratios used by HITRAN¹

For Earth, we show abundance-weighted absorption—the product of mixing ratio and cross-section—at 8 km and at 20 km, the former high in the troposphere and the latter in the stratosphere. For these figures, the axes labeled “absorption-weighted abundance” show the product of the mixing ratio and the molecular cross-section, which has units of area. The stratosphere shows ozone, and the low pressure helps separate the individual lines

¹ HITRAN uses terrestrial geochemical standard isotope ratios by default, although not to full precision. The geochemical standards differ in general from what is found in atmospheric gases. For example, both atmospheric CH₄ and atmospheric CO₂ are depleted, to different degrees, in the rare ¹³C — for methane, the difference is 4.7%. The mismatch between the HITRAN defaults and the real atmosphere can lead to mischief if one is not careful.

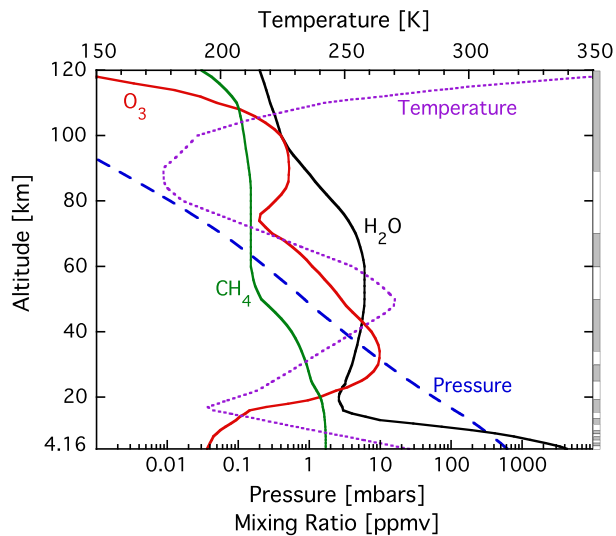


Fig. 1. The AFGL standard atmosphere that we use for computing atmospheric transmission over Mauna Kea. The surface at 4.16 km corresponds to the altitude of Mauna Kea. The 18 vertical intervals used in computing atmospheric transmission are indicated along the right-hand vertical axis.

and brings out some interesting details. We also compute transmission through the average atmospheric column above Mauna Kea. For the transmission computations we assume vertical incidence. We use 18 layers (indicated in Fig. 1) and include absorption by H₂O, CO₂, CH₄, O₃, and N₂O. We do not include scattering or atmospheric emission, which are negligible at 3.3 μm. Mauna Kea's elevation is taken into account by setting the surface at 4.16 km.

For Mars, we assume $T = 200$ K, 6.7 mbar total pressure, 95% CO₂ and 200 ppmv H₂O (consistent with 15 μm s of precipitable water, which is a reasonable average for a gas that is far from constant). The martian gas is spiked with 20 ppbv CH₄. We also include 20 ppbv O₃ but it does not prove important. For the spectral regions we are looking at there are no important lines of CO, O₂, or N₂, and N₂O's lines are weak and its abundance unknown.

3.1. Spacecraft observations

Formisano et al. (2004) use the planetary Fourier spectrometer (PFS) instrument on *Mars Express*, a spacecraft in orbit about Mars. Geminale et al. (2008) expand on this using the same instrument and methods over a two year baseline. The PFS data do not suffer from telluric contamination, but the spectral resolution is too coarse (1.3 cm⁻¹) and the signals too weak for methane to be identified directly. They therefore focus their attention on the Q branch of the ν₃ band at 3016–3019 cm⁻¹, which is the best choice at low resolution because the individual lines in the Q branch are tightly bunched together, such that their sum is 10× stronger than the adjacent lines in the R and P branches at PFS spectral resolution. Martian water vapor is not a major problem for the Q branch (Fig. 2). Methane is inferred indirectly: adding 10–60 ppbv CH₄ to their model appears to improve their model's fit at one wavelength, 3018 cm⁻¹ (Formisano et al., 2004). The model, which includes many parameters other than CH₄, is described by Geminale et al. (2008). The observations on orbit 559, which Geminale et al. (2008) present as their most compelling case, is fit with a model assuming 61 ppbv methane, 650 ppmv H₂O, and an ice cloud optical depth of 0.45. We note that, despite the low resolution of the PFS, the computed methane feature (essentially the width of the Q branch) in this observation is twice the width of the purported 3018 cm⁻¹ methane feature. If the spectral distortions inferred by modeling the PFS spectra are indeed caused by

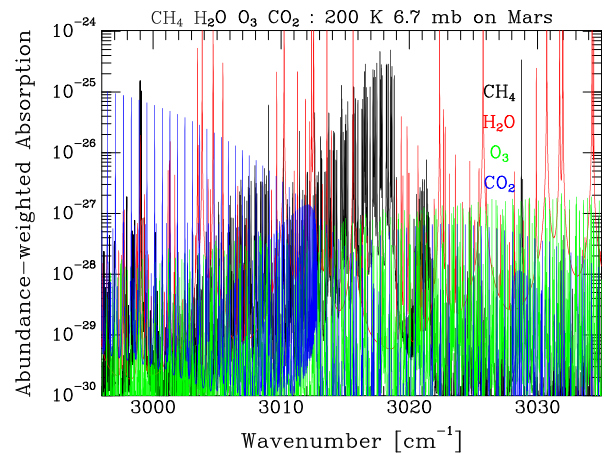


Fig. 2. Computed abundance-weighted absorption—the product of mixing ratio and cross-section—of the martian atmosphere at 200 K. Units are cm² per molecule of martian atmosphere. The atmosphere is spiked with 20 ppbv CH₄. The methane ν₃ Q branch has a large number of lines between 3016 and 3019 cm⁻¹. Methane is black, water red, CO₂ blue, and ozone green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

methane, the mean methane mixing ratio would be 14 ± 5 ppbv (Geminale et al., 2008), with no sign of a secular trend. The average measurement varies between 6.5 and 24.5 ppbv over the two year time span of the observations. One surprise is that variations of the 3018 cm⁻¹ feature do not always correlate with atmospheric path length — the longest path length discussed in Formisano et al. (2004) had no 3018 cm⁻¹ feature and is consistent with no methane. Another surprise is that the putative methane feature correlates with H₂O on hourly time scales over the course of a martian day (Geminale et al., 2008). Other surprises have been noted by Webster and Mahaffy (2010).

3.2. Ground-based Observations

Ground-based observations of martian methane are difficult because Mars must be viewed through Earth's atmosphere. Earth's atmosphere is ~60× thicker than Mars's and contains ~1800 ppbv methane. If we accept for argument that there are 20 ppbv methane on Mars, and that both atmospheres are viewed at the same angle, 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 ¹²CH₄ lines should be 2000× stronger than their putative martian counterparts. (To anticipate a point that will come up, using the atmospheric ¹²C/¹³C ratio of 93.4, a photon encounters 20 terrestrial ¹³CH₄ molecules for each putative martian ¹²CH₄ molecule.)

The martian lines are displaced from the core of the corresponding terrestrial lines by exploiting the Doppler shift when Mars is approaching or receding from Earth (Krasnopolsky et al., 2004; Krasnopolsky, 2007; Mumma et al., 2009). Relative velocities can exceed ~17 km/s. The Doppler shift for a relative velocity of 17 km/s is 0.17 cm⁻¹ at 3000 cm⁻¹, which is enough to separate the centers of the martian and telluric lines, but not enough to remove the martian lines from the wings of the much broader terrestrial lines.

3.2.1. The P4 lines

There are four strong P4 lines, centered at rest wavelengths of 2978.65, 2978.85, 2978.92, and 2979.01 cm⁻¹. Absorption by tropospheric air in the vicinity of the P4 lines is illustrated in Fig. 3. Vertical transmission through Earth's atmosphere is shown in

Fig. 4. Krasnopolsky et al. (2004) observed Mars with a maximum blueshift of 0.176 cm^{-1} in February 2003. The 2979.01 cm^{-1} line, which blueshifts to 2979.186 cm^{-1} , out of the core of the P4 group and beyond a telluric H_2O line at 2979.08 cm^{-1} , appears to dominate Krasnopolsky et al.'s reported results. Krasnopolsky et al.'s observations were taken using the Fourier Transform Spectrometer at the Canada–France–Hawaii Telescope. The nominal resolution of the instrument is about 0.02 cm^{-1} at 3000 cm^{-1} ($\nu/\Delta\nu \sim 1.8 \times 10^5$). The other three P4 lines cannot be seen in blueshift: the 2978.92 cm^{-1} is moved into the telluric water line, while the other two remain blocked by telluric methane. The locations of the P4 lines in the rest frame and at red and blue Doppler shifts are illustrated in Fig. 4.

The P4 lines can be a reasonable place to look for martian CH_4 from the ground, provided that martian methane is more abundant than a few ppbv. Fig. 5 shows absorption in the vicinity of P4 by a martian atmosphere with 200 ppmv water vapor and 20 ppbv O_3 spiked with 20 ppbv CH_4 . Martian lines are narrow because the pressure is low. The figure reveals a forest of weak isotopic CO_2 lines that set an effective background level that would preclude

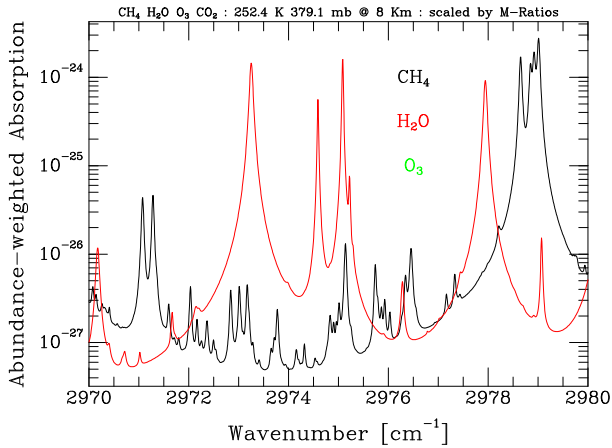


Fig. 3. Computed abundance-weighted absorption (cm^2 per molecule) of air at 8 km in the vicinity of methane's ν_3 P4 lines computed using HITRAN. The figure illustrates the structure of the P4 multiplet at 2979 cm^{-1} and nearby water vapor lines.

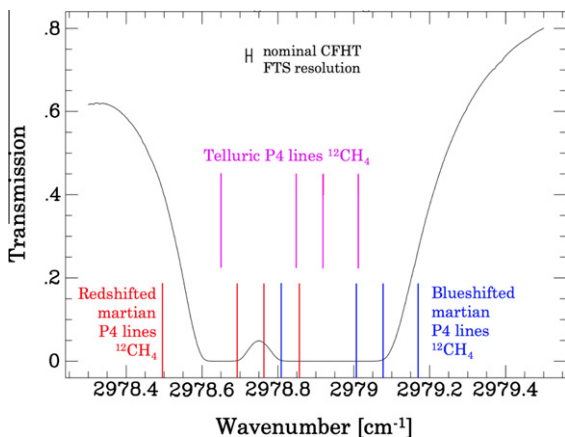


Fig. 4. Transmission through Earth's atmosphere in the vicinity of the ν_3 P4 methane lines. The wings of the P4 band are notably smooth. This makes the highest and lowest frequency lines of the four methane P4 lines relatively detectable when observed in blueshift or redshift, respectively. Doppler shifts of 0.16 cm^{-1} are assumed here for the illustration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

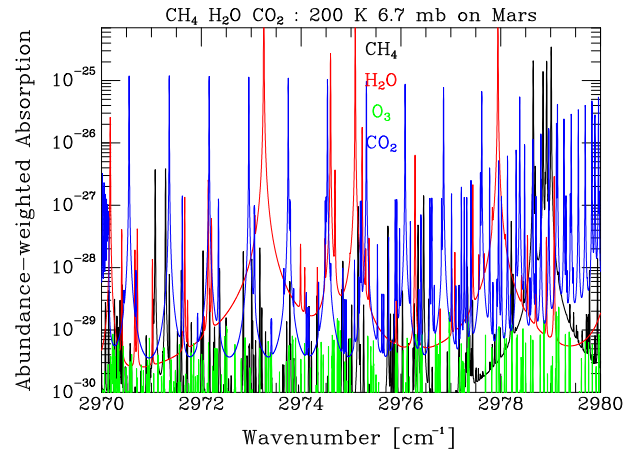


Fig. 5. Computed abundance-weighted absorption (cm^2) of the martian atmosphere spiked with 20 ppbv CH_4 in the vicinity of the methane ν_3 P4 lines (black). Confusion with isotopic lines of CO_2 (blue) can be a problem for CH_4 concentrations of 3 ppbv or less. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

detecting CH_4 at levels below ~ 3 ppbv, even for a space-based mission.

In the reported detection, the martian 2979.01 cm^{-1} line appears as a wavelike dip at the correct blueshifted frequency, somewhat deeper than adjacent wavelike dips that are reckoned noise or artifacts. Krasnopolsky et al. observed 14 other methane lines in the ν_3 band. Their other data are not shown, but the weighted sum of all their data shows the same wavelet structure as the P4 line, and hence appears to be dominated either by the P4 line or by consistent instrumental artifacts. Krasnopolsky et al. state that, if methane, the feature would be consistent with an abundance of 10 ± 3 ppbv. Their " 3.7σ " result, from one of fifteen lines, may not be greatly different from chance.

3.2.2. The R0 and R1 lines

Mumma et al. (2009) reported detection of significant, latitudinally variable methane on Mars using the R0 and R1 lines of the ν_3 band of $^{12}\text{CH}_4$. These observations were made using the Cryogenic Echelle Spectrograph (CSHELL) instrument at the NASA IRTF (Infrared Telescope Facility). The observations of the R0 and R1 lines are separate—the two lines were not both seen in the same observation. The R0 and R1 lines are attractive targets for ground-based work because they are moderately strong and they are effectively single lines, rather than multiplets. This minimizes the effects of line mixing and makes modeling absorption in the wings of the strong telluric $^{12}\text{CH}_4$ lines more robust. The tradeoff is that an observation of a single line leaves only the frequency as an identifying characteristic. The rest frequencies of the $^{12}\text{CH}_4$ R0 and R1 lines are 3028.75 cm^{-1} and 3038.50 cm^{-1} , respectively. The 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} . The apparent methane signature is easy to see in their Fig. 1, and it is seen at all latitudes in what are effectively latitudinal maps of Mars.

Mumma et al. (2009) 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} . Observations were made both with CSHELL and with NIRSPEC (the Near-Infrared Spectrograph) on Keck, a more powerful instrument. The upper limit appears to be ~ 3 ppbv. Krasnopolsky (2007) also looked for the R0 and R1 lines during the same apparition with CSHELL on IRTF. His data

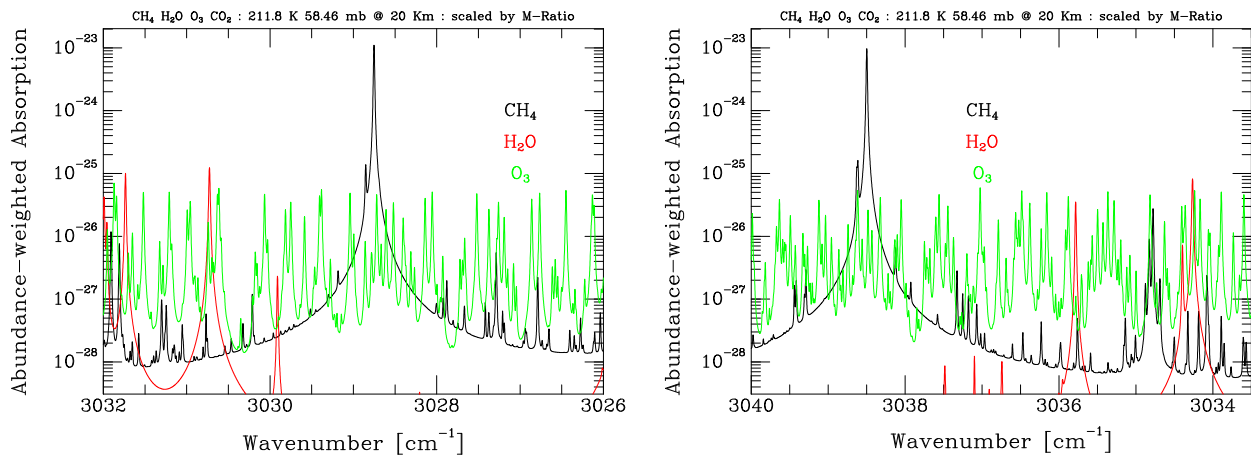


Fig. 6. Abundance-weighted absorption (cm^2) for Earth's stratosphere at 20 km in the immediate vicinity of the ν_3 $^{12}\text{CH}_4$ R0 (left) and R1 (right) lines. The low pressure of the stratosphere allows the different lines to be seen clearly. In particular, the ν_3 R1 line and R2 lines of $^{13}\text{CH}_4$ at 3028.85 cm^{-1} and 3038.62 cm^{-1} are in the blue wings of the $^{12}\text{CH}_4$ lines. Their placement is equivalent to blueshifting the $^{12}\text{CH}_4$ lines by 0.10 cm^{-1} and 0.12 cm^{-1} , respectively. The blue wing of the ν_3 $^{12}\text{CH}_4$ R0 and both wings of the R1 lines are affected by numerous ozone lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

were obtained in February 2006. The redshift of 0.174 cm^{-1} was then near its maximum value. Krasnopolsky reports upper limits on the order of ~ 20 ppbv. Krasnopolsky notes that the solar spectrum in this region is fairly bland but has dips as deep as a few percent (see his Fig. 11), which he treats as a possible complicating factor. The difference in the upper limits between observers using the same tool is surprising; the difference may be attributable to the more sophisticated methods that Mumma et al. use to reduce their data.

The redshift/blueshift dichotomy in the R0/R1 observations is interesting. Mumma et al. (2009) attribute the difference to seasonality. But there may be another explanation for a redshift/blueshift asymmetry hidden in methane's spectrum. Krasnopolsky (2007) notes in passing that the blue wings of the $^{12}\text{CH}_4$ R0 and R1 lines are "contaminated" by other telluric lines of water and methane. Krasnopolsky appears to be referring to strong lines of $^{13}\text{CH}_4$, i.e., methane made with carbon's minor isotope. These methane lines, which are not mentioned by Mumma et al. (2009), are well seen in Fig. 6.

Figs. 6–8 illustrate why the blueshifted retrievals are more challenging than the redshifted retrievals. Figs. 6 and 7 reveal strong lines of $^{13}\text{CH}_4$ superposed on the blue wings of the ν_3 $^{12}\text{CH}_4$ R0 and R1 lines. These are the $^{13}\text{CH}_4$ ν_3 R1 and R2 lines, respectively. The $^{13}\text{CH}_4$ R1 line is displaced to the blue from the center of the $^{12}\text{CH}_4$ R0 line by 0.10 cm^{-1} , and the $^{13}\text{CH}_4$ R2 doublet is displaced to the blue from the center of the $^{12}\text{CH}_4$ R1 line by 0.12 cm^{-1} . These are not directly resolved from martian methane blueshifted by 0.15 or 0.16 cm^{-1} using IRTF's CSHELL instrument, which has a nominal resolution of 0.075 cm^{-1} at 3030 cm^{-1} . The R0 line also contends with a weak water line displaced to the blue by 0.15 cm^{-1} . Fig. 9 shows how well the contending lines line up with the putative martian lines.

The telluric $^{13}\text{CH}_4$ lines are much stronger than the putative martian $^{12}\text{CH}_4$ lines. Methane on Earth is presently 1800 ppbv at 1 bar. The $^{12}\text{C}/^{13}\text{C}$ ratio in atmospheric methane is 93.4, which is 4.7% lighter than the terrestrial Pee Dee Belemnite (PDB) carbonate geochemical standard.² This implies that 1800 ppbv of $^{12}\text{CH}_4$ corre-

sponds to 19.3 ppbv $^{13}\text{CH}_4$, or $6.6\text{ }\mu\text{g}/\text{cm}^2$ above Mauna Kea (0.61 bars). On Mars, allowing for two passes through a 6.3 mbar atmosphere, the equivalent amount of methane would correspond to 530 ppbv of $^{12}\text{CH}_4$. The R0, R1, and R2 lines are 50–60% stronger at 200 K than at 280 K, and the R2 doublet is in combination about twice as strong as R0 or R1. When the calculation is done in detail we find that the R0 line of $^{12}\text{CH}_4$ at 200 K is intrinsically $1.7\times$ stronger than the R1 line of $^{13}\text{CH}_4$ at 275 K, and the $^{12}\text{CH}_4$ R1 line at 200 K is intrinsically $0.77\times$ the strength of the $^{13}\text{CH}_4$ R2 doublet at 275 K. We therefore infer that the telluric $^{13}\text{CH}_4$ R1 line is $\sim 15\times$ stronger than the R0 line produced by 20 ppbv of martian $^{12}\text{CH}_4$, and the telluric $^{13}\text{CH}_4$ R2 doublet is $\sim 35\times$ stronger than the R1 line produced by 20 ppbv of martian $^{12}\text{CH}_4$. When the relatively high strengths of the telluric isotopic lines are combined with the need to achieve super-resolution, errors in pressure broadening and pressure shifts of the CH_4 lines could easily mask (or produce) residuals that are interpreted as martian CH_4 .

Mumma et al. use a model of Earth's atmosphere as the basis for removing the effects of Earth's atmosphere. The model is tuned to the particular observation by exploiting information in the observed spectrum from wavelengths unaffected by Mars. This can be effective for O_3 and H_2O , which have many lines, but it is more difficult for $^{13}\text{CH}_4$, which has only the one line in any particular observation, and thus depends on the correction for the wings of the telluric $^{12}\text{CH}_4$ line and an assumed $^{12}\text{C}/^{13}\text{C}$ ratio. Mumma et al. do not describe their attempts to use a differential measurement (e.g., of a background star) to subtract Earth's spectral absorptions. Their model for telluric absorption is much more sophisticated than the models we have presented here, but the general approach is the same. In particular, Mumma et al.'s model makes use of the same HITRAN database that we use. Mumma et al. did not correct for the 4.7% isotopic difference between atmospheric and PDB methane (M. Mumma, personal communication). The 4.7% difference in using PDB rather than atmospheric methane isotopes would produce a signal as large as, but of opposite sign as, the reported detection that would show up as artificial emission at the wavelengths of the telluric $^{13}\text{CH}_4$ lines. The expected artifact is not apparent in any of the published retrievals. This could mean that Mumma et al. have undercounted martian $^{13}\text{CH}_4$ by a factor of two, it could mean that the uncertainty in their retrievals is comparable to the reported signal, or it could mean that their corrections for telluric $^{13}\text{CH}_4$ are insensitive to their corrections for telluric $^{12}\text{CH}_4$.

² HITRAN uses a $^{12}\text{C}/^{13}\text{C}$ ratio of $R = 0.0112348$, which is close to the PDB standard of $R_{\text{PDB}} = 0.0112372$ (e.g., Santamaria-Fernandez et al., 2008). Differences from the PDB standard are conventionally expressed in the $\delta^{13}\text{C}_{\text{PDB}}$ notation, which is defined by $\delta^{13}\text{C}_{\text{PDB}} = (R/R_{\text{PDB}} - 1) \times 1000$. Current atmospheric methane is variable but on average has $\delta^{13}\text{C}_{\text{PDB}} \approx -47$ per mil (or -4.7%). Hence $R_{\text{atm}} = (-47/1000 + 1) \times R_{\text{PDB}} = 0.010709051$, for which $^{12}\text{C}/^{13}\text{C} = 93.4$.

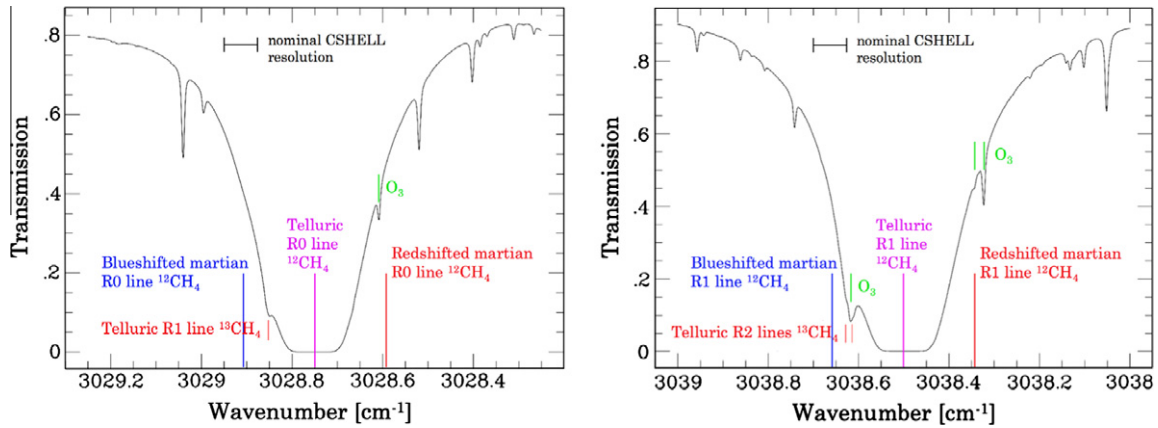


Fig. 7. Computed transmission through Earth's atmosphere in the immediate vicinity of the ν_3 $^{12}\text{CH}_4$ R0 (left) and R1 (right) lines. The ν_3 R1 and R2 lines of $^{13}\text{CH}_4$ at 3028.85 cm^{-1} and 3038.62 cm^{-1} are not fully resolved from blueshifted martian $^{12}\text{CH}_4$ lines by IRTF-CSHELL, but may be resolvable with newer more capable instruments. As described in the text, the $^{13}\text{CH}_4$ lines are at least $20\times$ stronger than the putative martian $^{12}\text{CH}_4$ lines, which makes them a significant source of confusion. The red wings of the ν_3 $^{12}\text{CH}_4$ R0 and R1 line are affected by narrow ozone lines. Stronger interference on the blue wing of the $^{12}\text{CH}_4$ R1 line combines the greater line strength of $^{13}\text{CH}_4$ R2 doublet with a tight cluster of O_3 lines between 3038.61 and 3038.62 cm^{-1} . Placement of martian lines on these plots assumes Doppler shifts of 0.16 cm^{-1} . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

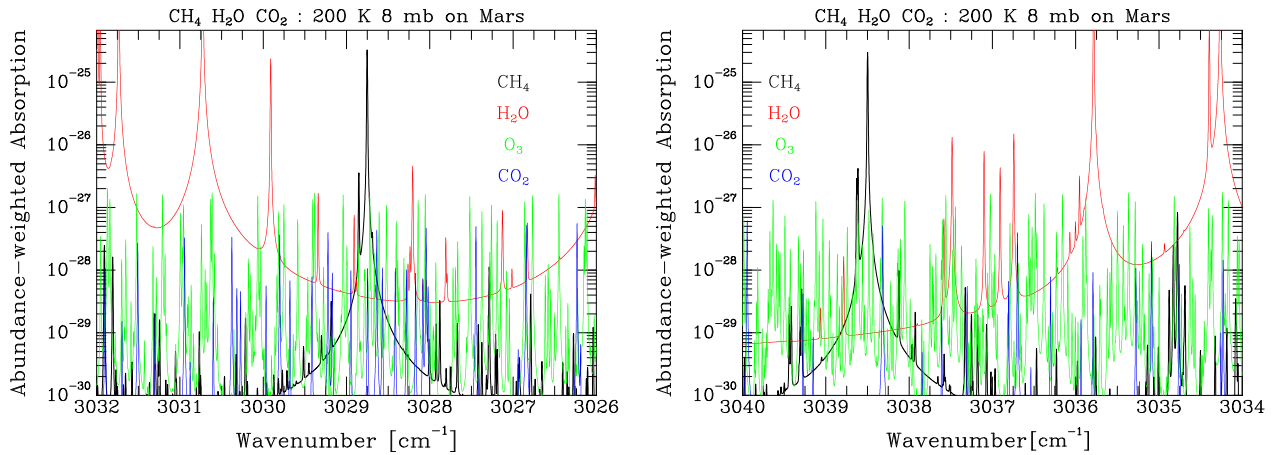


Fig. 8. Abundance-weighted absorption (cm^2) for Mars's atmosphere spiked with 20 ppbv CH_4 in the immediate vicinity of the ν_3 $^{12}\text{CH}_4$ R0 (left) and R1 (right) lines. Methane is black, water red, ozone green, and CO_2 blue. There are no obvious sources of confusion. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2.3. The P2 lines

The other reported detection of martian methane uses the ν_3 P2 lines of $^{12}\text{CH}_4$ (Mumma et al., 2009). The observations were taken on 29 May 2005, when Mars was approaching Earth at 11 km/s , giving a blueshift of 0.11 cm^{-1} . The relevant figure is their Fig. S2 (from the supplemental online material of Mumma et al.). Their figure shows a pronounced difference between the northern and southern hemispheres of Mars. In the north, there are lines of $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ on either side of the methane line. These are the R23 and R25 lines of the $\nu_2 + \nu_3$ band (Villanueva et al., 2008a,b). In the South, the CO_2 lines are much weaker if present. Instead there is a relatively strong line at the expected frequency of the martian $^{12}\text{CH}_4$ P2 doublet. The methane signal grows monotonically stronger to the south, and is strongest at the south pole. It is not stated how much methane the line would correspond to.

Figs. 10 and 11 illustrate the abundance weighted absorption in air and total atmospheric transmission through air in the vicinity of the ν_3 $^{12}\text{CH}_4$ P2 lines. In the rest frame the P2 lines are at 2999.06 and 2998.99 cm^{-1} . Fig. 10 shows that the P2 methane doublet coincides with a weaker but non-negligible water triad at rest frequencies of 2998.97 , 2999.00 , and 2999.16 cm^{-1} . These lines are

stronger than the putative martian methane line, and thus the same sorts of problems arise as arose for the R0 and R1 lines with $^{13}\text{CH}_4$.

Fig. 11 shows that the 0.11 cm^{-1} blueshift of the May 2005 observations is not really big enough to separate the the redder of a possible martian $^{12}\text{CH}_4$ P2 doublet from total telluric extinction. The line that remains is shifted into coincidence with H_2O at 2999.16 cm^{-1} .

The water lines introduce two complications to retrieving weak martian lines. The first is that water vapor is variable on short time scales in Earth's atmosphere. The second is that two of the three contaminating water lines are very sensitive to temperature. The line at 2998.97 cm^{-1} has an effective excitation temperature of 2060 K , i.e., to first approximation the population of the level and hence the line strength goes as $e^{-2060/T}$. This line coincides with the redder of the $^{12}\text{CH}_4$ P2 lines. The H_2O line (actually a close doublet) at 2999.16 cm^{-1} is even more sensitive to temperature, with an excitation temperature of 2870 K . At this point it is worth mentioning that HITRAN is not infallible, and that the data in HITRAN are sometimes uncertain. To give a specific example, the quoted uncertainty in the strength of H_2O 's 2999.16 cm^{-1} line is $5\text{--}10\%$

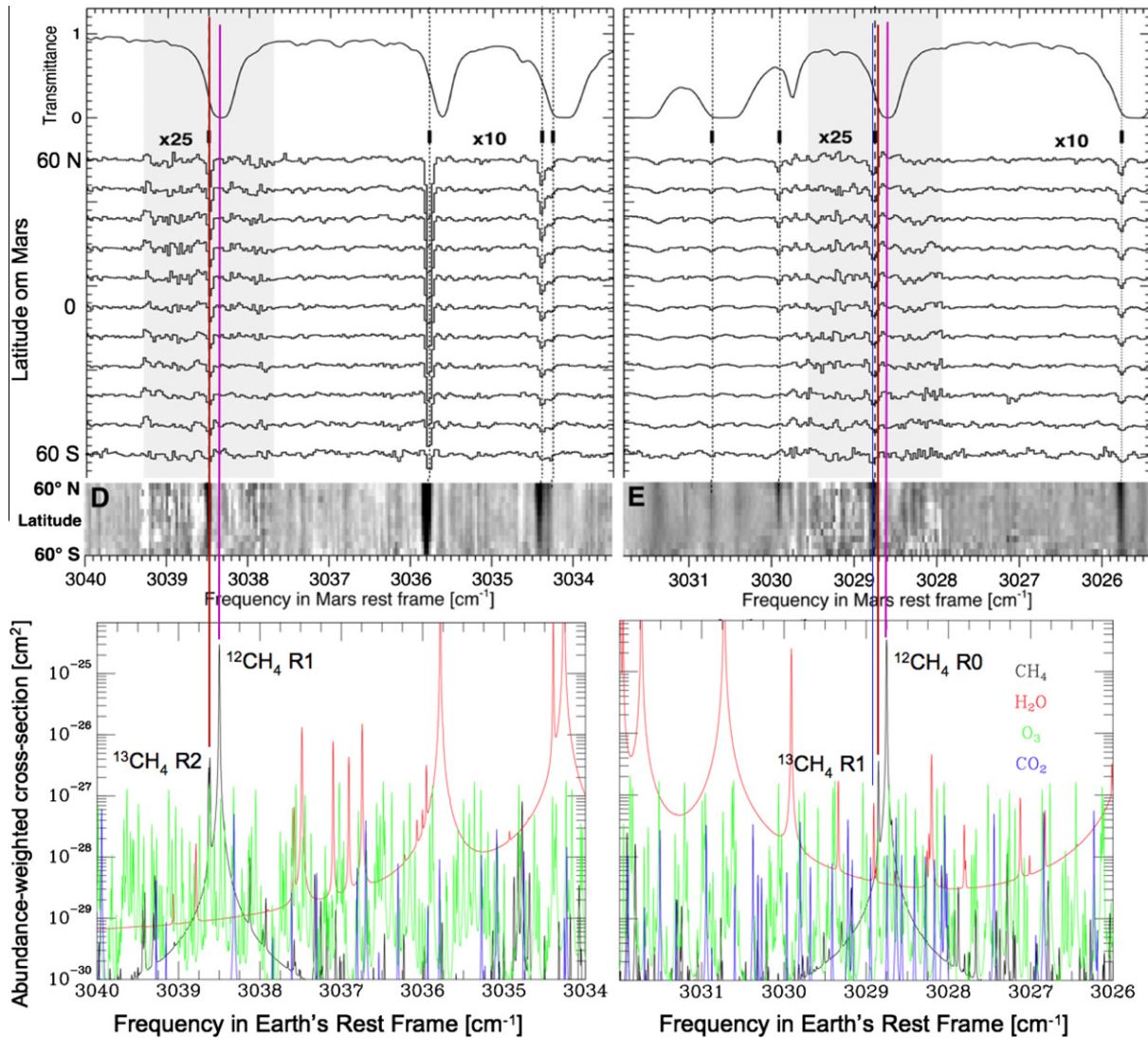


Fig. 9. The top panel shows Mumma et al.'s retrieval of martian methane using the blueshifted ν_3 $^{12}\text{CH}_4$ R0 and R1 lines. The curves labeled "transmittance" are their models of Earth's atmosphere. The lower panels use our Fig. 8 to show the locations and strengths of key lines at low pressures for which collisional broadening is negligible. The vertical lines draw correspondences between the published spectrum and telluric $^{12}\text{CH}_4$ lines (violet), telluric $^{13}\text{CH}_4$ lines (red), and telluric H_2O lines (blue). The reported martian methane lines correspond to strong lines of telluric $^{13}\text{CH}_4$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Rothman et al., 2009); the excitation temperature may also be imperfectly known, which is a serious issue for modeling a line as sensitive to temperature as 2999.16 cm^{-1} is.

At 20 ppbv on Mars, the bluer (and weaker) of the P2 lines would have a vertical optical depth on Mars of 0.022. We compute a nominal vertical optical depth of the H_2O 2999.16 cm^{-1} line of 0.27 above Mauna Kea. Thus the telluric water line is about $6\times$ stronger (allowing two passes through the martian atmosphere and ignoring the geometry) than the signal produced by 20 ppbv martian methane blueshifted to essentially the same wavelength.

With methane present, the ν_3 $^{12}\text{CH}_4$ P2 region on Mars would be complex. Fig. 12 shows abundance-weighted absorption in martian air with 20 ppbv CH_4 and 20 precipitable microns of H_2O at 225 K. The water and temperature are reasonable for the season ($L_s = 217$). For these conditions the H_2O lines are about $4\times$ weaker than the lines produced by 20 ppbv methane. As noted, these H_2O lines are very temperature sensitive, while the P2 lines of methane are not. Thus it is remotely possible that an anomalously warm wet spring day on Mars could explain the observation with martian water.

Also prominent in Fig. 12 are three isotopic CO_2 lines. They are the R25, R24, and R23 lines of the $\nu_2 + \nu_3$ band of $^{12}\text{C}^{16}\text{O}^{18}\text{O}$. The R24 line is very close in strength and placement to the ν_3 $^{12}\text{CH}_4$ P2 doublet for 20 ppbv methane. Mumma et al. were able to retrieve the R23 and R25 lines at 2999.5 cm^{-1} and 2998.3 cm^{-1} , respectively, but only in the northern hemisphere (there is a hint of R25 in the south), and they did not retrieve the R24 line in the middle: the $+0.11\text{ cm}^{-1}$ blueshift moves the R24 line at 2998.92 cm^{-1} to 2999.03 cm^{-1} , which puts it between the lines of the telluric CH_4 P2 doublet. Nondetection of the R24 line suggests that the uncertainty in the retrievals near the heart of the telluric methane P2 lines is considerable.

The hemispheric asymmetry in CO_2 is at first sight surprising. The explanation may be path length through the martian atmosphere (M. Mumma, personal communication): (i) The southern hemisphere has on average a significantly higher elevation, so that the atmosphere is thinner there; this causes a 30% difference between hemispheres. (ii) On 29 May 2005, Earth was at its southernmost declination in the martian sky, which made the slant

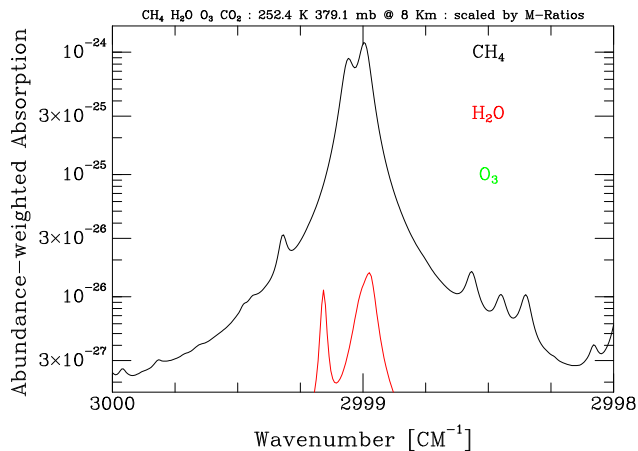


Fig. 10. Computed abundance-weighted absorption (cm^2) at 8 km altitude in air in the immediate vicinity of the ν_3 $^{12}\text{CH}_4$ P2 lines. The interval 2998–3000 cm^{-1} corresponds to Mumma et al.'s Fig. S2 (from the supplemental online material of Mumma et al.); it is a subset of the full spectral window. The ν_3 $^{12}\text{CH}_4$ P2 lines (black) are at 2999.06 and 2998.99 cm^{-1} . The methane doublet coincides with a weaker but very temperature sensitive H_2O triplet (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

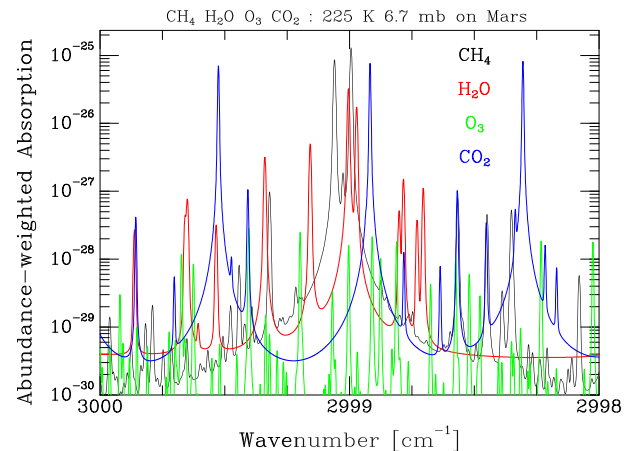


Fig. 12. Abundance-weighted absorption (cm^2) for Mars in the immediate vicinity of the ν_3 $^{12}\text{CH}_4$ P2 lines. These are computed at 225 K and 20 precipitable microns of water. Spiking the martian atmosphere with 20 ppbv methane turns this into a complicated region. The H_2O lines (red) are within a factor of a few of the 20 ppbv ν_3 $^{12}\text{CH}_4$ P2 lines (black). Also interesting are the R23, R24, and R25 lines of the $\nu_2 + \nu_3$ band of $^{12}\text{C}^{16}\text{O}^{18}\text{O}$. These are comparable in strength to the lines produced by the methane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

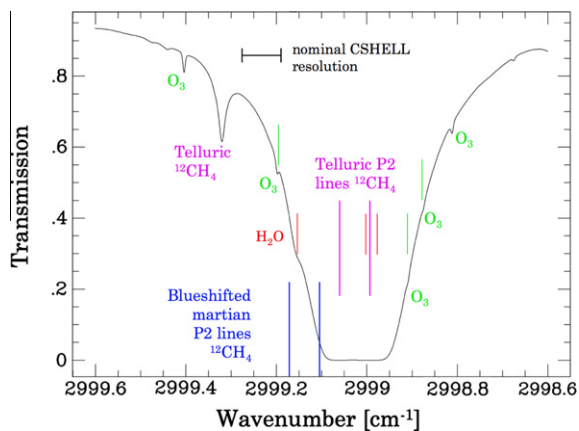


Fig. 11. Computed transmission through Earth's atmosphere in the immediate vicinity of the ν_3 $^{12}\text{CH}_4$ P2 lines. The blueshift of 0.11 cm^{-1} corresponds to that used by Mumma et al. in their detection. This blueshift is insufficient to separate the redder of the martian P2 lines from telluric methane, while placing the other in near coincidence with a stronger telluric H_2O line that is very sensitive to temperature. The methane line at 2999.33 cm^{-1} is from the R9 series of the $\nu_2 + \nu_4$ band. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

path through the northern hemisphere's atmosphere exceptionally long.

The difference in CO_2 between hemispheres is not attributable to temperature because the R23, R24, and R25 $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ lines all rise from the vibrational ground state and are relatively insensitive to temperature (Fig. 13). For these particular lines, rotational excitations correspond to excitation temperatures on the order of 250–300 K. There would be a modest temperature dependence if the other Rn, Qn and Pn lines could be ignored, but in fact all the lines are affected and the whole suite of lines must be renormalized (the partition function) to take into account that a molecule can only be in one state. When the excitation and partition function are both taken into account, we find that the R23 and R25 lines are insensitive to temperature for conditions relevant to Mars (Fig. 13). The full suite of Rn and Pn lines (there are dozens) provides an excellent thermometer by fitting $1/T_{\text{rot}}$ to a straight line, as shown by

Villanueva et al., 2008a (their Fig. 5). The key point with the CO_2 lines is that the temperature information is in the slope, not in the absolute strength of individual lines.

In summary, ground-based detection of the P2 CH_4 requires correction of an interference with temperature-sensitive absorption by telluric H_2O at 2999.16 cm^{-1} that is far stronger than the putative martian signal.

4. Discussion and summary

Variable methane in quantities and lifetimes reported in the literature is inconsistent with Mars's atmospheric chemistry, both in the short term when compared to the detailed knowledge of methane atmospheric chemistry gained over the past several decades in Earth science, and in the long term in the context of the chemical stability of O_2 in the martian atmosphere. Thus short-lived abundant methane on Mars should be regarded as an extraordinary claim. Is the claim supported by extraordinary evidence?

The various reported detections of methane discussed here are all very challenging. A common feature of the detections is that in each methane is seen at exactly one wavelength. A single line of a spectrum is not a fingerprint. Thus the apparent consistency of the different reports of methane plays a big part in the credibility of all.

The spacecraft measurements made from *Mars Express* are obviously at the limits of the resolution and sensitivity of the PFS instrument. These are the observations that show variable methane to be a persistent feature of Mars. The interpretation of the variance at 3018 cm^{-1} as methane depends on, among other things, a multi-parameter model of the martian atmosphere and surface. The model fits as shown are not in fact very good: methane's ν_3 Q branch spans almost 3 cm^{-1} , which corresponds to two or three resolution elements in the PFS spectra, yet the putative methane feature is confined to a single 1.3 cm^{-1} resolution element. Moreover, there are other nearby wavelengths where the model fit is equally bad but cannot be changed by adding methane.

Ground-based measurements by Krasnopolsky et al. (2004) use the Doppler shift to move the bluest of the four strong ν_3 P4 lines into the blue wing of Earth's P4 lines. This particular observation has relatively few problems with Earth's atmosphere, although there is some interference from martian isotopic CO_2 lines.

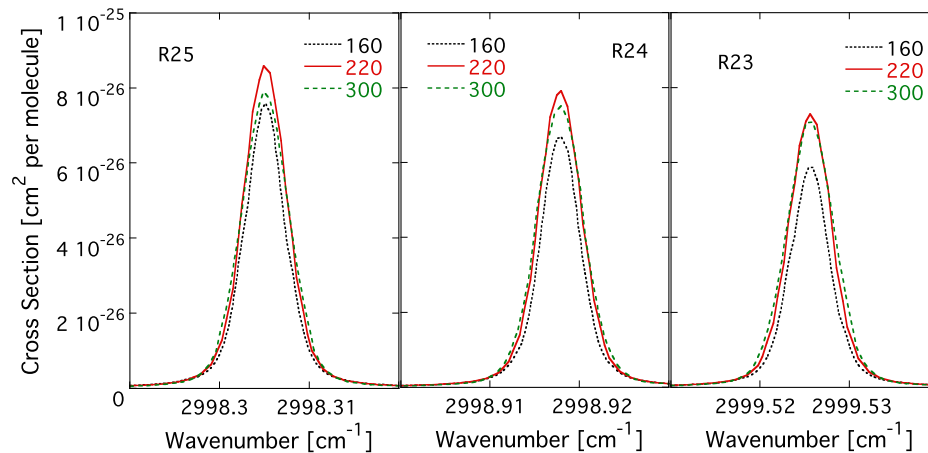


Fig. 13. Computed abundance-weighted absorption cross-sections for the $\nu_2 + \nu_3$ R25, R24, and R23 $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ lines at 6.7 mbars and three temperatures (160 K, 220 K, 300 K). These lines are insensitive to temperature under martian conditions.

However, the observation shows a pronounced wavelike structure that looks alarmingly like an instrumental artifact. The deepest of the minima corresponds to the wavelength of martian CH_4 , but the adjacent minima would be noise.

Ground-based measurements by Mumma et al. (2009) show much stronger signals. Detections are reported at three wavelengths, corresponding to methane's ν_3 R0 and R1 lines and the ν_3 P2 doublet. All are retrieved at several latitudes across the apparent disk of Mars. The signal grades linearly with martian latitude, which Mumma et al. regard as evidence that the signal is intrinsic to Mars as opposed to being an artifact of signal processing. The same linear gradient is seen in martian water vapor in the same spectra.

However, it must be stressed that the published spectra are inseparable from the models used to process the data. These models describe the pressure, temperature, and constituent structure of Earth's atmosphere, and address radiative transfer through the model atmosphere. These models are described in general terms but not to a level of detail where they could be reproduced. In particular, the specific details pertinent to the reported observations are not discussed. We therefore constructed our own atmospheric models to better understand the specific hurdles encountered while measuring martian methane from Earth. What we found is that the three specific wavelengths where detections are reported are particularly affected by undocumented terrestrial contamination.

The P2 doublet is in competition with a triad of water vapor lines, two of which are very temperature sensitive. When the observation was made, the 0.11 cm^{-1} Doppler blueshift was only big enough to move one component of the martian P2 doublet out of the core of the telluric P2 lines. But the 0.11 cm^{-1} blueshift moves the other component into coincidence with a stronger and very temperature sensitive telluric H_2O line. The sensitivity of this H_2O line to the details of the model atmosphere and uncertainties in the HITRAN database would make it very difficult for any model to correct for it.

The issue with viewing martian methane in blueshift in the wings of the telluric $^{12}\text{CH}_4$ R1 and R0 lines is that both of these observations contend with contamination by telluric $^{13}\text{CH}_4$. The telluric $^{13}\text{CH}_4$ lines are challenging because (i) the telluric $^{13}\text{CH}_4$ lines are one to two orders of magnitude stronger than the putative martian $^{12}\text{CH}_4$ lines; (ii) the martian lines are not directly resolved from the telluric $^{13}\text{CH}_4$ lines by the instrument used for the observations; and (iii) there are no other available $^{13}\text{CH}_4$ lines in the observed spectra to provide an independent basis for removing them. By contrast, the red wings of the R1 and R0 lines are less strongly affected by atmospheric confusion, with the chief problem being

narrow O_3 lines, of which there are many at other wavelengths that do provide an independent basis for correcting for them. Consequently the redshifted martian R1 and R0 methane lines should be easier to retrieve. But for these observations, Mumma et al. recover little or no martian methane, consistent with an upper limit on the order of 3 ppbv.

It is possible to do better from Earth. Higher resolution observations made with newer more capable instruments at bigger telescopes are being made today. Higher resolution observations over a range of different redshifts would refine the lower limit obtained from the R0 and R1 lines. Another possibility is using SOFIA (the Stratospheric Observatory for Infrared Astronomy) to observe from the stratosphere, which is above almost all the water and 85% of Earth's methane, and which also exploits the low pressure where interfering lines are narrower (Lacy et al., 2005). Third, Sonnabend et al. (2008) describe a campaign using heterodyne observations made in the ν_4 band that their models project can recover methane at the 10 ppbv levels; however, these observations as planned address solitary lines, which makes identification of a weak signal with methane problematic unless it can be established independently that methane is present.

It is possible to do *much* better from Mars. The NASA Mars Science Laboratory (MSL) carries a remarkable chemistry package that includes capability of obtaining very high-resolution spectra of the $^{12}\text{CH}_4$ ν_3 R3 triplet at 3057.7 cm^{-1} (Webster and Mahaffy, 2010). The experiment will exploit the R3 triplet's characteristic spacings and strengths to identify methane convincingly at the 1 pptv level. Other lines in the same narrow spectral window enable obtaining the $^{13}\text{C}/^{12}\text{C}$ and D/H ratios in methane, if methane is abundant enough.

The ESA-NASA 2016 ExoMars Trace Gas Orbiter mission is expected to have the capability of detecting methane and other trace gases at levels below 10 pptv (Zurek et al., 2010). Along with the measurement of other trace gases (e.g., SO_2 , H_2S , HCl , O_3 , CO , NO_x), the orbiter should be able to determine if Mars currently emits geothermal gases and, if so, how they interact with Mars's oxidizing atmosphere. In particular, the mission should resolve the questions that remain after MSL about the actual level of methane on Mars and its source.

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