

Atmospheric photochemistry above possible martian hot spots

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Abstract

Considering the possibility of outgassing from some localized sources on Mars, we have developed a one-dimensional photochemical model that includes methane (CH₄), sulfur dioxide (SO₂) and hydrogen sulfide (H₂S). Halogens were considered but were found to have no significant impact on the martian atmospheric chemistry. We find that the introduction of methane into the martian atmosphere results in the formation of mainly formaldehyde (CH₂O), methyl alcohol (CH₃OH) and ethane (C₂H₆), whereas the introduction of the sulfur species produces mainly sulfur monoxide (SO) and sulfuric acid (H₂SO₄). Depending upon the flux of the outgassed molecules from possible hot spots, some of these species and the resulting new molecules may be detectable locally, either by remote sensing (e.g., with the Planetary Fourier Spectrometer on Mars Express) or in situ measurements.

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1. Introduction

Although there is no evidence of volcanism on Mars today, outgassing from small, localized sources, the hot spots, may not be ruled out. The models of recent ground water seepage and surface runoff particularly at the middle and high latitudes (Malin and Edgett, 2000), based on certain Mars Global Surveyor images, give a tantalizing possibility that even now Mars could be active from time to time at least in some places. Associated with such water seepage, or even otherwise, there may be outgassing of the typical terrestrial outgassing species –CH₄, SO₂, H₂S, and the halogens. None of these species have yet been detected in “global” observations of the martian atmosphere. Any localized sources, if present, are likely to go undetected in such observations due to dilution by averaging and the relatively short photochemical lifetimes of the species. A tentative detection of 0.5 ppm of formaldehyde (CH₂O) in the equatorial region during northern spring (Korablev et al., 1993), if confirmed, could, however, imply a large flux of methane from a localized source into the martian atmo-

sphere. With the above in mind, and due to considerable interest in the question of extinct or extant life on Mars, we have developed a one-dimensional photochemical model, considering the possibility that CH₄, SO₂ and H₂S from any outgassing sources may be introduced into the martian atmosphere. From this model we predict the abundances of the various new molecules that are expected to be formed in the ensuing atmospheric chemistry, in the hope of guiding future remote sensing and in situ measurements of chemical markers of possible hot spots on Mars. This brief report summarizes the main points of our findings. The reader is referred to Wong et al. (2003) for a detailed discussion of the model.

We begin the hot spot photochemical calculations with a “normal” martian atmosphere model, similar to the models of Krasnopolsky (1993), Atreya and Gu (1994), and Nair et al. (1994). The details of the “normal” atmosphere model including the updated list of photochemical reactions along with their rate coefficients are given in Wong et al. (2003). Here we discuss the points pertinent to the hot spot chemistry. For each chemical species, the model calculates the density as a function of altitude from the ground up to 220 km. Water content is the global averaged value of 10 pr-µm

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(1 pr- $\mu\text{m} = 10^{-4} \text{ g cm}^{-2} \text{ H}_2\text{O} = 3.35 \times 10^{18} \text{ H}_2\text{O molecules cm}^{-2}$; 1 pr- $\mu\text{m} \sim 15 \text{ ppm}$ of H_2O for uniformly mixed H_2O). We introduce SO_2 , H_2S and CH_4 , beginning with their current global average upper limits, and then consider progressively larger abundances over possible outgassing sources. New species and reactions added for calculation of hot spot chemistry are described in the next two sections. Since there is little significant interaction between the sulfur species and the hydrocarbon species, and since their concentrations are relatively low, in the model the two types of chemistry are considered separately. The effect of outgassed halogen species on the martian atmosphere is found to be unimportant (Wong et al., 2003).

2. Sulfur chemistry

The presence of SO_2 and H_2S in the atmosphere of Mars has been speculated previously (e.g., Farquhar et al., 2000; Wänke and Dreibus, 1994). The upper limits of SO_2 and H_2S are 0.1 ppm each for globally averaged observations (Maguire, 1977). In the present work, we investigate the sulfur photochemistry in the martian atmosphere from outgassing sources. The main reactions of sulfur chemistry and their rate coefficients are listed in Wong et al. (2003). The principal reaction pathways are shown in Fig. 1 and will be discussed later in this section.

In the model, we first study the photochemistry of each of these two gases as independent outgassing species. We start with SO_2 as the only outgassed species, at 0.1 ppm at the surface. In subsequent model runs, we

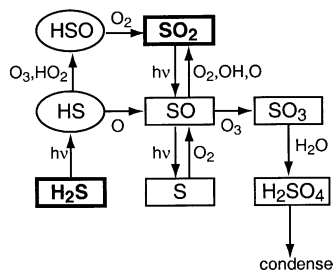


Fig. 1. Important reaction pathways for sulfur species in the martian atmosphere.

increase its concentration gradually until it reaches 100 ppm. We do the same with H_2S outgassing. Then we have both gases outgassing from the surface together, and increase the concentration of each from 0.1 to 100 ppm. The results of a few investigations are listed in Table 1; these models correspond to the cases where both gases are outgassed.

Only for the purpose of illustration, the result of one case (Model C) is summarized here. In this case, the surface mixing ratio of each outgassed species is set to 100 ppm. However, this value could be larger or smaller for each species in the real situation. The resulting mixing ratios of SO_2 , H_2S , and SO at 10 km are 1.7×10^{-4} , 1.8×10^{-5} , and 1.7×10^{-7} , respectively (see Table 1). The number densities of important species are plotted in Fig. 2.

Once in the atmosphere, SO_2 will be photodissociated to produce sulfur monoxide (SO). The reaction of SO with O_2 or OH recycles some SO_2 , while the reaction with O_3 forms sulfur trioxide (SO_3). SO_3 quickly combines with water vapor to form sulfuric acid (H_2SO_4), which condenses in the lower atmosphere. The outgassing of H_2S alone gives similar results as the outgassing of SO_2 . This is due to the fact that the outgassed H_2S is rapidly converted to SO_2 (see Fig. 1). After H_2S is released into the atmosphere, it undergoes photodissociation to form mercapto radical (HS). HS quickly reacts with O_3 to form HSO, which upon reaction with O_2 forms SO_2 . The subsequent chemistry then follows that

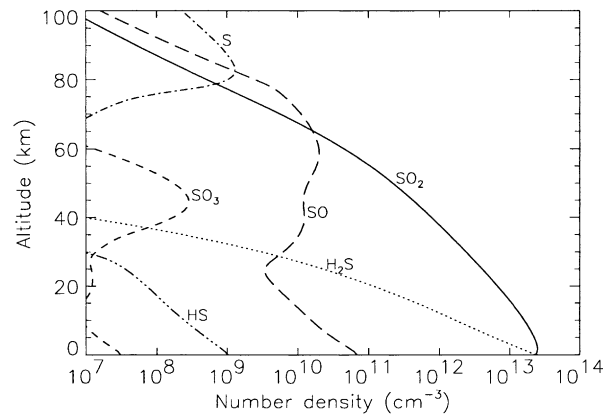


Fig. 2. Number densities of important species vs. altitude calculated in Model C, with 100 ppm each of H_2S and SO_2 at the surface of Mars.

Table 1
Results for sulfur chemistry in the Mars photochemical model

		Model A		Model B		Model C	
		Mixing ratio	Column	Mixing ratio	Column	Mixing ratio	Column
Outgassing species	$\text{SO}_2, \text{H}_2\text{S}$	$10^{-7}, 10^{-7}$	–	$10^{-5}, 10^{-5}$	–	$10^{-4}, 10^{-4}$	–
Major species at 10 km	SO_2	1.3×10^{-7}	9.8×10^{15}	1.7×10^{-5}	1.7×10^{18}	1.7×10^{-4}	1.8×10^{19}
	H_2S	2.2×10^{-8}	7.6×10^{14}	3.0×10^{-6}	1.3×10^{17}	1.8×10^{-5}	7.4×10^{17}
	SO	1.2×10^{-9}	1.7×10^{15}	9.1×10^{-9}	4.1×10^{16}	1.7×10^{-7}	7.8×10^{16}

The column abundance (column) is number of molecules per cm^2 above 10 km altitude.

of SO₂. The photochemical lifetime of SO₂ is 1.4×10^7 s (160 days), and that of H₂S is 7.9×10^5 s (9 days).

3. Hydrocarbon chemistry

The upper limit of CH₄ from globally averaged observations is 0.02 ppm (Maguire, 1977). We use the photochemical model to calculate the abundances of new species that get formed upon the introduction of CH₄ into the martian atmosphere by outgassing. The list of reactions is given in Wong et al. (2003). The principal reaction pathways are shown in Fig. 3.

Starting with 0.02 ppm at the surface, we increase the CH₄ abundance above any possible hot spots gradually until it reaches a mixing ratio of 100 ppm over the hot spot. Table 2 summarizes a sample of the model results. For the purpose of illustration, the result for a case with 100 ppm CH₄ (Model F) is outlined here. The most abundant species are CH₄, CH₂O, methyl alcohol (CH₃OH), and ethane (C₂H₆), and the resulting mixing ratios at 10 km are 1.0×10^{-4} , 2.8×10^{-11} , 4.3×10^{-12} and 6.4×10^{-12} , respectively (see Table 2). The number densities of important species for this case are plotted in Fig. 4.

At high altitudes (>80 km), CH₄ is photodissociated into CH, ³CH₂, ¹CH₂ and CH₃, and its oxidation by O(¹D) forms CH₃. ³CH₂ reacts with CO₂ to form CH₂O. At the low altitudes, the oxidation of methane by OH forms CH₃. CH₃ reacts with O to form CH₂O, and

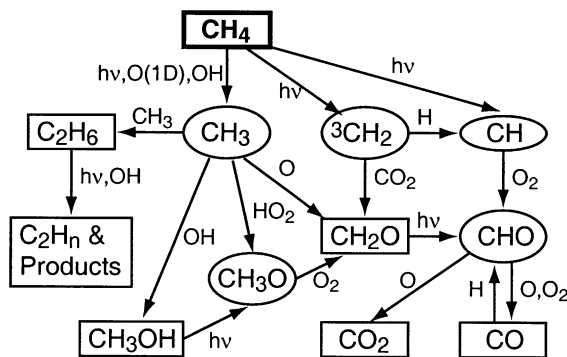


Fig. 3. Important reaction pathways of hydrocarbon chemistry in the martian atmosphere.

Table 2
Results for hydrocarbon chemistry in the Mars photochemical model

		Model D		Model E		Model F	
		Mixing ratio	Column	Mixing ratio	Column	Mixing ratio	Column
Outgassing species	CH ₄	2×10^{-8}	–	10^{-6}	–	10^{-4}	–
Major species at 10 km	CH ₄	2×10^{-8}	2.0×10^{15}	1×10^{-6}	1.0×10^{17}	1×10^{-4}	1.0×10^{19}
	CH ₂ O	6.0×10^{-15}	4.0×10^9	2.9×10^{-13}	2.0×10^{11}	2.8×10^{-11}	1.6×10^{13}
	CH ₃ OH	1.4×10^{-15}	2.1×10^8	4.3×10^{-14}	8.1×10^9	4.3×10^{-12}	8.2×10^{11}
	C ₂ H ₆	2.1×10^{-18}	2.3×10^5	6.4×10^{-16}	9.7×10^7	6.4×10^{-12}	9.6×10^{11}

The column abundance (column) is number of molecules per cm² above 10 km altitude.

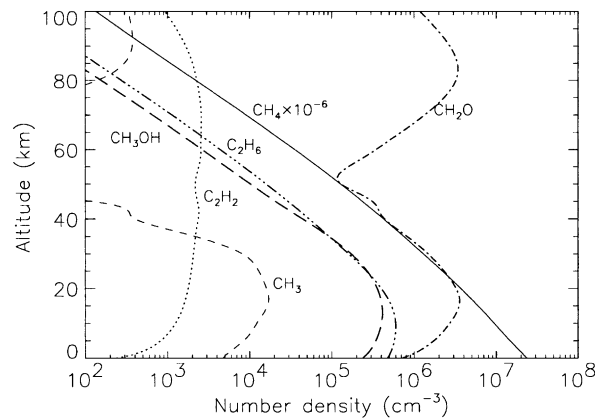


Fig. 4. Number densities of important species vs. altitude calculated in Model F, with 100 ppm of CH₄ at the surface of Mars.

with OH to form CH₃OH. C₂H₆ is produced by recombination of CH₃. The model finds that the abundances of hydrocarbons derived from the methane photochemistry are very low even when the concentration of methane is relatively large in the atmosphere. The reason is that CH₄ does not dissociate efficiently to start the hydrocarbon chemistry. Photolysis of CH₄ is largely shielded by the much more abundant CO₂ whose absorption cross section overlaps that of CH₄. In the lower atmosphere, the most effective way to break down methane is by reaction with OH, which is quickly removed by CO and O.

From our model, we find that the photochemical lifetime of CH₄ is about 670 years, which is the longest amongst the principal hydrocarbon species (lifetimes of CH₂O, CH₃OH and C₂H₆ are 7.5 h, 74 and 25 days, respectively). Therefore, CH₄ may be easier to detect even far from the source region, provided that its source flux is reasonably large. On the other hand, CH₂O has a relatively short lifetime of several hours. Therefore, if the previous tentative detection of CH₂O (0.5 ppm, Korablev et al., 1993) is confirmed by future observations, it would imply a nearly continuous supply of methane to the atmosphere. Moreover, the amount of methane required would have to be much greater than the “global” upper limit of 20 ppb derived from Mariner 9 IRIS observations (Maguire, 1977), since the models produce only 30 ppt of CH₂O with 100 ppm of CH₄ (Model F, Table 2). On the other hand, CH₂O itself

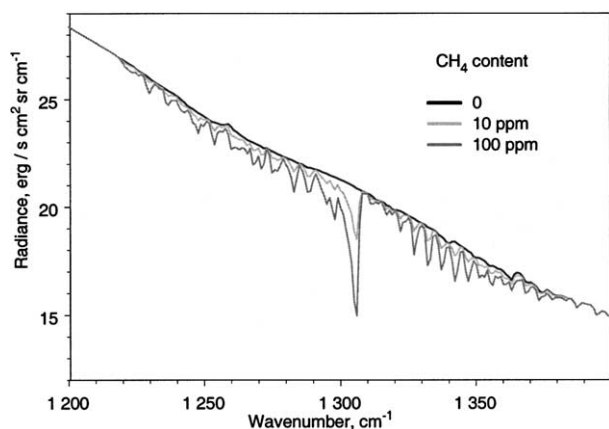


Fig. 5. Simulated PFS spectra for methane at mixing ratios 0, 20 ppb, 10 ppm, 100 ppm.

could also be outgassed from the interior, or formed in surface reactions.

4. Conclusion

We have shown that if outgassing is taking place somewhere on Mars today, only a handful of new species with significant abundance would be formed as a result of photochemical processes involving the products of outgassing. In particular, the outgassed H_2S and SO_2 would produce significant amounts of only SO in the gas phase. H_2SO_4 is expected to condense out. Similarly, photochemistry of any outgassed CH_4 would produce appreciable amounts of only CH_2O and CH_3OH , but the hydrocarbon photochemical products would be less abundant than the sulfur species, starting with the same mixing ratios of the outgassed species. Thus, the best candidates for the chemical markers of any hot spots on Mars are SO_2 , H_2S , CH_4 , possibly SO , CH_2O , and CH_3OH . The largest source of methane in the earth's atmosphere is methanogenic bacteria living in anaerobic soils in tropical forests, swamps and rice paddies and in the guts of cattle and other grass eating animals, with smaller contributions from fossilized matter. Methane and its products could serve as possible biomarkers in the martian atmosphere as well.

The Planetary Fourier Spectrometer (PFS) on board Mars Express can be used to search for the molecules

discussed in this paper. PFS has the spatial resolution and spectral range necessary for detecting small localized sources and some of the outgassing species. We have generated simulated PFS spectra for various species to predict the sensitivity of the instrument. One sample simulated spectrum for methane is shown in Fig. 5. The instrument is capable of detecting methane mixing ratios above 10 ppm in a "single" spectrum. The signal to noise ratio could be increased substantially by binning the spectra, even surpassing the Mariner 9 detection limit of 20 ppb. Depending upon the experience in flight, the actual detection limit may be different than in the simulation. For example, signal-to-noise ratio could be poorer due to the effect of larger than usual aerosol (dust and haze) opacity.

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