Isotopic fractionation of methane in the martian atmosphere

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Abstract

The existence of methane in the martian atmosphere may be an indicator of subsurface life. Biological processes are known to fractionate the common isotopologues of methane, and hence measuring these isotopic ratios may yield constraints on the nature of the methane source. Any measurement of the isotopic ratios of atmospheric methane must consider the additional fractionation due to photochemistry in order to quantify the isotopic ratios of the source. Using a one-dimensional photochemical model, we find that photochemistry has a small (4.5‰) contribution to $\delta^{13}C(CH_4)$ but has a large (114‰) contribution to $\delta D(CH_4)$. Confirmation of these fractionation values will require additional laboratory data on key model inputs, particularly the ultraviolet absorption cross sections of $^{13}CH_4$ and kinetic rate coefficients for the reactions of $^{13}CH_4$ and CH_3D with OH and O(^{1}D) at pressures and temperatures relevant to the martian atmosphere.
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Keywords: Exobiology; Mars, atmosphere; Photochemistry

1. Introduction

The recent tentative detection of methane in the martian atmosphere (Formisano et al., 2004; Krasnopolsky et al., 2004; Mumma et al., 2003) raises the question of its origin, as the martian atmosphere is an oxidizing environment where the lifetime of methane is on the order of 200 years. A number of possible sources have been suggested, such as subsurface biology (Weiss et al., 2000; Summers et al., 2002), volcanism (Wong et al., 2003), or cometary impacts (Kress and McKay, 2004).

It is possible to discriminate between terrestrial methane sources by measuring the relative abundance of the three common isotopologues CH_4, CH_3D, and $^{13}CH_4$. For example, biogenic methane generally has $\delta^{13}C(CH_4)$ lighter than $-60‰$ and $\delta D(CH_4)$ lighter than $-150‰$, while thermogenic (e.g., volcanic) methane generally has $\delta^{13}C(CH_4)$

heavier than $-50‰$ and $\delta D(CH_4)$ heavier than $-275‰$ (Cicerone and Oremland, 1988; Tyler, 1992). The reference isotopic standards for $\delta^{13}C$ and δD are Pee Dee belemnite and Standard Mean Ocean Water, respectively. Here we have used the δ symbol to represent the isotopic enhancement of a sample, defined by

$$\delta = 1000\big[(r/R) - 1\big], \tag{1}$$

where r is the isotopic ratio (e.g., D/H) of the sample and R is the isotopic ratio of the reference. The units of δ are "permil" (‰), or parts per thousand.

Photochemistry will additionally fractionate atmospheric methane. Based on the source and atmospheric values of terrestrial $\delta D(CH_4)$, Tyler (1992) inferred an isotopic shift for $\delta D(CH_4)$ of 210‰ due to atmospheric chemistry. Saueressig et al. (2001) found enhancements of up to 30‰ for $\delta^{13}C(CH_4)$ and 300‰ for $\delta D(CH_4)$ in their photochemical model of the terrestrial stratosphere, in good agreement with the observed isotopic ratios.

If the degree of photochemical fractionation of the methane family can be quantified, measurements of these

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isotopic ratios in the martian atmosphere can provide a constraint on the isotopic ratios of the source, and possibly distinguish biological sources from non-biological ones (Yung and DeMore, 1999; Summers et al., 2002).

2. Photochemical model

Our one-dimensional photochemical model is identical to case "f" of Nair et al. (1994), with the addition of CH_4, CH_3D, and $^{13}CH_4$. Surface fluxes for the methane species are specified as boundary conditions. We assume that there are no photochemical sources for these species and that the only losses are due to photolysis or reaction with $O(^1D)$ or OH.

Photochemical cross sections for CH_4 and CH_3D are taken from Lee et al. (2001). Since the photochemical cross sections for $^{13}CH_4$ have not been measured, we estimate them using the differences in the ground state zero point vibrational energies (ZPEs) between CH_4 and $^{13}CH_4$. We assume a unit quantum yield for photodissociation as the ultraviolet photon energies are significantly larger than the C–H bond strength. This method has been previously used to estimate photochemical cross sections of the heavier isotopologues of N_2O (Yung and Miller, 1997).

The ZPEs for CH_3D and $^{13}CH_4$ relative to CH_4 are -599 ± 1 and -25.5 ± 0.5 cm^{-1}, respectively. These correspond to blue shifts of 0.9 and 0.04 nm, respectively, at 120 nm. The CH_3D cross sections predicted by this method agree well with the measured values of Lee et al. (2001) from 105 to about 130 nm, but are smaller at longer wavelengths where the cross sections are changing rapidly. The ZPE shift for $^{13}CH_4$ is small enough that the predicted cross sections do not significantly differ from those of CH_4. The uncertainty in the $^{13}CH_4$ cross sections is thus dominated by the assumption that the CH_3D and $^{13}CH_4$ cross sections as a function of wavelength have identical shapes.

Rate coefficients for the reactions of CH_3D and $^{13}CH_4$ with $O(^1D)$ and OH were computed using the kinetic isotope effect (KIE) factors measured by Saueressig et al. (2001) and the corresponding CH_4 reaction coefficients from DeMore

et al. (1997). Table 1 shows these rate coefficients, as well as the photodissociation coefficient calculated at the top of the model atmosphere (240 km). At 200 K, the uncertainty in the rate coefficients for the reaction of CH_4 with $O(^1D)$ and OH are 40 and 30%, respectively (DeMore et al., 1997). The 2σ uncertainties in the KIE values are on the order of a few percent (Saueressig et al., 2001). The KIE uncertainties are more important for this study, as we are interested in the relative loss rates among the methane family members, not their absolute rates.

Surface fluxes specified as lower boundary conditions for each methane species are listed in Table 2. The flux for CH_4 (ϕ_0) was chosen to reproduce the observed surface mixing ratio of 10^{-8} (Formisano et al., 2004; Krasnopolsky et al., 2004). The fluxes for CH_3D (ϕ_1) and $^{13}CH_4$ (ϕ_2) were determined by

$$\phi_1 = 4 * f_{D1} * f_{D2} * f_{D3} * \phi_0,$$
$$\phi_2 = f_{C1} * f_{C2} * f_{C3} * \phi_0,$$

where $f_{D1} = 1.5576 \times 10^{-4}$ is the terrestrial D/H standard value (Fegley, 1995), $f_{D2} = 5.2$ is the enrichment factor for deuterium on Mars relative to Earth (Bjoraker et al., 1989; Owen et al., 1988; Krasnopolsky et al., 1997), $f_{D3} = 0.710$ is the enrichment factor for a biogenic source (Tyler, 1992), $f_{C1} = 1.1235 \times 10^{-2}$ is the terrestrial $^{13}C/^{12}C$ standard value (Fegley, 1995), $f_{C2} = 1$ is the enrichment factor for ^{13}C on Mars relative to Earth (Nier and McElroy, 1977), and $f_{C3} = 0.943$ is the enrichment factor for a biogenic source (Tyler, 1992). There is significant (up to 100‰) uncertainty in the value of martian atmospheric $\delta^{13}C$ (Jakosky, 1991), but for the purposes of this paper a precise value is not required. The enrichment factors for biogenic sources are assumed to be the same as the terrestrial values.

3. Results

The calculated surface mixing ratios, column abundances, and column-integrated lifetimes for the methane species are shown in Table 3. The column-integrated loss rates and timescales for each photochemical sink are shown in Table 4. Profiles of all other species in the model are nearly unchanged from those in case "f" of Nair et al. (1994), as the addition of trace amounts of methane is an insignificant perturbation to the standard model.

Since photolysis is not effective as a destruction mechanism below ~ 60 km, we find a lifetime of 380 years at the surface. This is longer than the surface lifetime of 300 years

Table 1
Rate coefficients for methane loss reactions

Reaction	Rate coefficient
$CH_4 + h\nu$	2.924×10^{-6}
$CH_4 + O(^1D)$	1.5×10^{-10}
$CH_4 + OH$	$2.45 \times 10^{-12} e^{-1775/T}$
$CH_3D + h\nu$	2.908×10^{-10}
$CH_3D + O(^1D)$	1.42×10^{-10}
$CH_3D + OH$	$2.23 \times 10^{-12} e^{-1824/T}$
$^{13}CH_4 + h\nu$	2.924×10^{-6}
$^{13}CH_4 + O(^1D)$	1.48×10^{-10}
$^{13}CH_4 + OH$	$2.45 \times 10^{-12} e^{-1775/T}$

The units for photolysis and two-body reactions are s^{-1} and cm^3 s^{-1}, respectively.

Table 2
Lower boundary conditions

Species	Surface flux (cm^{-2} s^{-1})
CH_4	3.460×10^5
CH_3D	7.960×10^2
$^{13}CH_4$	3.670×10^3

found by Summers et al. (2002), who used a rate coefficient for the reaction $O + HO_2$ that is 50% of that used by Nair et al. (1994). When using this value, we obtain the same surface lifetime of 300 years. $O + HO_2$ is the dominant sink for odd oxygen (O and O_3) in the martian atmosphere. Using a smaller rate coefficient for this reaction increases the amount of atmospheric O_3 and hence increases the rate of CH_4 destruction by $O(^1D)$, which is produced by photolysis of O_3.

From the column-integrated lifetimes, we see that photolysis is the largest contributor to methane destruction, but does not discriminate between the different isotopologues. Reaction with OH is the second most important destruction pathway, and removes CH_4 and $^{13}CH_4$ significantly faster than CH_3D. Reaction with $O(^1D)$ is marginally faster for CH_4 and $^{13}CH_4$ than for CH_3D.

In order to compute δ values using Eq. (1), we take r to be the ratio of concentrations (e.g., $[CH_3D]/[CH_4]$) and R to be the ratio of surface fluxes (e.g., ϕ_1/ϕ_0). From the fluxes and calculated mixing ratios in Tables 2 and 3, we find that $\delta D(CH_4) = 114‰$ and $\delta^{13}C(CH_4) = 4.5‰$ at the surface. These values remain nearly constant up to 100 km, as shown in Fig. 1. Above ~ 120 km, $^{13}CH_4$ and CH_3D fall off in abundance relative to the lighter CH_4 due to molecular diffusion. We have not included reactions of methane with ionic species in this model, which may affect the isotopic fractionation in the ionosphere and above.

4. Conclusions

If methane is present in the martian atmosphere, a measurement of the relative abundances of its common isotopologues $^{13}CH_4$ and CH_3D may serve to constrain the nature of its source. These atmospheric measurements will have to be corrected for photochemical processes which will modify the relative abundances of the methane species from their source values.

We expect the lower atmosphere to be enriched in the heavier methane isotopologues relative to the source. The measured atmospheric $^{13}CH_4/CH_4$ ratio should be very close (4.5‰) to the emissions by the source, while the measured atmospheric CH_3D/CH_4 ratio should be appreciably higher (114‰) than the source emissions, primarily due to the more rapid reaction of CH_4 with OH.

Figure 2 shows how the measured isotopic ratio of atmospheric methane should differ from the isotopic ratio of the source. We take the source composition to be $\delta^{13}C(CH_4) = -57‰$ and $\delta D(CH_4) = -290‰$, the same as for terrestrial sources (Tyler, 1992). In this case the measured $\delta^{13}C(CH_4)$ would be $-52‰$ and $\delta D(CH_4)$ would be $-176‰$.
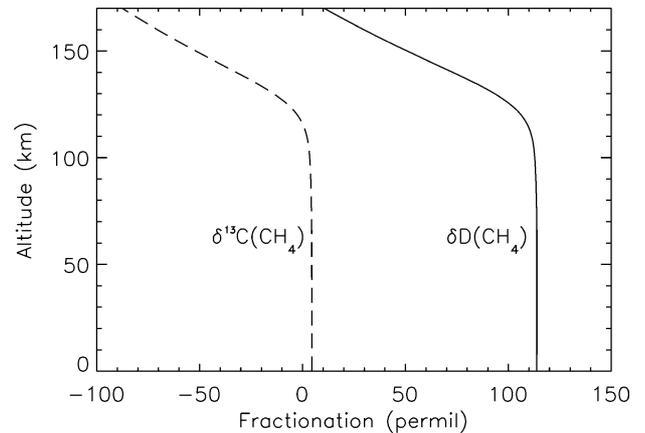
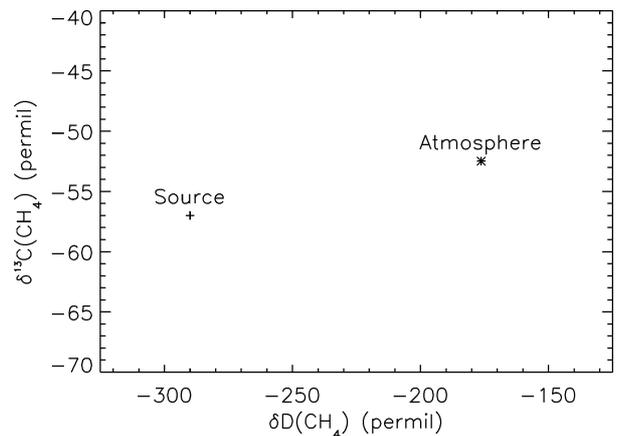Fig. 1. Calculated vertical profiles of $\delta^{13}C(CH_4)$ and $\delta D(CH_4)$.

Fig. 2. Isotopic composition of a CH_4 source (assumed to be the same as terrestrial) and the expected atmospheric composition.

Table 3
Surface mixing ratios, column amounts, and column lifetimes

Species	Surface mixing ratio	Column abundance (cm^{-2})	τ (years)
CH_4	9.993×10^{-9}	2.305×10^{15}	211
CH_3D	2.561×10^{-11}	5.907×10^{12}	235
$^{13}CH_4$	1.065×10^{-10}	2.456×10^{13}	212

Table 4
Column integrated loss rates and timescales for methane isotopologues

	$h\nu$ column rate (cm^{-2} s^{-1})	τ (years)	OH column rate (cm^{-2} s^{-1})	τ (years)	$O(^1D)$ column rate (cm^{-2} s^{-1})	τ (years)
CH_4	1.700×10^5	430	1.098×10^5	665	6.702×10^4	1090
CH_3D	4.347×10^2	431	2.010×10^2	931	1.620×10^2	1155
$^{13}CH_4$	1.808×10^3	430	1.165×10^3	668	7.048×10^2	1104

Significant uncertainties in this study are the photolysis rate of $^{13}CH_4$, as well as values for the kinetic isotope effects for the reactions of $^{13}CH_4$ and CH_3D with OH and $O(^1D)$. Further laboratory measurements will be extremely useful in order to design and conduct experiments that can measure the isotopic fractionation of CH_4 on Mars to the required precision to detect biogenic signatures.

Acknowledgments

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