Isotopic fractionation of methane in the martian atmosphere

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Received ________________; accepted ________________

Submitted to Icarus, 17 August 2004

11 pages, 4 tables, 2 figures
Proposed running head: Methane Fractionation on Mars

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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. We find that photochemical processing of the methane family in the atmosphere has a small (4.5\%) contribution to $\delta^{13}C(CH_4)$ but has a large (90\%) contribution to $\delta D(CH_4)$.

Subject headings: Exobiology; Mars, atmosphere; Photochemistry
1. Introduction

The recent tentative detection of methane in the martian atmosphere (Encrenaz, 2004; Maillard 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., 2004), 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$_3$D, and $^{13}$CH$_4$. For example, biogenic methane generally has $\delta^{13}$C(CH$_4$) lighter than $-60\%_o$ and $\delta D$(CH$_4$) lighter than $-150\%_o$, while thermogenic (e.g. volcanic) methane generally has $\delta^{13}$C(CH$_4$) heavier than $-50\%_o$ and $\delta D$(CH$_4$) heavier than $-275\%_o$ (Cicerone and Oremland, 1988; Tyler, 1992). The reference isotopic standards for $\delta^{13}$C and $\delta D$ are Pee Dee belemnite and Standard Mean Ocean Water, respectively.

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 $210\%_o$ due to atmospheric chemistry. Saueressig et al. (2001) found enhancements of up to $30\%_o$ for $\delta^{13}$C(CH$_4$) and $300\%_o$ 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 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$_3$D, and $^{13}$CH$_4$. Surface fluxes for these species were specified as boundary conditions, and we assume that the only losses are due to photolysis or reaction with O($^1$D) or OH.

Photochemical cross sections for CH$_4$ and CH$_3$D 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$_2$O (Yung and Miller, 1997).

The ZPEs for CH$_3$D and $^{13}$CH$_4$ relative to CH$_4$ are -599 and -25.5 cm$^{-1}$, respectively. These correspond to blue shifts of 0.9 and 0.04 nm, respectively, at 120 nm. The CH$_3$D 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. The ZPE shift for $^{13}$CH$_4$ is small enough that the predicted cross sections do not significantly differ from those of CH$_4$.

Rate coefficients for the reactions of CH$_3$D and $^{13}$CH$_4$ with O($^1$D) and OH were computed using the kinetic isotope effects measured by Saueressig et al. (2001) and the corresponding CH$_4$ reaction coefficients from DeMore et al. (1997). Table 1$^{E1}$ shows these rate coefficients, as well as the photodissociation coefficient calculated by the model at the top of the model atmosphere (240 km).

$^{E1}$NOTE TO EDITOR: Insert Table 1
Surface fluxes specified as lower boundary conditions for each are listed in Table 2. The flux for CH$_4$ ($\phi_0$) was chosen to reproduce the observed surface mixing ratio of $10^{-8}$ (Encrenaz, 2004; Maillard et al., 2004). We note that this surface flux of $3.440 \times 10^5$ cm$^{-2}$ s$^{-1}$ is smaller than the potential flux from a subsurface biosphere that derives its energy source from the photochemical products in the atmosphere (Weiss et al., 2000).

The fluxes for CH$_3$D ($\phi_1$) and $^{13}$CH$_4$ ($\phi_2$) were determined by

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

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. Discussion

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

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E2NOTE TO EDITOR: Insert Table 2
E3NOTE TO EDITOR: Insert Table 3
and timescales for each photochemical sink are shown in Table 4\textsuperscript{E4}. 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 $\sim 60$ km, we find a lifetime of 380 years at the surface. This is longer than the surface lifetime of 300 years 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$_3$D. Reaction with $O(^1D)$ is marginally faster for CH$_4$ and $^{13}$CH$_4$ than for CH$_3$D.

We define the isotopic shift $\delta$ as

$$\delta = 1000[r/R - 1],$$

where $r$ is the ratio of concentrations (e.g. $[CH_3D]/[CH_4]$) and $R$ is the ratio of surface fluxes (e.g. $\phi_1/\phi_0$). From the fluxes and calculated mixing ratios in Tables 2 and 3, we find that $\delta D(CH_4) = 90\%_o$ and $\delta^{13}C(CH_4) = 4.5\%_o$ at the surface. These values remain

\textsuperscript{E4}NOTE TO EDITOR: Insert Table 4
nearly constant up to 100 km, as shown in Fig. 1. Above \( \sim 120 \) km, \(^{13}\text{CH}_4\) and \(^{3}\text{CH}_3\text{D}\) fall off in abundance relative to the lighter \(^{12}\text{CH}_4\) 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.

We expect the lower atmosphere to be enriched in the heavier methane isotopologues relative to the source. The measured atmospheric \(^{13}\text{CH}_4\)/\(^{12}\text{CH}_4\) ratio should be very close to the emissions by the source, while the measured atmospheric \(^{3}\text{CH}_3\text{D}\)/\(^{12}\text{CH}_4\) ratio should be appreciably higher than the source emissions, primarily due to the more rapid reaction of \(^{12}\text{CH}_4\) with \(\text{OH}\).

Fig. 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 \(\delta^{13}\text{C}(\text{CH}_4) = -57\%\) and \(\delta D(\text{CH}_4) = -290\%\), the same as for terrestrial sources (Tyler, 1992). In this case the measured \(\delta^{13}\text{C}(\text{CH}_4)\) would be \(-52\%\) and \(\delta D(\text{CH}_4)\) would be \(-200\%\).

Significant uncertainties in this study are the photolysis rate of \(^{13}\text{CH}_4\), as well as values for the kinetic isotope effects for the reactions of \(^{13}\text{CH}_4\) and \(^{3}\text{CH}_3\text{D}\) with \(\text{OH}\) and \(\text{O}(^{1}\text{D})\). Further laboratory measurements will be extremely useful in order to design and conduct experiments that can measure the isotopic fractionation of \(^{12}\text{CH}_4\) on Mars to the required precision to detect biogenic signatures.

We thank M. Gerstell for a critical reading of the manuscript. This work was supported in part by an NSF grant and the NASA Astrobiology Institute at JPL.

\(^{E5}\)NOTE TO EDITOR: Insert Fig. 1

\(^{E6}\)NOTE TO EDITOR: Insert Fig. 2
REFERENCES


This manuscript was prepared with the AAS \LaTeX macros v5.2.
Table 1. Rate coefficients for methane loss reactions. The units for photolysis and two-body reactions are s$^{-1}$ and cm$^3$ s$^{-1}$, respectively.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
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</thead>
<tbody>
<tr>
<td>CH$_4$ + h$\nu$</td>
<td>2.924 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>CH$_4$ + O(1D)</td>
<td>1.5 $\times$ 10$^{-10}$</td>
</tr>
<tr>
<td>CH$_4$ + OH</td>
<td>2.46 $\times$ 10$^{-12}$ e$^{-1780/T}$</td>
</tr>
<tr>
<td>CH$_3$D + h$\nu$</td>
<td>2.908 $\times$ 10$^{-10}$</td>
</tr>
<tr>
<td>CH$_3$D + O(1D)</td>
<td>1.42 $\times$ 10$^{-10}$</td>
</tr>
<tr>
<td>CH$_3$D + OH</td>
<td>1.89 $\times$ 10$^{-12}$ e$^{-1780/T}$</td>
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<tr>
<td>$^{13}$CH$_4$ + h$\nu$</td>
<td>2.924 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>$^{13}$CH$_4$ + O(1D)</td>
<td>1.5 $\times$ 10$^{-10}$</td>
</tr>
<tr>
<td>$^{13}$CH$_4$ + OH</td>
<td>2.46 $\times$ 10$^{-12}$ e$^{-1780/T}$</td>
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Table 2. Lower boundary conditions

<table>
<thead>
<tr>
<th>Species</th>
<th>Surface Flux (cm$^{-2}$ s$^{-1}$)</th>
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<tbody>
<tr>
<td>CH$_4$</td>
<td>$3.440 \times 10^5$</td>
</tr>
<tr>
<td>CH$_3$D</td>
<td>$7.910 \times 10^2$</td>
</tr>
<tr>
<td>$^{13}$CH$_4$</td>
<td>$3.640 \times 10^3$</td>
</tr>
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</table>
Table 3. Surface mixing ratios, column amounts, and column lifetimes

<table>
<thead>
<tr>
<th>Species</th>
<th>Surface mixing ratio</th>
<th>Column abundance (cm(^{-2}))</th>
<th>(\tau) (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>(1.000 \times 10^{-8})</td>
<td>(2.307 \times 10^{15})</td>
<td>212</td>
</tr>
<tr>
<td>CH(_3)D</td>
<td>(2.507 \times 10^{-11})</td>
<td>(5.784 \times 10^{12})</td>
<td>231</td>
</tr>
<tr>
<td>(^{13})CH(_4)</td>
<td>(1.063 \times 10^{-10})</td>
<td>(2.452 \times 10^{13})</td>
<td>213</td>
</tr>
</tbody>
</table>
Table 4. Column integrated loss rates and timescales for methane isotopologues

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$</th>
<th></th>
<th>CH$_3$D</th>
<th></th>
<th>$^{13}$CH$_4$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>column rate</td>
<td>$\tau$</td>
<td>column rate</td>
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<tr>
<td></td>
<td>(cm$^{-2}$ s$^{-1}$)</td>
<td>(years)</td>
<td>(cm$^{-2}$ s$^{-1}$)</td>
<td>(years)</td>
<td>(cm$^{-2}$ s$^{-1}$)</td>
<td>(years)</td>
</tr>
<tr>
<td>h$\nu$</td>
<td>1.701 $\times$ 10$^5$</td>
<td>430</td>
<td>4.256 $\times$ 10$^2$</td>
<td>431</td>
<td>1.805 $\times$ 10$^3$</td>
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<tr>
<td>OH</td>
<td>1.076 $\times$ 10$^5$</td>
<td>679</td>
<td>2.085 $\times$ 10$^2$</td>
<td>879</td>
<td>1.140 $\times$ 10$^3$</td>
<td>682</td>
</tr>
<tr>
<td>O($^{1}$D)</td>
<td>6.706 $\times$ 10$^4$</td>
<td>1090</td>
<td>1.586 $\times$ 10$^2$</td>
<td>1156</td>
<td>7.036 $\times$ 10$^2$</td>
<td>1100</td>
</tr>
</tbody>
</table>
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.
Fig. 1.— Nair et al.
Fig. 2.— Nair et al.