Measurement of the Isotopic Signatures of Water on Mars; Implications for Studying Methane

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Related Talks:

Michael J. Mumma: Absolute Measurement of Methane on Mars

Geronimo Villanueva: Methane and Water on Mars: Maps of Active Regions and their Seasonal Variability
Outline:

- $[\text{HDO}]/[\text{H}_2\text{O}]$

- Isotopologues of Methane

- Model to Predict measurement of $[^{13}\text{CH}_4]/[^{12}\text{CH}_4]$

- Considerations for the future
Measurements of [HDO]/[H$_2$O] on Mars

26 March, 3:50-4:10 UT, Centered at 150°-156°W, L$_s$ = 50°

H$_2$O Setting

HDO Setting

Eq. Width = 0.0050 cm$^{-1}$
Noise = 0.0002 cm$^{-1}$

Eq. Width = 0.0041 cm$^{-1}$
Noise = 0.0002 cm$^{-1}$

3 row extracts, 4.6°N, 26 March 2008
Column Densities of HDO and H₂O 150°-156° W

\[
\frac{[\text{HDO}]}{[\text{H₂O}]} \text{ wrt. SMOW}
\]

SMOW ratio = 0.312 x 10^{-3}
Isotopic Signatures of Methane in the Earth’s Atmosphere:

$^{12}\text{CH}_4$ 0.99827  
$^{13}\text{CH}_4$ 0.01110  
$^{12}\text{CH}_3\text{D}$ 0.00062  

from HITRAN

Variations of this ratio provide insights into the origins of Methane, whether abiotic or microbial.

Models of Earth’s atmosphere for measured conditions above Mauna Kea.

Line By Line Radiative Transfer Model (Clough et al. (2005), *JQSRT*, 91, 233-244.

A. Methane, Water, Ozone, Ethane, Carbon Dioxide.

B. Methane
Targeted Methane Transitions:  
(from JavaHAWKS/HITRAN)

P4 Region (~ 2978.6 cm\(^{-1}\), T=210K

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{12}\text{CH}_4)</td>
<td>2978.6505</td>
<td>9.784E-20</td>
</tr>
<tr>
<td>(^{13}\text{CH}_4^*)</td>
<td>2978.6926</td>
<td>1.769E-21</td>
</tr>
<tr>
<td>(^{13}\text{CH}_4^*)</td>
<td>2978.8083</td>
<td>1.058E-21</td>
</tr>
<tr>
<td>(^{12}\text{CH}_4)</td>
<td>2978.8481</td>
<td>6.564E-20</td>
</tr>
<tr>
<td>(^{13}\text{CH}_4^*)</td>
<td>2978.8932</td>
<td>1.061E-21</td>
</tr>
<tr>
<td>(^{12}\text{CH}_4)</td>
<td>2978.9201</td>
<td>9.83E-20</td>
</tr>
</tbody>
</table>

\[(Wn.)/(\Delta Wn.) = 70904\]

\[I(^{13}\text{CH}_4)/I(^{12}\text{CH}_4) = 0.018\]

Transitions in Red are Being compared.

* P5 transition
**P2, ~2998.9 cm⁻¹)**

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<tr>
<td>$^{12}\text{CH}_4$</td>
<td>2998.9939</td>
<td>7.15E-20</td>
</tr>
<tr>
<td>$^{12}\text{CH}_4$</td>
<td>2999.0602</td>
<td>4.77E-20</td>
</tr>
<tr>
<td>$^{13}\text{CH}_4^*$</td>
<td>2999.0634</td>
<td>3.13E-22</td>
</tr>
</tbody>
</table>

$(\text{Wn.})/(\Delta \text{Wn.}) > 900000$

$I(^{13}\text{CH}_4)/I(^{12}\text{CH}_4) = 0.0066$

* P3

**R0**

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<tr>
<td>$^{12}\text{CH}_4$</td>
<td>3028.7523</td>
<td>1.53E-19</td>
</tr>
<tr>
<td>$^{13}\text{CH}_4^*$</td>
<td>3028.8519</td>
<td>1.60E-21</td>
</tr>
</tbody>
</table>

$(\text{Wn.})/(\Delta \text{Wn.}) = 30400$

$I(^{13}\text{CH}_4)/I(^{12}\text{CH}_4) = 0.011$

* R1
\( \frac{(Wn.)/(\Delta Wn.)}{(Wn.)/(\Delta Wn.)} = 26000 \)

\( \frac{I(^{13}CH_4)}{I(^{12}CH_4)} = 0.023 \)

*R2

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<tbody>
<tr>
<td>(^{12}CH_4 )</td>
<td>3038.4984</td>
<td>1.445E-19</td>
</tr>
<tr>
<td>(^{13}CH_4^*)</td>
<td>3038.6144</td>
<td>1.968E-21</td>
</tr>
<tr>
<td>(^{13}CH_4^*)</td>
<td>3038.6285</td>
<td>1.312E-21</td>
</tr>
</tbody>
</table>
### Summary:

R1 is the targeted transition.

$^{13}\text{CH}_4$ (R2) is to the blue side of $^{12}\text{CH}_4$ (R1)

Del dot of -16.0 km/sec shifts wavenumber by .16 cm$^{-1}$
- Best transition to retrieve $^{13}\text{CH}_4$ through the Earth’s Atmosphere from those listed here.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$(Wn.)/(\Delta Wn.)$</th>
<th>$I(^{13}\text{CH}_4)/I(^{12}\text{CH}_4)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4</td>
<td>70904</td>
<td>0.018</td>
</tr>
<tr>
<td>P2</td>
<td>&gt; 900000</td>
<td>0.007</td>
</tr>
<tr>
<td>R0</td>
<td>30400</td>
<td>0.011</td>
</tr>
<tr>
<td>R1</td>
<td>26000</td>
<td>0.023</td>
</tr>
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</table>
Components of Atmospheric Model Used to Retrieve Gas Column Densities on Mars:

- Solar Model (based on Hase et al., JQRST, 102, (2006), 450-463)
- Mars Atmosphere Model*, Incoming (LBLTRM model)
- Surface Blackbody Component
- Mars Atmosphere Model*, Outgoing (LBLTRM model)
- Earth Terrestrial Model (LBLTRM model)
- Doppler shift between Sun and Mars (r dot)
- Doppler shift between Mars and Earth (del dot)

* 10 pr-microns H₂O, 40 ppb CH₄
\[ [\text{CH}_4] = 40 \text{ ppb} \]
Resolution = 75000
Relative velocity = -16.5 km/sec
Using noise = 0.0002 cm\(^{-1}\)

\[
\begin{align*}
S/N(H_2O) &= 49.4 \\
S/N^{(12)CH_4} &= 6.4 \\
S/N^{(13)CH_4} &= 0.2
\end{align*}
\]
Model
P4 Transition

Ground-based:

Space-based:
Ground-Base Measurements of $^{13}$CH$_4$/^{12}$CH$_4$:

- High Spectral Resolution ($> 75000$)
- Sufficient Doppler Shift ($> 15$ km/sec)
- Better S/N
  * Measure and Add Multiple Absorption Lines Simultaneously
  * More sensitive detectors
Possible Near Future Measurements:

- CRIRES on VLT
  * $R > 100000$
  * Altitude $\sim 2600$ m
  * precipitable terrestrial Water Vapor $\sim 3.0$ mm
  * Multiple lines of Methane

- iSHELL on NASA-IRTF (funded proposal)
  * $R \sim 70000$
  * Altitude $\sim 4200$ m
  * precipitable terrestrial Water Vapor $\sim 1.0-2.0$ mm
  * Cross disperse Spectrograph
    - Multiple Lines.
Suggested Future Work:

- High Resolution Space Based Near IR Spectrograph

- Detection/Models for $^{12}\text{CH}_3\text{D}$