A Possible Solution to the Early Mars Problem: Experimentally Verified Collision-Induced Absorption Cross-Sections of CO_2-H_2 And CO_2-CH_4 Complexes

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Introduction

Geological evidence on Mars strongly suggests there was once liquid water on its surface. Yet most atmospheric models of ancient Mars have difficulty producing sufficient warming to raise the surface temperature above 0°C.

A recent study by Wordsworth *et al.* [1] suggested that previously unaccounted-for collision-induced absorption (CIA) by carbon dioxide (CO_2) and hydrogen gas (H_2), and by CO_2 and methane (CH_4) could provide the additional atmospheric absorption needed to trap enough radiation to raise the Martian surface temperature above freezing.

CIA cross-sections for CO_2-H_2 and CO_2-CH_4 complexes do not exist in the literature over the full spectral and temperature range desired, so the authors could only use computational methods to simulate the CIA absorption cross-sections that they themselves identify in the study as needing experimental validation.

Recent work done by Turbet *et al.* [2], have investigated CIA of CO_2-H_2 and CO_2-CH_4 complexes at room temperature in the range of 40-640 cm^{-1}.

Theory

Collisions between molecules momentarily form a two-molecule complex that has its own absorption spectrum; this is known as collision induced absorption and are typically broad band features.

The absorption of light passing through a gas mixture is given by Beer's Law:

$$I = I_o e^{-L(\rho_{CO_2}\sigma_{CO_2}+\rho_x\sigma_x+\rho^2_{CO_2}\sigma_{CO_2+CO_2}+\rho^2_x\sigma_{x+x}+\rho_{CO_2}\rho_x\sigma_{CO_2+x})}$$

where I_o is the intensity of light before passing through the mixture, I is the intensity of light after absorption, L is the pathlength of light through the mixture, ρ_{CO2} is the density of CO_2, ρ_x is the density of either H_2 or CH_4, and the σ are the absorption cross-sections for individual molecule absorption or CIA absorption depending on the subscript.

Single species cross-sections are known, as are some of the self CIA cross-sections.

Experimental Details

- Experiments were performed at the FAR-IR beamline of the Canadian Light Source (CLS) Synchrotron.
- The FAR-IR beamline has a White cell that was used to detect the weak CIA absorption features.
- The White cell has a maximum pathlength of 7274.93±6 cm, and a maximum pressure of 1 atm.
- Safety protocols at the CLS limit explosive gas mixtures to maximum 20% CH_4 and 8.3% H_2.

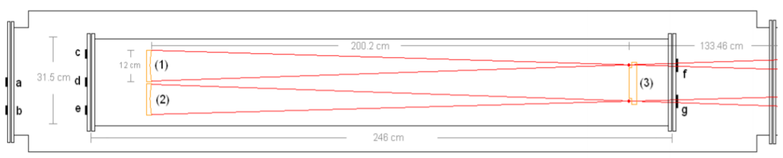

Fig. 1: White cell schematic. Mirrors are placed at both ends of the cell. A beam of light bounces between the mirror multiple times before exiting the cell, allowing for a pathlength much longer than the length of the cell. The cell is nested inside a second vacuum chamber to isolated it from environmental affects.

- No combination of beamsplitter, windows, and detector covers the full spectral range, so the experiment is divided into two optical regimes:
  1. 30-600 cm^{-1}: polypropylene windows, Si bolometer detector, and mylar beamsplitter.
  2. 500-2000 cm^{-1}: KBr windows and beamsplitter, and MCT detector.

Data Analysis

- The single absorption lines, and self CIA features must be subtracted from the spectra to determine the CIA.
- Single molecule absorption lines are simulated using the HITRAN Application Programming Interface (HAPI).
- HAPI does not include line broadening effects due to CO_2 and H_2, hence residual effects will remain in the spectra after line subtraction.
- Spectra is smoothed with a 5 cm^{-1} running mean to further remove noise.

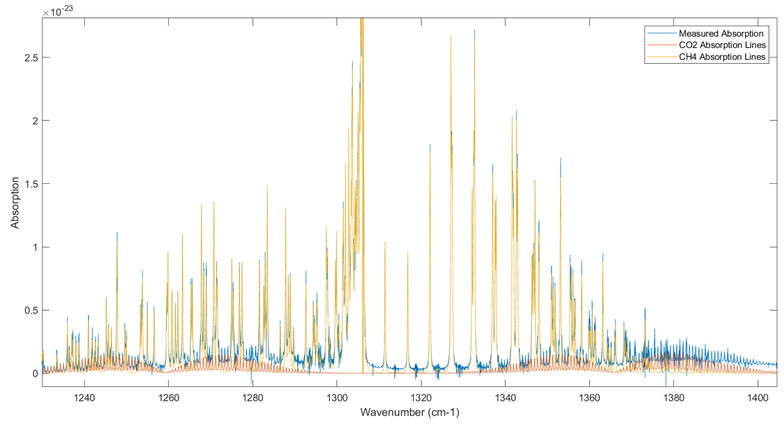

Fig. 2: Example of absorption lines that need to be removed from the measured cross-section.

Methane-Carbon Dioxide CIA

- Experimental measurements of CO_2-CH_4 CIA at three different temperatures.
- Agreement with Turbet *et al.* [2] that the experimental results are weaker than the theoretical predictions of Wordsworth *et al.* [1].
- Water vapour contamination in the spectra below 600 cm^{-1}.
- Difficulty removing the single molecule absorption by CH_4 due to CO_2 line broadening is causing anomalous intensity values for 1200-1500 cm^{-1}.

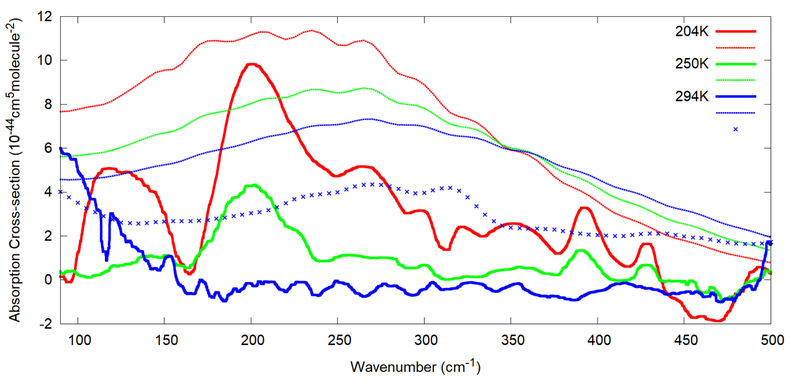

Fig. 3: CO2-CH4 CIA from this work (solid lines) along with comparisons to Wordsworth *et al.* (dotted lines) [1] and Turbet *et al.* (X line) [3].

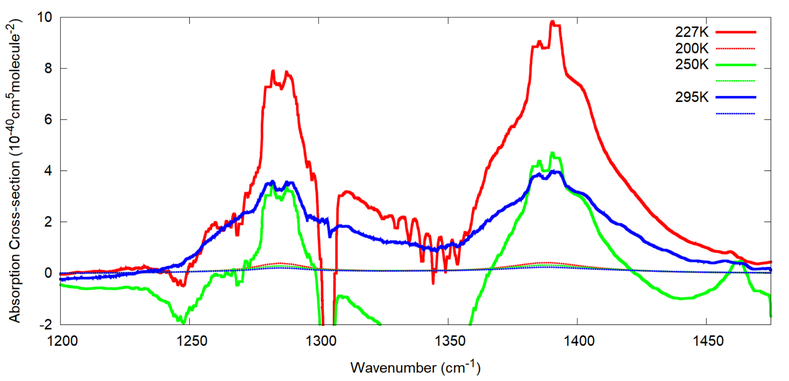

Fig. 4: CO2-CH4 CIA from this work (solid lines) along with comparisons to Wordsworth *et al.* (dotted lines, increased by a factor of 1000) [1]. CO_2-CO_2 CIA is assumed to be 0 in this spectral range.

Hydrogen-Carbon Dioxide CIA

- Experimental measurements of CO_2-H_2 CIA at three different temperatures.
- Water vapour present in the higher temperature measurements causing difficulty with calculation of CIA.
- Agreement with Turbet *et al.* [2] that the experimental results are weaker than the theoretical predictions of Wordsworth *et al.* [1] below 500 cm^{-1} for the 203 K measurement.
- CO_2 line broadening due to H_2 is causing anomalous intensity values from 500 to 1000 cm^{-1}.

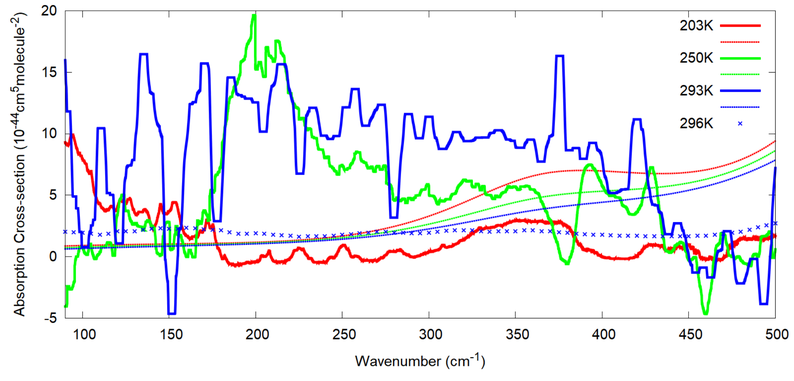

Fig. 5: CO2-H2 CIA from this work (solid lines) along with comparison to Wordsworth *et al.* (dotted lines) [1] and Turbet *et al.* (X line) [3].

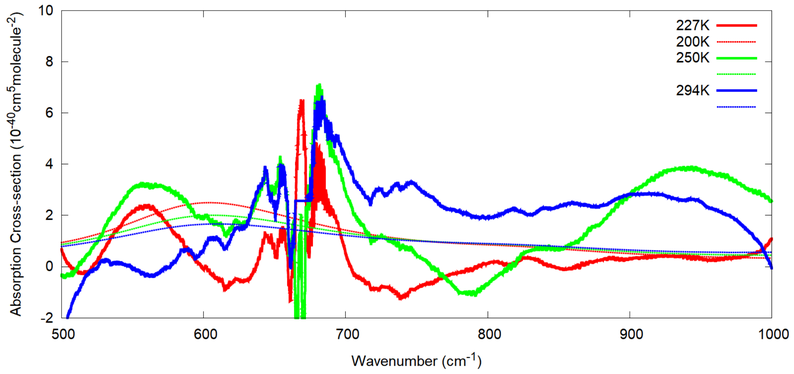

Fig. 6: CO2-H2 CIA from this work (solid line) along with comparison to Wordsworth *et al.* (dotted line, increased by a factor of 1000) [1]. Due to complete absorption by CO_2, nothing can be resolved in the range of 670-680 cm^{-1}. CO_2-CO_2 CIA is assumed to be 0 in this spectra range.

Conclusions

- First temperature dependent experimental measurements of CO_2-H_2 and CO_2-CH_4 CIA.
- First experimental measurements of CO_2-H_2 and CO_2-CH_4 CIA above 600 cm^{-1}.
- Below 600 cm^{-1}, CO_2-CH_4 CIA agrees with the position and general shape of the calculation by Wordsworth *et al.* [1], however the amplitude is weaker than predicted.
- Above 600 cm^{-1}, CO_2-CH_4 CIA does exhibit the two peak structure as predicted, but it is shifted to lower wavenumbers. Due to difficulty removing the single molecule absorption by CH_4 and CO_2, constraining the amplitude of the CIA absorption is on going.
- Above 600 cm^{-1}, CO_2-H_2 CIA does appear to exhibit the CIA absorption structure as predicted, but due to saturation by CO_2 and H_2 broadening effects, the full nature of the absorption remains unknown.

References: [1] Wordsworth, R., Y. Kalugina,S. Lokshtanov, A. Vigasin, B. Ehlmann,J. Head, C. Sanders, and H. Wang (2017), Transient reducing greenhouse warming on early Mars, Geophys. Res. Lett., 44, 665–671, doi:10.1002/2016GL071766.
[2] Martin Turbet, Ha Tran, Olivier Pirali, François Forget, Christian Boulet, Jean-Michel Hartmann, Far infrared measurements of absorptions by CH4+CO2 and H2+CO2 mixtures and implications for greenhouse warming on early Mars (2019), Icarus, 321, 189-199.
[3] Gruszka M, and Borysow A., Computer simulation of the far infrared collision induced absorption spectra of gaseous CO2 (1998), Mol Phys, 93, 1007-16.