Stronger Greenhouse Effect on Early Mars: Collision-Induced Absorption by CO2-H2 and CO2-CH4 Complexes

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Introduction

- Geological evidence on Mars strongly suggests there was once liquid water on its surface.
- 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.
- CIA 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.
- By filling the gas cell with a single gas first, I_o can absorb the terms of the exponential that only depend on that gas.

Experimental Details

- Experiments were performed at the FAR-IR beamline of the Canadian Light Source (CLS) Synchrotron.
- Applications for beamtime at the CLS is a highly competitive process; this project was awarded two weeks of beamtime.
- 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.

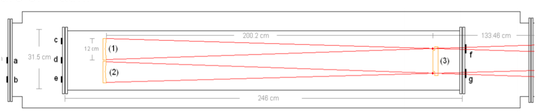

Fig. 1: White cell schematic. Mirrors are placed at both ends of the cell. A beam of light bounces between the mirror multiple times before exiting the cell, allowing for a pathlength much longer than the length of the cell. The cell is nested inside a second vacuum chamber to isolated it from environmental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

- Safety protocols at the CLS limit explosive gas mixtures to maximum 20% CH_4 and 8.3% H_2.
- No combination of beamsplitter, windows, and detector covers the full spectral range, so the experiment is divided into two optical regimes:
  1. Below 600 cm^{-1}, polypropylene windows, Si bolometer detector, and mylar beamsplitter are used.
  2. Above 500 cm^{-1}, KBr windows and beamsplitter, and MCT detector are used.

Carbon Dioxide CIA

- Experimental measurements of CO_2-CO_2 CIA at three different temperatures.
- Strange signal observed around 70 cm^{-1}, unclear what caused it.
- General agreement with calculations by Gruszka and Borysow [3].
- 250 K result weaker than expected.

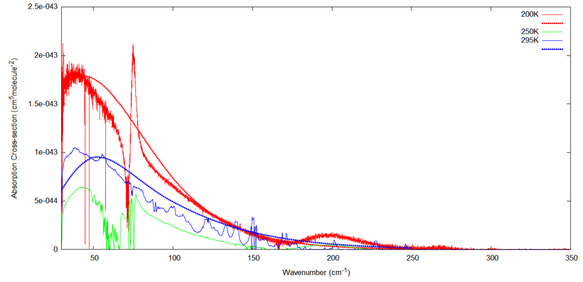

Fig. 2: CO_2-CO_2 CIA from this work (solid lines) along with comparisons to Gruszka and Borysow (dotted lines) [3].

Methane-Carbon Dioxide CIA

- Experimental measurements of CO_2-CH_4 CIA at three different temperatures.
- 250 K result stronger than expected, although this is likely due to insufficient removal of CO_2-CO_2 CIA due to the weak measurement found in the above section.
- Agreement with Turbet *et al.* [2] that the experimental results are weaker than the theoretical predictions of Wordsworth *et al.* [1].
- Difficulty removing the single molecule absorption by CH_4 and CO_2 is causing anomalous intensity values above 600 cm^{-1}.

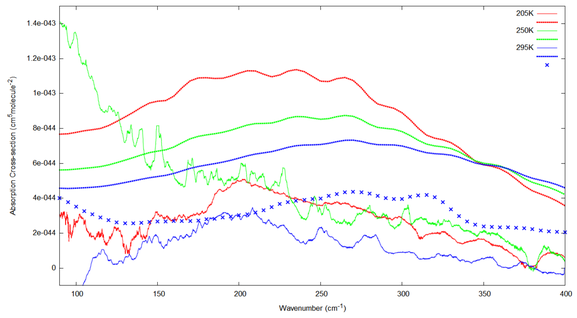

Fig. 3: CO2-CH4 CIA from this work (solid lines) along with comparisons to Wordsworth *et al.* (dotted lines) [1] and Turbet *et al.* (X line) [3].

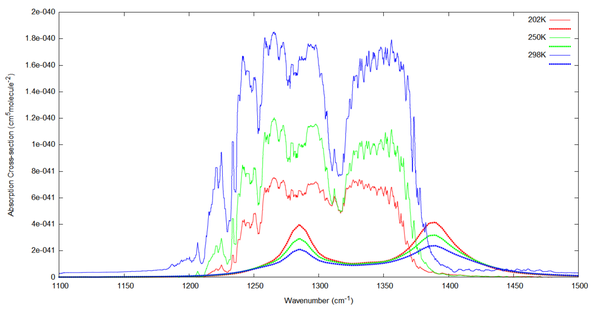

Fig. 4: CO2-CH4 CIA from with work (solid lines) along with comparisons to Wordsworth *et al.* (dotted lines) [1], which are increased by a factor of 100. CO_2-CO_2 CIA is assumed to be 0 in this spectral range.

Hydrogen-Carbon Dioxide CIA

- Experimental measurements of CO_2-H_2 CIA at three different temperatures.
- Significant water contamination present in the 250 K measurement.
- Agreement with Turbet *et al.* [2] that the experimental results are weaker than the theoretical predictions of Wordsworth *et al.* [1] below 600 cm^{-1}.
- Absorption by CO_2 is causing anomalous intensity values from 550 to 1000 cm^{-1}.

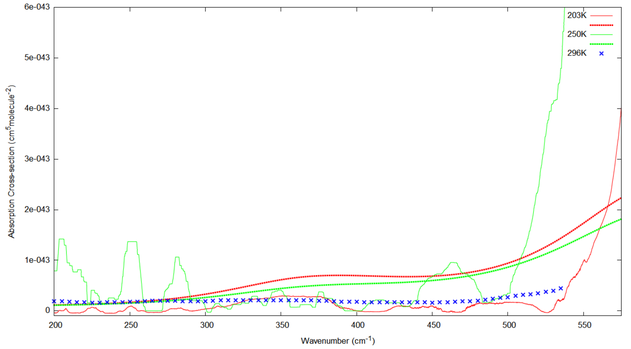

Fig. 5: CO2-H2 CIA from this work (solid lines) along with comparison to Wordsworth *et al.* (dotted lines) [1] and Turbet *et al.* (X line) [3].

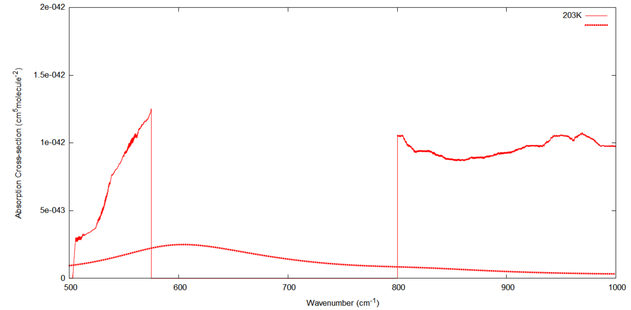

Fig. 6: CO2-H2 CIA from this work (solid line) along with comparison to Wordsworth *et al.* (dotted line) [1]. Due to complete absorption by CO_2, nothing can be resolved in the range of 575-800 cm^{-1}. CO_2-CO_2 CIA is assumed to be 0 in this spectra range.

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}.
- CO_2-CO_2 CIA results agree with the calculations by Gruszka and Borysow [3] at room temperature. However at lower temperatures small scale structure is seen, although overall shape and amplitude agrees with their theoretical calculations.
- Below 600 cm^{-1}, CO_2-H_2 and 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 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.