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

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Abstract

An unanswered question in planetary science is how could the early Martian atmosphere have maintained a greenhouse effect sufficient to allow for liquid water on the surface? A recent study by Wordsworth et al. (DOI:10.1002/2016GL071766) suggested that previously unaccounted-for collision-induced absorption (CIA) by carbon dioxide (CO2) and hydrogen gas (H2), and by CO2 and methane (CH4) could provide the additional atmospheric absorption needed to trap enough radiation to raise the Martian surface temperature above freezing. However, as CIA cross-sections for CO2-H2 and CO2-CH4 complexes do not exist in the literature, 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. Preliminary results will be presented from experimental measurements of the CIA cross-sections for CO2-H2 and CO2-CH4 complexes performed using Fourier Transform Spectroscopy. We have obtained Beam-time at the Canadian Light Source Far-IR beamline in late October and early November which will allow us to derive Cross-sections over a spectral range of 0-3000 cm-1 and a temperature range of 200-350 K. In addition to allowing us to experimentally validate the hypothesis of Wordsworth, the cross-sections so obtained can also be applied to other planetary systems with CO2-rich atmospheres, such as Venus, and will be useful to terrestrial spectroscopists.

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.

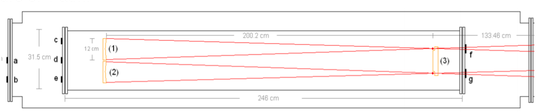

Fig. 1: White cell schematic. Mirrors are placed at both ends of the cell. A beam of light bounces between the mirror multiple times before exiting the cell, allowing for a pathlength much longer than the length of the cell. The cell is nested inside a second vacuum chamber to isolated it from environmental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

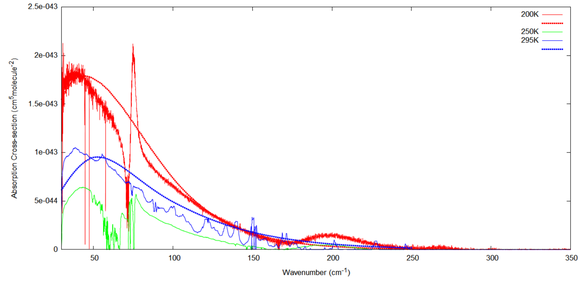

Fig. 2: CO_2-CO_2 CIA from this work (solid lines) along with comparisons to Gruszka and Borysow (dotted lines) [3].

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}.

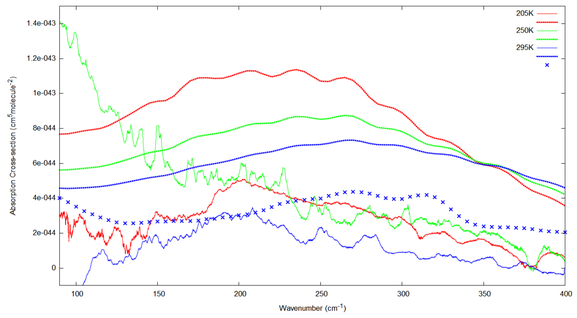

Fig. 3: CO2-CH4 CIA from this work (solid lines) along with comparisons to Wordsworth *et al.* (dotted lines) [1] and Turbet *et al.* (X line) [3].

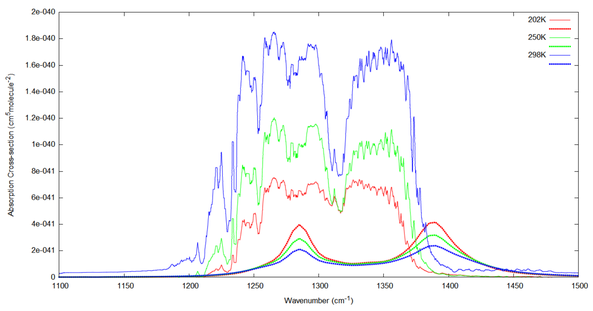

Fig. 4: CO2-CH4 CIA from with work (solid lines) along with comparisons to Wordsworth *et al.* (dotted lines) [1], which are increased by a factor of 100. CO_2-CO_2 CIA is assumed to be 0 in this spectral range.

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}.

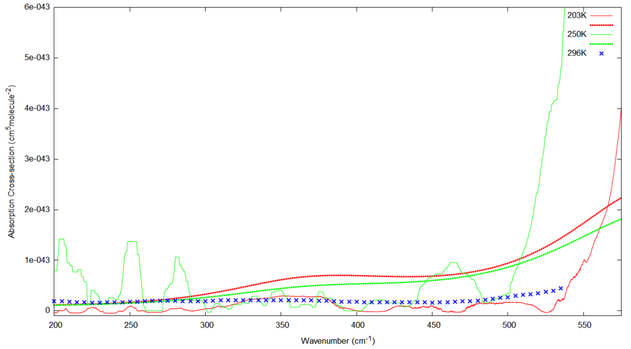

Fig. 5: CO2-H2 CIA from this work (solid lines) along with comparison to Wordsworth *et al.* (dotted lines) [1] and Turbet *et al.* (X line) [3].

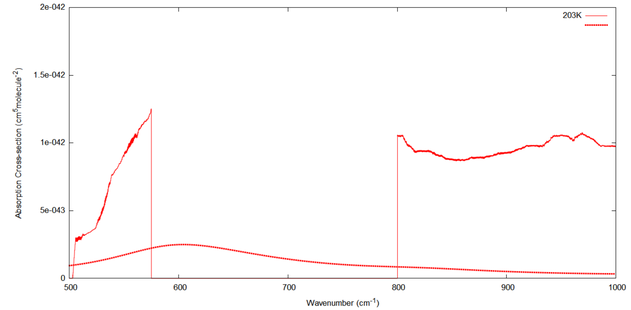

Fig. 6: CO2-H2 CIA from this work (solid line) along with comparison to Wordsworth *et al.* (dotted line) [1]. Due to complete absorption by CO_2, nothing can be resolved in the range of 575-800 cm^{-1}. CO_2-CO_2 CIA is assumed to be 0 in this spectra range.

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.