

# Collision-Induced Absorption of $\text{CH}_4\text{-CO}_2$ and $\text{H}_2\text{-CO}_2$ Complexes and Their Effect on the Ancient Martian Atmosphere

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## Abstract

Experimental measurements of collision-induced absorption (CIA) cross-sections for  $\text{CO}_2\text{-H}_2$  and  $\text{CO}_2\text{-CH}_4$  complexes were performed using Fourier transform spectroscopy over a spectral range of 100-500 cm and a temperature range of 200-300 K. These experimentally derived CIA cross-sections agree with the spectral range and temperature dependence of the calculation by \citeA{Robin}, however the amplitude is half of what was predicted. Furthermore, the CIA cross-sections reported here agree with those measured by \citeA{Turbet}. The CIA cross-sections can be applied to planetary systems with  $\text{CO}_2$ -rich atmospheres, such as Mars and Venus, and will be useful to terrestrial spectroscopists.

Additionally, radiative transfer calculations of the early Mars atmosphere were performed and showed that  $\text{CO}_2\text{-CH}_4$  CIA would require surface pressure greater than 3 bar for a 10% methane atmosphere to achieve 273 K at the surface.  $\text{CO}_2\text{-H}_2$ , however, liquid water is possible with 5% hydrogen and less than 2 bar of surface pressure.

# Collision-Induced Absorption of CH<sub>4</sub>-CO<sub>2</sub> and H<sub>2</sub>-CO<sub>2</sub> Complexes and Their Effect on the Ancient Martian Atmosphere

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## Key Points:

- First temperature-dependent experimental measurements of CO<sub>2</sub>-H<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub> CIA cross-sections
- Radiative transfer calculations of the early Mars atmosphere were performed using the newly acquired CIA cross-sections
- Surface temperatures above 273 K can be reached if surface pressures exceed 3 bar for 10% CH<sub>4</sub> or 2 bar for a 5% H<sub>2</sub> atmosphere

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## Abstract

Experimental measurements of collision-induced absorption (CIA) cross-sections for CO<sub>2</sub>-H<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub> complexes were performed using Fourier transform spectroscopy over a spectral range of 100-500 cm<sup>-1</sup> and a temperature range of 200-300 K. These experimentally derived CIA cross-sections agree with the spectral range and temperature dependence of the calculation by Wordsworth et al. (2017), however the amplitude is half of what was predicted. Furthermore, the CIA cross-sections reported here agree with those measured by Turbet et al. (2019). The CIA cross-sections can be applied to planetary systems with CO<sub>2</sub>-rich atmospheres, such as Mars and Venus, and will be useful to terrestrial spectroscopists.

Additionally, radiative transfer calculations of the early Mars atmosphere were performed and showed that CO<sub>2</sub>-CH<sub>4</sub> CIA would require surface pressure greater than 3 bar for a 10% methane atmosphere to achieve 273 K at the surface. CO<sub>2</sub>-H<sub>2</sub>, however, liquid water is possible with 5% hydrogen and less than 2 bar of surface pressure.

## Plain Language Summary

Temperature-dependent experimental measurements of collision-induced absorption (CIA) cross-sections for CO<sub>2</sub>-H<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub> complexes were measured for the first time over a spectral range of 100-500 cm<sup>-1</sup> and a temperature range of 200-300 K. These experimentally derived CIA cross-sections are half as strong as what was predicted by Wordsworth et al. (2017), but agree with those measured by Turbet et al. (2019), strengthening our confidence in these results. The CIA cross-sections can be applied to planetary systems with CO<sub>2</sub>-rich atmospheres, such as Mars and Venus, and will be useful to terrestrial spectroscopists. Additionally, simulations of the early Mars atmosphere were performed and showed that a surface pressure greater than 3 bar for a 10% methane atmosphere or 5% hydrogen and less than 2 bar of surface pressure to achieve liquid water at the surface of Mars.

## 1 Introduction

Geological evidence suggests that there was once liquid water on ancient Mars (Ramirez & Craddock, 2018; Craddock & Howard, 2002; Mangold et al., 2004; Stepinski & Stepinski, 2005; Barnhart et al., 2009; Hynek et al., 2010; Matsubara et al., 2013); this leads to an unanswered question of how could the early Martian atmosphere have maintained a greenhouse effect sufficient to allow for water on the surface present as a liquid? Ramirez et al. (2014) proposed the idea that collision-induced absorption (CIA) between carbon dioxide (CO<sub>2</sub>) and hydrogen gas (H<sub>2</sub>) from volcanic events could provide the additional atmospheric absorption needed to trap enough radiation to raise the ancient Martian surface temperature above freezing. However, there were no measured CO<sub>2</sub>-H<sub>2</sub> CIA cross-sections available in the literature at the time of Ramirez et al. (2014), so N<sub>2</sub>-H<sub>2</sub> was used as a proxy, but they had argued that CO<sub>2</sub>-H<sub>2</sub> CIA should be stronger. This was followed up in a study by Wordsworth et al. (2017), wherein they simulated the CIA of CO<sub>2</sub>-H<sub>2</sub> and CIA of CO<sub>2</sub> and methane (CH<sub>4</sub>), and their simulations did show that CO<sub>2</sub>-H<sub>2</sub> CIA was stronger than N<sub>2</sub>-H<sub>2</sub> CIA. Wordsworth et al. (2017) derived their CIA by performing *ab initio* calculations of the zeroth spectral moment of a CO<sub>2</sub>-H<sub>2</sub>/CH<sub>4</sub> system, and then approximating the spectra as a linear combination of CO<sub>2</sub>-CO<sub>2</sub> and H<sub>2</sub>-H<sub>2</sub> or CH<sub>4</sub>-CH<sub>4</sub> CIAs with the weighting determined by the *ab initio* calculation. The theoretical cross-sections from Wordsworth et al. (2017) have strong absorption features in the range of 0-600 cm<sup>-1</sup> and 1200-1500 cm<sup>-1</sup> for CO<sub>2</sub>-CH<sub>4</sub>; for CO<sub>2</sub>-H<sub>2</sub>, absorption was predicted to be a broad feature over the range of 0-1500 cm<sup>-1</sup>. While this approximation appears to give accurate results, there can be significant deviations. For example, for CO<sub>2</sub>-CH<sub>4</sub> above 1000 cm<sup>-1</sup>, there are no CH<sub>4</sub>-CH<sub>4</sub> CIA cross-sections in the literature, so a linear combination ends up simply as scaled CO<sub>2</sub>-CO<sub>2</sub> CIA cross-section. For these reasons,

69 experimental validation of this linear combination approximation method are still required  
 70 (Karman et al., 2019).

71 Additional modeling by Ramirez (Ramirez, 2017) used the cross-sections from Wordsworth  
 72 et al. (2017) in more sophisticated Martian climate models and found that the inclusion  
 73 of CIA between CO<sub>2</sub> and H<sub>2</sub> does result in a warm and wet early Mars that agrees with  
 74 the paleopressure and climate stability constraints with only 1% hydrogen concentrations.  
 75 Unfortunately, computing CIA cross-sections is quite challenging, and to date, the only  
 76 CIA cross-sections for CO<sub>2</sub>-H<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub> complexes in the literature are limited to  
 77 room temperature, a spectral range of 60 to 535 cm<sup>-1</sup>, and a resolution of 1 cm<sup>-1</sup> (Turbet  
 78 et al., 2019); which found that the experimentally derived CIA cross-sections are weaker  
 79 than predicted by Wordsworth et al. (2017), but still stronger than N<sub>2</sub>-H<sub>2</sub> CIA.

80 This paper expands upon the experimental work of Turbet et al. (2019), detailing  
 81 the first temperature-dependent experimental measurements of CO<sub>2</sub>-H<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub>  
 82 CIA. Given that experimentally derived CIA cross-sections are more reliable than pre-  
 83 dicted ones, these new experimentally derived cross-sections are used in early Mars cli-  
 84 mate models to improve our understanding of the impact CIA may have had on the cli-  
 85 mate of ancient Mars.

## 86 2 Laboratory Measurements of Collision-Induced Absorption

### 87 2.1 Experimental Procedure and Data Analysis

88 Experiments were performed at the Far-IR beamline of the Canadian Light Source  
 89 (CLS) Synchrotron facility. The IR absorption spectra were obtained using a Bruker IFS  
 90 125HR Fourier transform spectrometer connected to a temperature-controllable White-  
 91 type cell with a pathlength of 7275 ± 6 cm. Experiments were performed using a glo-  
 92 bar source, mylar beamsplitter, polypropylene windows, and Si bolometer detector. Spec-  
 93 tra were recorded at an unapodized resolution of 0.05 cm<sup>-1</sup> (maximum optical path dif-  
 94 ference of 20 cm). Each measurement consisted of 300-500 co-added spectra. Temper-  
 95 ature control was provided by a recirculating chiller. The chiller was capable of reach-  
 96 ing temperatures as low as 203 K with the cell containing gas at atmospheric pressure.

97 The gas samples were commercial products from Praxair with stated high purities  
 98 of greater than 99%. The cell was evacuated using a Varian turbo pump. The pressure  
 99 in the gas cell was measured using a combination of a 10 and 1000 Torr MKS baratron  
 100 pressure gauges. At each temperature, measurements were made at two pressure com-  
 101 binations as detailed in Table 1. Empty cell scans were performed between filled cell runs  
 102 to monitor baseline stability. Due to safety limitations when using explosive gases at the  
 103 CLS, the mixing ratio of H<sub>2</sub> in CO<sub>2</sub> was restricted to a maximum 8.3%; while for CH<sub>4</sub>  
 104 in CO<sub>2</sub>, the mixing ratio was restricted to maximum 20%. Methane experiments were  
 105 performed by first filling the cell with methane, followed by adding CO<sub>2</sub>. The H<sub>2</sub> exper-  
 106 iments were performed using pre-mixed H<sub>2</sub>-CO<sub>2</sub> gas cylinders as indicated in Table 1.

107 The absorption of light by a medium at a given pressure and temperature (P, T)  
 108 can be described by the well-known Beer-Lambert Law:

$$109 \quad I(\tilde{\nu}) = I_o(\tilde{\nu})e^{-\chi(\tilde{\nu})} \quad (1)$$

110 where  $I(\tilde{\nu})$  is the intensity at wavenumber  $\tilde{\nu}$  after passing through the gas sample (filled-  
 111 cell measurement) and  $I_o(\tilde{\nu})$  is the incident intensity (empty-cell measurement).  $\chi(\tilde{\nu})$  is  
 the optical depth, which for a mixture of CO<sub>2</sub> and another gas in a cell is given by:

$$\begin{aligned} \chi(\tilde{\nu}) = & L(\rho_{CO_2}\sigma_{CO_2}(\tilde{\nu}) + \rho_x\sigma_x(\tilde{\nu})) \\ & + \rho_{CO_2}^2\sigma_{CO_2+CO_2}(\tilde{\nu}) + \rho_x^2\sigma_{x+x}(\tilde{\nu}) \\ & + \rho_{CO_2}\rho_x\sigma_{CO_2+x}(\tilde{\nu}) \end{aligned} \quad (2)$$

Table 1: Summary of experimental conditions for CIA experiments with CO<sub>2</sub> and CH<sub>4</sub> or H<sub>2</sub>.

Temperature (K)	Total Pressure (Torr)	CH <sub>4</sub> Pressure (Torr)	% H <sub>2</sub>
293.80±0.05	750.1±0.08	156.5±0.05	0
293.40±0.05	762.5±0.15	76.7±0.05	0
250.10±0.05	743.6±0.11	152.0±0.06	0
250.15±0.08	687.0±0.12	80.1±0.05	0
204.05±0.08	751.0±0.17	150.7±0.06	0
203.20±0.05	760.4±0.30	75.8±0.06	0
292.60±0.05	745.3±0.31	0	4.009
293.12±0.06	742.4±0.13	0	8.312
250.01±0.05	718.1±0.33	0	4.009
250.45±0.15	741.7±0.44	0	8.312
203.30±0.05	756.4±0.19	0	3.987
203.50±0.05	757.5±0.25	0	8.270

112 where  $L$  is the cell length,  $\rho$  is the density of the gas, and  $\sigma(\tilde{\nu})$  are the absorption cross-  
113 sections for either single gas species or CIA of mixed species depending on the subscript  
114 ( $x$  designating either H<sub>2</sub> or CH<sub>4</sub>). The density of a gas in the cell is related to the pres-  
115 sure by:

$$\rho_x = \frac{P_x T_o}{P_o T} N_L \quad (3)$$

116 where  $P_o$  and  $T_o$  are standard conditions for pressure and temperature, and  $N_L$  is Loschmidt's  
117 constant.

118 Single gas species absorption cross-sections exist in the literature for CH<sub>4</sub>, H<sub>2</sub>, and  
119 CO<sub>2</sub> (Gordon et al., 2017); while CIA cross-sections exist for CO<sub>2</sub>-CO<sub>2</sub> (Gruszka & Bo-  
120 rysow, 1997), CH<sub>4</sub>-CH<sub>4</sub> (Borysow & Frommhold, 1987), and H<sub>2</sub>-H<sub>2</sub> (Abel et al., 2011)  
121 at the temperatures and spectral region investigated in this study. The absorption ef-  
122 fects from single gas species, CO<sub>2</sub>-CO<sub>2</sub> CIA, CH<sub>4</sub>-CH<sub>4</sub> CIA, and H<sub>2</sub>-H<sub>2</sub> CIA are sim-  
123 ulated using the HITRAN Application Programming Interface (HAPI) (Kochanov et al.,  
124 2016). These absorption effects are then subtracted from the optical depth. Addition-  
125 ally, there was some water contamination in the cell, which requires the subtraction of  
126 water absorption lines from the measured optical depth; however, since the concentra-  
127 tion of water is unknown, the optical depth was fit to match the absorption spectra of  
128 water in contaminated regions, using the density of water as a free parameter. The re-  
129 moval of these unwanted absorption features is not perfect, since there are small differ-  
130 ences between the simulated lines from HAPI and the measured spectra. A 7 cm<sup>-1</sup> me-  
131 dian filter was applied to remove any remaining narrow features. Lastly, the baseline was  
132 adjusted to account for fluctuations in light intensity between empty- and full-cell mea-  
133 surement runs. Wavenumbers of known zero optical depth are used to fit a linear base-  
134 line to the spectra.

135 Once the optical depth has been cleaned of the unwanted absorption effects, the  
136 CIA absorption cross-sections can be found via a linear fit of optical depth versus pres-

137 sure for a given temperature and wavenumber. All fits have a forced convergence of  $\chi =$   
 138 0 for  $P = 0$ , with

$$\chi(\tilde{\nu}) = \frac{P_x T_o}{P_o T} N_L L \sigma(\tilde{\nu}). \quad (4)$$

139 Sources of error include subtraction of unwanted absorption features (10%), tem-  
 140 perature fluctuations ( $\pm 0.2$  K), baseline adjustment (10%), and pressure readout ( $\pm 0.08$   
 141 Torr). These errors are propagated in the calculation of the optical depth to determine  
 142 its uncertainty. The uncertainty of the optical depth is used to assign weights in the lin-  
 143 ear fit against pressure to find the absorption cross-section. The final uncertainty is the  
 144 sum, in quadrature, of the linear fit error, pathlength uncertainty ( $\pm 6$  cm), and sample  
 145 purity error ( $\pm 1.0\%$ ), expressed at the  $3\sigma$  confidence interval.

## 146 2.2 Collision-Induced Absorption Cross-sections

147 Measured CO<sub>2</sub>-CH<sub>4</sub> and CO<sub>2</sub>-H<sub>2</sub> CIA cross-sections as a function of temperature  
 148 are shown in Figures 1 and 2, respectively. Below 100 cm<sup>-1</sup>, the limit of the detector be-  
 149 gins to be reached and the amplitude of the cross-section becomes less reliable; above  
 150 500 cm<sup>-1</sup>, CO<sub>2</sub> lines begin to saturate the detector, preventing the detection of other  
 151 types of absorption.

152 At room temperature, the measurement from this work for CO<sub>2</sub>-CH<sub>4</sub> CIA agree  
 153 with the experimental results from Turbet et al. (2019), and its observed that the the-  
 154 oretical prediction of Wordsworth et al. (2017) overestimates the CIA by roughly a fac-  
 155 tor of 2. Looking at the temperature dependence of the CIA, the predicted increase in  
 156 strength with decreasing temperature is also observed. Once again, Wordsworth et al.  
 157 (2017) overestimates the CIA by roughly a factor of 2 at these colder temperatures.

158 Similar results are observed in the CO<sub>2</sub>-H<sub>2</sub> CIA measurements, as seen for CO<sub>2</sub>-  
 159 CH<sub>4</sub>, although the uncertainty in the derived CIA is larger overall. Due to the exper-  
 160 imental safety limitations on the amount of hydrogen gas permitted in the gas cell, it  
 161 was difficult to resolve the CO<sub>2</sub>-H<sub>2</sub> CIA from the noise, especially at higher tempera-  
 162 tures where the CIA effect is weaker, hence the uncertainty is higher compared to the  
 163 CO<sub>2</sub>-CH<sub>4</sub> CIA measurements. Despite this, an overestimation factor of 2 can still be in-  
 164 ferred when comparing the prediction from Wordsworth et al. (2017) to the experimen-  
 165 tal measurements, including the measurement by Turbet et al. (2019).

166 Ultimately, these results agree with the prediction of Wordsworth et al. (2017) when  
 167 it comes to the spectral range, and temperature dependence. However, the Wordsworth  
 168 et al. (2017) prediction consistently overestimates the strength of the CIA by a factor  
 169 of 2. At room temperature, these results agree within combined errors with the exper-  
 170 imental cross-sections of Turbet et al. (2019), strengthening our confidence in those num-  
 171 bers. There appears to be more internal structure in the CIA cross-sections reported in  
 172 this work compared to those of Turbet et al. (2019). This may be due to the increased  
 173 resolution of this experiment or residual of incompletely removed unwanted absorption  
 174 lines.

175 Attempts were also made to observe the CIA above 500 cm<sup>-1</sup>, using an MCT de-  
 176 tector and KBr windows/beamsplitter. However in this regime, absorption lines from CO<sub>2</sub>  
 177 and CH<sub>4</sub> were so strong that in order to not saturate the detector, less than 0.05 Torr  
 178 of those gas species was used. With such a small amount of gas present, there was no  
 179 longer enough to produce a measurable CIA signal above the noise.

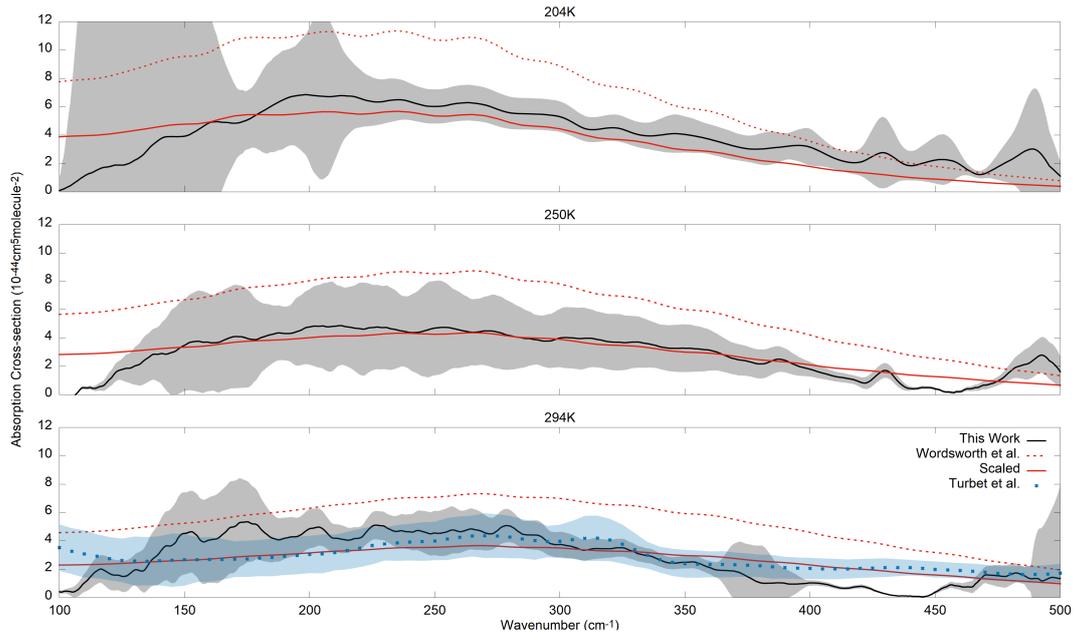


Figure 1: Experimental cross-section of  $\text{CO}_2\text{-CH}_4$  CIA from this work (solid black line) along with comparisons to Wordsworth et al. (2017) (red dotted line), Wordsworth et al. (2017) prediction scaled by a factor of 0.5 (red solid line) to provide better agreement with the results from this work, and Turbet et al. (2019) measurement (blue X line). Uncertainty is represented by the shading around the experimentally derived measurements.

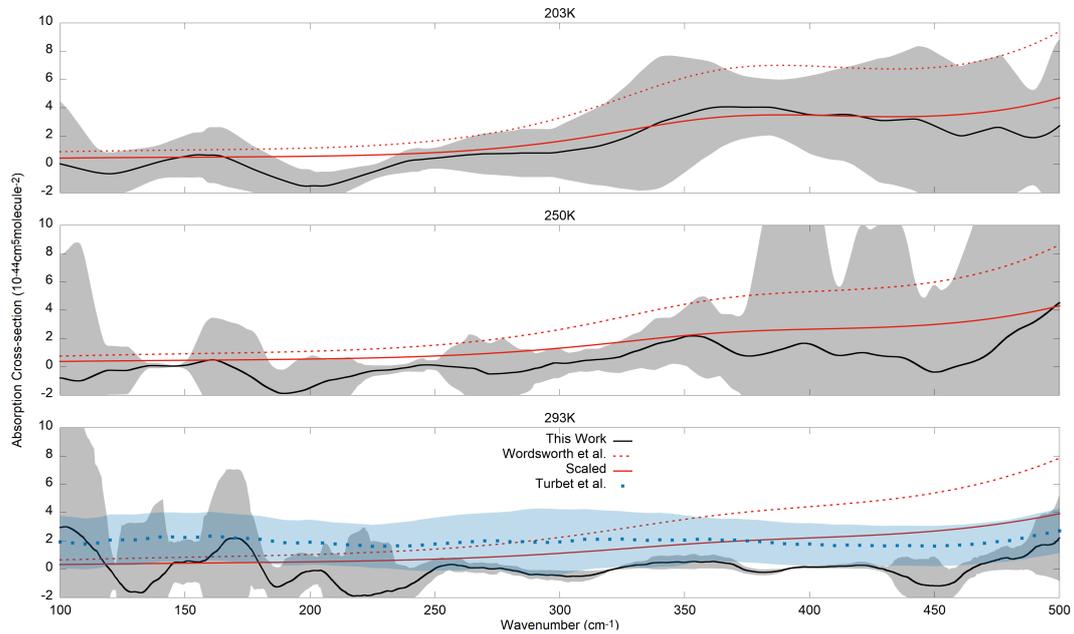


Figure 2: Experimental cross-section of  $\text{CO}_2\text{-H}_2$  CIA from this work (solid black line) along with comparisons to Wordsworth et al. (2017) (red dotted line), Wordsworth et al. (2017) prediction scaled by a factor of 0.5 (red solid line) to provide better agreement with the results from this work, and Turbet et al. (2019) measurement (blue X line). Uncertainty is represented by the shading around the experimentally derived measurements.

### 3 Implications for Ancient Mars

#### 3.1 Climate Model Details

Wordsworth et al. (2017) and Ramirez (Ramirez, 2017) investigated the effect on the ancient Martian climate by including the predicted CIA cross-sections in their radiative transfer models. However as noted in Section 2.2, there is a systematic overestimation in the predicted CIA for both CO<sub>2</sub>-H<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub> by a factor of 2. Therefore, it is worth revisiting these climate calculations with experimentally verified CIA absorption values. Since the experimental CIA do not cover the full spectral range needed for radiative transfer modeling, it is assumed that the scaling factor of 2 needed to adjust the Wordsworth et al. (2017) CIA is consistent across the full spectral range. A scaled Wordsworth et al. (2017) CIA was used in a single-column radiative climate model following the same procedure as outlined below (Ramirez et al., 2014; Ramirez, 2017):

This model follows a moist adiabat at warmer temperatures and relaxes to a CO<sub>2</sub> adiabat when temperatures become cold enough for CO<sub>2</sub> to condense (Ramirez et al., 2014, 2014). The model uses the correlated-k technique to compute absorption for CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, and H<sub>2</sub> across 38 solar intervals, 55 infrared intervals, five temperatures (100, 200, 300, 400, and 600 K), and for eight pressures (10<sup>-5</sup>–10<sup>2</sup> bar). At the low temperatures considered here (<300 K), the HITRAN (Gordon et al., 2017) line list was utilized to compute k-coefficients at all wavelengths for CO<sub>2</sub> and H<sub>2</sub>O, and in the thermal infrared for CH<sub>4</sub>. The far wings of water vapor are modeled using the *Baranov Paynter Serio* (BPS) water vapor continuum (Paynter & Ramaswamy, 2011), which allows for accurately computed water vapor absorption at warm temperatures. However, the HITRAN line list is still incomplete for CH<sub>4</sub> at visible and near-infrared wavelengths (Kassi et al., 2008). Instead, near-infrared CH<sub>4</sub> k-coefficients for wavelengths under 1 micron from Karkoschka (Karkoschka, 1994) were combined with those from Irwin et al. (1996) for the spectral range between 1 and 4.5 microns. Rayleigh scattering for H<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> (Ramirez et al., 2014; Snee & Ubachs, 2005) was included. CO<sub>2</sub>-CH<sub>4</sub> and CO<sub>2</sub>-H<sub>2</sub> CIA are incorporated, both from Wordsworth et al. (2017), and the CIA scaled by 0.5 to match the above experimental results. CO<sub>2</sub>-CO<sub>2</sub> CIA is modeled following the procedure in Wordsworth et al. (2010), using experimental data from Baranov et al. (2004) and Gruszka and Borysow (1997).

Overall, the new CIA yield significantly cooler mean surface temperatures as shown in Figures 3a and 3b, when comparing the results from this work (solid lines) to the previous work (dashed lines). Mean surface temperatures above 273 K can be reached with the new CIA if surface pressures exceed ~3 bar for a 10% CH<sub>4</sub> atmosphere. However, current studies on geologic observations suggest that the pressure on early Mars during valley network formation was no higher than ~2 bar (Kite et al., 2014; Hu et al., 2015; Kurokawa et al., 2017). Another issue is that for CH<sub>4</sub> concentrations above a CH<sub>4</sub>/CO<sub>2</sub> ratio of 0.1, photochemical hazes form that cool the planet, canceling the greenhouse effect (Haqq-Misra et al., 2008). Ultimately, CO<sub>2</sub>-CH<sub>4</sub> absorption is not as promising as initially argued in Wordsworth et al. (Wordsworth et al., 2017). CO<sub>2</sub>-H<sub>2</sub>, however, still seems much more promising, as liquid water is possible with 5% hydrogen and less than 2 bar of surface pressure.

The planetary albedo plots are calculated here using the updated CIA and compared to those found in (Ramirez, 2017); as in that study, the planetary albedo decreases with increasing CH<sub>4</sub> or H<sub>2</sub> concentrations since this causes the overall atmospheric scattering to decrease. Comparing the effect of scaled versus unscaled CIA on planetary albedo, the albedo does not change significantly with the updated CIA for CO<sub>2</sub>-CH<sub>4</sub> as shown in Figures 3c and 3d; this is primarily because water vapor amounts are still small at these temperatures. However with updated CO<sub>2</sub>-H<sub>2</sub> CIA, there is a slight change in planetary albedo. This is because H<sub>2</sub> has a larger impact on the surface temperature (Figures 3a and 3b) compared to CH<sub>4</sub>, which in turn increases the amount of water vapor in the atmosphere, resulting in the increased sensitivity of the planetary albedo to changes in CO<sub>2</sub>-H<sub>2</sub> CIA. Additionally, atmospheres with CH<sub>4</sub> will have a lower planetary albedo than

those with H<sub>2</sub> is in part due to the increased absorption of CH<sub>4</sub> at solar wavelengths, which reduces the planetary albedo compared to H<sub>2</sub>.

Following the analysis in (Ramirez, 2017), a comparison of temperature-altitude profiles for a fully-saturated 3 bar CO<sub>2</sub> early Mars atmosphere containing 1% CH<sub>4</sub> or 5% H<sub>2</sub> for a fully-saturated 2 bar CO<sub>2</sub> atmosphere were also performed using the updated CIA from this work. As seen in Figures 3e and 3f, there is little change in the temperature profile in the upper atmosphere when using Wordsworth et al. (2017) CIA or scaled CIA from this work; however at the surface there is  $\sim 10$  K difference in temperature.

## 4 Conclusions

This report details the first temperature-dependent experimental measurements of CO<sub>2</sub>-H<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub> CIA. It was found that below 600 cm<sup>-1</sup>, the experimentally derived CIA cross-sections agree with the spectral range and temperature dependence of the calculations by Wordsworth et al. (2017), however the amplitude is half of what was predicted. Furthermore, the CIA cross-sections reported here agree within combined uncertainty with those measured by Turbet et al. (2019), strengthening our confidence in these results.

With improved spectra, radiative transfer calculations of the early Mars atmosphere were performed and showed that CO<sub>2</sub>-CH<sub>4</sub> CIA is not as promising as initially argued in Wordsworth et al. (Wordsworth et al., 2017) for producing a warm and wet early Mars. CO<sub>2</sub>-H<sub>2</sub>, however, still seems much more promising, as liquid water is possible with 5% hydrogen and less than 2 bar of surface pressure.

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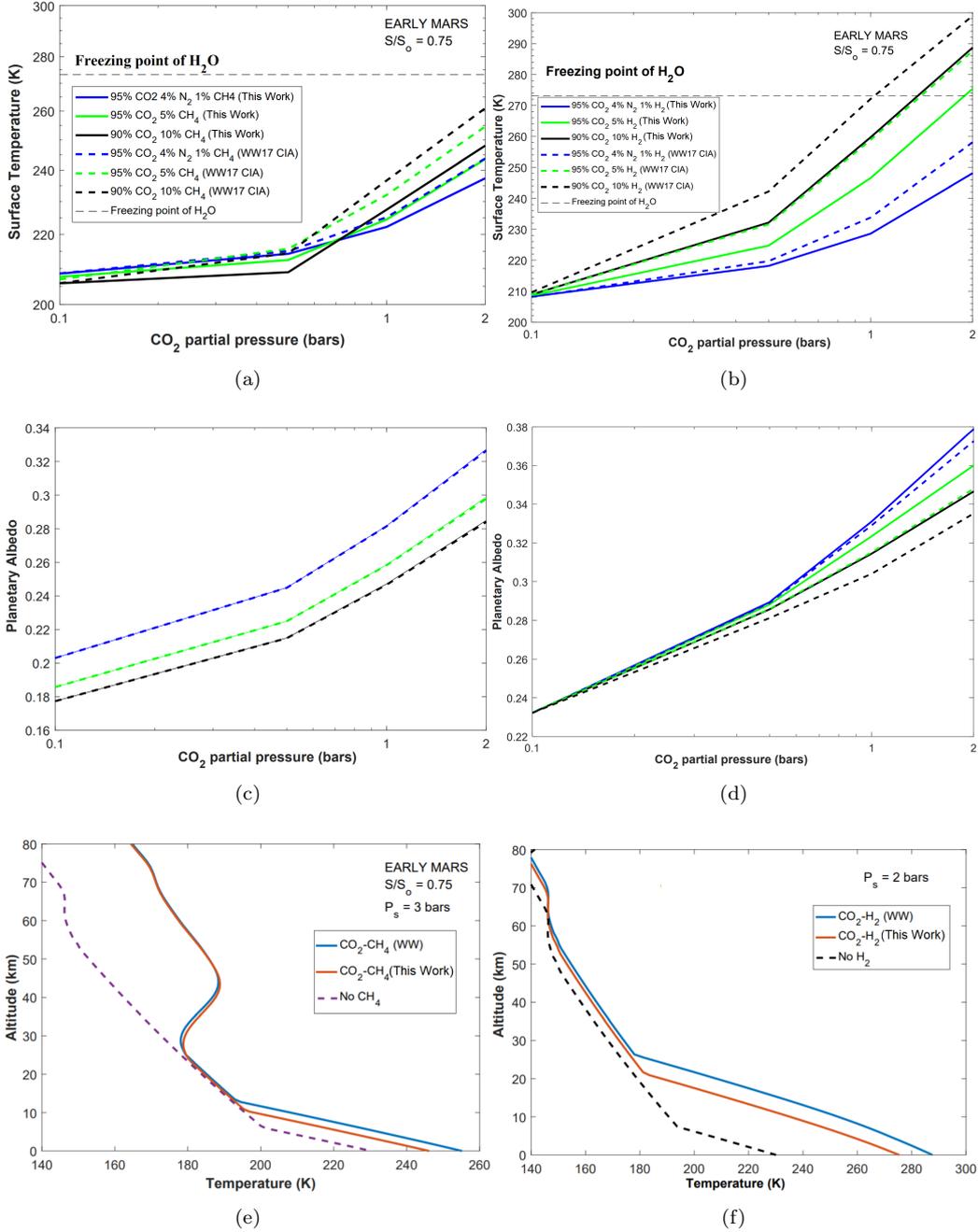


Figure 3: Early Mars climate modeling for atmospheres containing CH<sub>4</sub> or H<sub>2</sub>. Dotted lines designate unscaled CIA from Wordsworth et al. (2017), while solid lines use CIA values scaled by 0.5. The model assumes that the effective stellar flux received by Mars  $\sim 4$  billion years ago, is 75% of the present-day flux ( $S/S_0=0.75$ ). First row: modeled surface temperature as a function of CO<sub>2</sub> partial pressure (log scale), at 1%, 5%, and 10% CH<sub>4</sub> (a) or H<sub>2</sub> (b). Second row: Mars' planetary albedo as a function of CO<sub>2</sub> partial pressure, at 1%, 5%, and 10% CH<sub>4</sub> (c) or H<sub>2</sub> (d). Third row: temperature-altitude profiles for a fully-saturated CO<sub>2</sub> early Mars atmosphere from Ramirez (2017) for atmospheres containing no CH<sub>4</sub> or H<sub>2</sub> (dashed line), 1% CH<sub>4</sub> (e) or 5% H<sub>2</sub> (f) using Wordsworth et al. (2017) CIA (blue line), and 1% CH<sub>4</sub> (e) or 5% H<sub>2</sub> (f) using CIA from this work (red line).

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