Measurements and semi-empirical calculations of CO$_2$+CH$_4$ and CO$_2$+H$_2$ collision-induced absorptions across a wide range of wavenumbers and temperatures. Application for the prediction of early Mars surface temperature.

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Abstract

Reducing atmospheres have recently emerged as a promising scenario to warm the surface of early Mars enough to drive the formation of valley networks and other ancient aqueous features that have been detected so far on the surface of Mars. Here we present a series of experiments and calculations to better constrain CO$_2$+CH$_4$ and CO$_2$+H$_2$ collision-induced absorptions (CIAs) as well as their effect on the prediction of early Mars surface temperature. First, we carried out a new set of experimental measurements (using the AILES line of the SOLEIL synchrotron) of both CO$_2$+CH$_4$ and CO$_2$+H$_2$ CIAs. These measurements confirm the previous results of Turbet et al. 2019, Icarus vol. 321, while significantly reducing the experimental uncertainties. Secondly, we fitted a semi-empirical model to these CIAs measurements, allowing us to compute the CO$_2$+CH$_4$ and CO$_2$+H$_2$ CIAs across a broad spectral domain (0-1500cm$^{-1}$) and for a wide range of temperatures (100-600K). Last, we performed 1-D numerical radiative-convective climate calculations (using the LMD Generic Model) to compute the surface temperature expected on the surface of early Mars for several CO$_2$, CH$_4$ and H$_2$ atmospheric contents, taking into account the radiative effect of these revised CIAs. These calculations demonstrate that thick CO$_2$+H$_2$-dominated atmospheres remain a viable solution for warming the surface of Mars above the melting point of water, but not CO$_2$+CH$_4$-dominated atmospheres. Our calculated CO$_2$+CH$_4$ and CO$_2$+H$_2$ CIA spectra and predicted early Mars surface temperatures are provided to the community for future uses.

Keywords: Mars, spectroscopy, measurement, calculations, methane, hydrogen, collision-induced absorptions, climate, surface temperature

1. Introduction

Understanding how the early Martian climate could have been warm enough for liquid water to flow on the surface is still one of the major enigmas of planetary science (Wordsworth et al. 2016, Haberle et al., 2017). Reducing atmospheres have recently emerged as one of the most promising scenarios to solve this enigma (Ramirez et al., 2014, Wordsworth et al., 2017). Specifically, it has been proposed that significant amounts of hydrogen and methane could have accumulated in the atmosphere of early Mars 3-4 billion years ago through (i) volcanic outgassing from a reduced mantle (Ramirez et al., 2014), (ii) serpentinization (Chassefière et al., 2016), (iii) radiolysis (Tarnas et al., 2018), (iv) clathrate release e.g. after atmospheric collapse and reinflation events (Kite et al., 2020) or (v) impact-induced thermochemistry (Haberle et al., 2019).

The community's recent interest in this scenario stems mostly from the fact that H$_2$ and CH$_4$ are the only known yet plausible gases that could theoretically raise the surface temperature of a CO$_2$-dominated early Martian atmosphere above the melting point of water, i.e. the typical temperature required to form aqueous mineralogic and geomorphologic features visible today on the surface of Mars.
It has been shown that reducing gases CH₄ and H₂ can in fact produce a strong greenhouse effect in a CO₂-dominated atmosphere via their far-infrared absorptions (CIAs) induced by collisions with CO₂ (Ramírez et al., 2014, Wordsworth et al., 2017). Initially, the modelling of these CIAs was based, due to lack of relevant data, on the CIAs of H₂-N₂ and CH₄-N₂ pairs, respectively (Ramírez et al., 2014).

Since the initial work of Ramírez et al. (2014), significant efforts have been made to better constrain the intensity and spectral shape of CO₂+CH₄ and CO₂+H₂ CIAs. First, Wordsworth et al. (2017) provided theoretical calculations of these CIAs, using a semi-empirical model that assumes that the shape of the spectrum of CO₂+H₂ (CO₂+CH₄, respectively) CIA can be approximated as a linear combination of CO₂+CO₂ and H₂+H₂ (CH₄+CH₄, respectively) CIAs, which are known (Richard et al., 2012, Karman et al., 2019). The relative contribution of the two pure gas CO₂+CO₂ and H₂+H₂ (CH₄+CH₄, respectively) CIAs was taken equal to what is necessary to fit N₂+H₂ (N₂+CH₄, respectively) for which measurements have been performed, with N₂+N₂ and H₂+H₂ (CH₄+CH₄, respectively) pure gas CIAs. The integrated CO₂+H₂ (CO₂+CH₄, respectively) CIA spectrally integrated intensity was then predicted based on ab initio calculations of the zeroth order spectral moment (Wordsworth et al. 2017). With this model, Wordsworth et al. (2017) showed that the H₂-CO₂ and CH₄-CO₂ CIAs are more intense than the H₂-N₂ and CH₄-N₂ CIAs, respectively, mostly as a result of the fact that CO₂ has larger polarizability and multipole moments than N₂.

Turbet et al. (2019) then performed the first measurements of those H₂-CO₂ and CH₄-CO₂ CIAs. They showed that Wordsworth et al. (2017) had likely overestimated their average contribution, possibly by a factor of 1.6-1.7, at room temperature, and in the 50-550cm⁻¹ spectral range.

Knowing precisely the value of these CIAs is crucial to evaluate the true greenhouse effect of reducing atmospheres, and more specifically to estimate the minimum amount of H₂ (or CH₄, respectively) in a thick CO₂-dominated atmosphere required to warm the surface of early Mars above the melting point of water. This calculation is critical to assess the credibility of the reducing early Mars atmosphere scenario. On the one hand, maintaining hydrogen concentration above a few percent in the early Mars atmosphere would be difficult, given the predicted escape rates of hydrogen to space (Batalha et al., 2015). On the other hand, accumulating methane concentration in excess of 10% in the early Mars atmosphere should lead to the formation of photochemical hazes (Trainer et al., 2006), leading to a significant cooling of the surface. With the CIAs calculated in Wordsworth et al. (2017), only a few % of CH₄ and/or H₂ in a CO₂-dominated atmosphere could suffice to warm early Mars enough for surface liquid water to become stable (Wordsworth et al., 2017, Ramírez, 2017).

Here we performed a series of experiments and calculations to better constrain CO₂+CH₄ and CO₂+H₂ collision-induced absorption spectra as well as to determine their impact on the prediction of early Mars surface temperature. We present in Section 2 the results of our latest measurements of the CO₂+H₂ and CO₂+CH₄ CIAs. In Section 3, we present our semi-empirical model and show the results of our calculated CIAs. In Section 4, we use a numerical climate model to estimate the effect of these CIAs on surface temperature of early Mars. In Section 5, we present our conclusions as well as discuss future pathways to improve these calculations.

2. Updated experimental CIA measurements

After the first measurement campaign of CO₂+H₂ and CO₂+CH₄ CIAs carried in April 2018 and whose results were presented in Turbet et al. (2019), a second set of experiments was carried in September 2018. A total of fourteen CO₂+H₂ infrared spectra (14 spectra between 301 and 942
mbar, for a mixture of \(~ 50\% \text{ CO}_2 \) and \(~ 50\% \text{ H}_2 \) and thirteen \text{CO}_2+\text{CH}_4\) infrared spectra (13 spectra between 301 and 930 mbar, for a mixture of \(~ 50\% \text{ CO}_2 \) and \(~ 50\% \text{ CH}_4 \)) were recorded during one week, using the experimental setup (AILES line, at the SOLEIL synchrotron facility) detailed in Section 2.1 of Turbet et al. (2019). These spectra were then post-treated and converted into two collision-induced absorption (CIA) spectra (see Fig. 1; green spectra) using the methodology described in Section 2.2 of Turbet et al. (2019).

![Figure 1: In green, H\(_2\)+CO\(_2\) CIA (top panel) and CH\(_4\)+CO\(_2\) CIA (bottom panel) measured in this work at room temperature (symbols with error bars) in September 2018 measurement campaign. In black, the previously measured (Turbet et al., 2019) H\(_2\)+CO\(_2\) CIA (top panel) and CH\(_4\)+CO\(_2\) CIA (bottom panel), also at room temperature.](image)

Fig. 1 shows the resulting experimental CIA spectra (green spectra), obtained at room temperature (296 K) between \(~ 50 \) and \(~ 550 \text{ cm}^{-1} \). Newly recorded \text{CO}_2-\text{H}_2 \) and \text{CO}_2-\text{CH}_4\) spectra are both compatible within error bars with the previous measurements (black spectra) of Turbet et al. (2019).
While this gives us more confidence on the reliability of these experimental CIAs, we encourage independent measurements to further test these results (Godin et al., 2019). The uncertainties on the CO$_2$+H$_2$ CIA measurements (Fig. 1, top panel) have significantly reduced when compared to Turbet et al. (2019). This stems from the fact that particular care was taken to ensure that the Helium-cooled Si-bolometer detector had reached its steady-state temperature of 4.2 K. For our CO$_2$+CH$_4$ measurements (Fig. 1, bottom panel) as well as for the measurements presented in Figure 7 of Turbet et al. (2019), it turns out that the detector had not fully reached its steady-state equilibrium temperature, thus adding an extra source of uncertainty. The stability of the detector temperature (at 4.2 K) is key to keeping a stable baseline from one experiment to the next (as well as relative to reference spectra), and thus maximizing the signal to noise ratio of the CIA measurements.

The new experimental CIAs presented in Fig. 1 are used for the calibration of the semi-empirical CIA model described in the next Section. The goal of this model is to cover a wider temperature and wavenumber range than in the experiments.

3. Predictions of CIAs across a wide range of wavenumbers and temperatures

The most rigorous method for the calculation of CIA spectra is a close-coupling approach which fully takes into account the anisotropy of the interaction potential (see Karman et al., 2015). However, this approach remains hardly tractable with CO$_2$ as a collisional partner, due to the number of collisional channels that must be taken into account and subsequent computer cost.

In this section, we present the results of a tractable but more simple, semi-empirical model designed to calculate CIA spectra in the temperature and spectral ranges of interest for early Mars. Specifically, this model allows to compute the roto-translational band of the CIA spectra of CO$_2$-H$_2$ and CO$_2$-CH$_4$ pairs with the following two objectives:

i Being in agreement with the available experimental data (see Fig. 1) obtained at room temperature and for a rather limited spectral range.

ii But giving the possibility to calculate the CIA spectra over all frequencies between 0 and 1500 cm$^{-1}$ and at temperatures between 100 and 600 K.

Detailed information on this semi-empirical model (construction of the model, validation against experiments) can be found in Appendix A.

Figure 2 shows the results of our calculated CO$_2$+H$_2$ and CO$_2$+CH$_4$ CIAs at 200 K and 300 K between 0 and 1200 cm$^{-1}$, compared with the results of Wordsworth et al. (2017) as well as with the experimental results presented in the previous section (see Fig. 5 and 8 in Appendix A for a more detailed comparison). Our computed CIAs at room temperature match closely with the experimental results presented in Turbet et al. (2019) and in the Section 2 of this paper. The CIAs calculated with our semi-empirical model are also consistently weaker than those predicted in Wordsworth et al. (2017) in the main infrared window of CO$_2$, between 200 and 550 cm$^{-1}$. This not only confirms the result of Turbet et al. (2019) but also extends it to a broader range of temperatures.

Our calculated CIAs are provided as ascii files in the Supplementary Materials of this paper. They are used for the numerical climate calculations presented in the next Section. The goal of these climate calculations is to quantitatively evaluate the greenhouse effect of CO$_2$+CH$_4$ and CO$_2$+H$_2$ atmospheres on the surface temperature of early Mars.
Figure 2: $H_2+CO_2$ CIA (top panels) and $CH_4+CO_2$ CIA (bottom panels) calculated in Wordsworth et al. 2017 (dashed lines) and calculated in this work (solid lines), at temperatures of 200K (black) and 300K (blue). In the zoomed region, we also added (blue error bars) the experimental CIAs presented in Section 2. More detailed comparisons of the calculated CIAs with the room temperature measurements are provided in Appendix A (Fig. 5 and 8).

4. Effect of revised CIAs on the surface temperature of early Mars

We used the LMD Generic numerical climate model in (1D time-marching radiative-convective mode, as in Turbet & Tran, 2017) to perform numerical simulations of CO$_2$-dominated atmospheres (complemented with $H_2$, CH$_4$ and H$_2$O), under Noachian Mars insolation conditions (75% of present-day Mars insolation). The LMD Generic model has previously been used to simulate the surface and atmosphere of early Mars in 3D mode (Forget et al. 2013, Wordsworth et al., 2013, 2015, Turbet et al., 2017, 2020, Turbet & Forget, 2019) and in 1D mode (Wordsworth et al., 2010, Turbet & Tran, 2017, Turbet et al., 2020).
Following Wordsworth et al. (2017), we performed numerical climate calculations for atmospheres of various surface pressures (0.5-2bar), as well as various hydrogen (0.005-0.1) and methane (0.005-0.1) mixing ratios, now including the CO$_2$-H$_2$ and CO$_2$-CH$_4$ collision-induced absorption parameterizations presented in Section 3. The calculations were performed over 30 atmospheric layers from the surface up to a minimum atmospheric pressure of ~10 Pa. Following Wordsworth et al. (2017), CO$_2$, H$_2$ and CH$_4$ mixing ratios were assumed to be constant in the 30 atmospheric layers. H$_2$O mixing ratio was calculated at each layer assuming a constant tropospheric relative humidity of 0.8. Figure 3 compares our results with those of Wordsworth et al. (2017), for both CO$_2$+H$_2$ (upper panel) and CO$_2$+CH$_4$ (lower panel) atmospheres, and a total atmospheric surface pressure of 2 bar, which corresponds roughly to the upper estimate during the Noachian epoch (Kite, 2019) based on small crater statistics records (Kite et al., 2014) and maximum escape rates extrapolated from MAVEN observations (Jakosky et al., 2018). A more detailed Figure (i.e. comparing results across several surface pressures) is also proposed in Appendix B.

**Figure 3:** This figure shows calculated surface temperature for a 2 bar atmosphere under early Mars condition (75% of present-day Mars insolation; surface albedo taken equal to 0.2), assuming a CO$_2$+H$_2$ atmosphere (upper panel) and a CO$_2$+CH$_4$ atmosphere (lower panel). Black lines show the calculated surface temperatures as a function of H$_2$ and CH$_4$ mixing ratios, using the CIA parameterizations presented in Section 3. For comparison, we added blue lines, which are the calculated surface temperatures of CO$_2$-H$_2$ and CO$_2$-CH$_4$ atmospheres, respectively, taken from Wordsworth et al. (2017). The horizontal dashed black lines indicate the melting temperature of water, i.e. 273.15K.
Figure 3 (upper panel) shows that in a CO₂-dominated 2 bar atmosphere, a ~6% H₂ mixing ratio is required to warm the surface above the melting point of water. This mixing ratio estimate is approximately twice that calculated with the CO₂-H₂ CIA parameterization of Wordsworth et al. 2017. For a CO₂+CH₄ atmosphere (Fig. 3, lower panel), we calculated that the maximum surface temperature that can be reached is ~263K, about 8K lower than calculated with the CO₂-CH₄ CIA parameterization of Wordsworth et al. 2017. This is maximal in the sense that for CH₄/CO₂ mixing ratios higher than roughly 0.1, it is expected that reflective, anti-greenhouse haze would be produced (Trainer et al. 2006). This result confirms that CO₂ and CH₄ alone (possibly complemented with N₂ and H₂O) are unable to warm the surface of early Mars above the melting point of water. This makes H₂ the most efficient known and plausible gas to warm the surface of Mars above the melting point of water.

Finally, we performed several sensitivity tests to better understand the influence of the wavelength coverage and of the temperature dependence of the CO₂-H₂ CIA on the calculated surface temperatures. In the first, we artificially suppressed the temperature dependence of the CO₂+H₂ CIA and fixed the CIA to its 300K value. Doing this led, for a 1bar CO₂ atmosphere with 10% H₂, to a 12K decrease of the surface temperature, highlighting the importance of knowing accurately the temperature dependence of the CIA. In a second test, we artificially cut the CO₂+H₂ CIA wavelength coverage beyond 550cm⁻¹ (i.e. we retained only the 0-550cm⁻¹ part of the CIA). Doing this led, for a 1bar CO₂ atmosphere with 10% H₂, to an 8K decrease of the surface temperature. Again, this demonstrates that it is not only important to quantify the CIA between 0 and 550 cm⁻¹ (because there is a major CO₂ atmospheric window around 350cm⁻¹; corresponding to the low-frequency wing of the ν₂ band of CO₂) but also between 800 and 1200cm⁻¹ (corresponding to the high-frequency wing of the ν₂ band of CO₂).

5. Conclusions and future work

In this paper, we performed a series of experiments and calculations to better constrain the CO₂+CH₄ and CO₂+H₂ collision-induced absorptions (CIAs) as well as their effect on the prediction of early Mars surface temperature. First, we carried a new set of experimental measurements (using the AILES line of the SOLEIL synchrotron) of both CO₂+CH₄ and CO₂+H₂ CIAs. These measurements confirm the previous results of Turbet et al. (2019) while significantly reducing the uncertainties on the CIA determinations. Secondly, we fitted a semi-empirical model on these CIAs measurements, allowing us to compute CO₂+CH₄ and CO₂+H₂ CIAs across a broad spectral domain (0-1500cm⁻¹) and for a wide range of temperatures (100-600K). These CIAs are provided in the Supplementary Materials of this paper. Last, we performed 1-D numerical climate calculations (using the LMD Generic Model) to compute the surface temperature expected on the surface of early Mars for several CO₂, CH₄ and H₂ partial pressures, taking into account the radiative effect of the revised CIAs. We found that the concentration of H₂ required to warm the surface of early Mars above the melting point of water is 2-3 times higher than previously reported in Wordsworth et al. (2017). However, we showed that a CO₂+CH₄ atmosphere (assuming a total CO₂ surface pressure lower or equal to 2bar, and a CH₄/CO₂ ratio lower or equal to 0.1) should be unable to warm the surface of early Mars above 273K. This demonstrates that H₂ remains the only known and plausible gas that may possibly raise the annual mean surface temperature of early Mars over the melting temperature of water.

In the future, there are several ways to make progresses on our understanding of the reducing atmosphere scenario which we now – according to our results – suggest renaming the “H₂ scenario” or “H₂ hypothesis”. First, independent measurements of CO₂+H₂ and/or CO₂+CH₄ CIAs in a range of wavenumbers and temperatures as large as possible (e.g. see ongoing efforts in Godin et al., 2019) would be helpful to validate the experimental results presented in our work and in the work
Specifically, measurements of the CIAs in the high frequency part of the \( \nu_2 \) band (i.e. below 15\( \mu \)m band) and/or at very low or high temperatures would be useful to validate and constrain the semi-empirical model presented in our work.

Then, sophisticated models such as anisotropic fully quantum calculations (Karman et al., 2015) could be developed to produce reliable CIA spectra. Preliminary calculations show however that this approach will be computationally very expensive. Another strategy could be to perform classical molecular dynamics simulations (CMDS), in the same vein than Hartmann et al. (2011), taking possibly into account anisotropic effects as they were shown to be important in our analysis.

Finally, the “H\(_2\) scenario” could be evaluated with 3-dimensions Global Climate Models (GCMs). The sophisticated climate models can be used not only to better evaluate the necessary concentration of H\(_2\) required to warm the surface of Mars, but can also be used to get insights on the nature of the hydrological cycle expected in such environments. For instance, GCMs can be used to predict erosion spatial patterns which can then be compared with observations of the ancient surfaces of Mars. There are currently many efforts being made to move toward this direction with the 3-D LMD Generic GCM (Turbet, 2018, Turbet & Forget 2019), the NASA AMES GCM (Steakley et al., 2019) and the DRAMATIC GCM (Takeshi Kuroda, personal communication).

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Appendix A - Semi-empirical CIA model

In this Appendix, we describe in details how we constructed our semi-empirical model of CO₂-H₂ and CO₂-CH₄ CIs.

A.1. CO₂-H₂

We first start this Appendix by introducing the various terms and approximations necessary for the readers to understand the content and philosophy of our semi-empirical models of CO₂+H₂ (and CO₂+CH₄) collision-induced absorptions.

The induced dipole (ID): As discussed by Poll & Hunt (1976), the spherical components of the ID in a space fixed system, for a pair of linear molecules can be written in terms of coupled spherical harmonics specified by four indices $\lambda_1, \lambda_2, \Lambda \land \Lambda$ satisfying some general constraints. Following a preliminary study of Cherepanov et al. 2016 (see p.28), showing that the short range components of the ID are negligible for distances $R$ (between the centers of mass) greater than about $7a_0$, we have limited the ID to its long range components. We have taken into account all the components as given in the appendix of Hartmann et al. (2011). Note that all the molecular parameters appearing in these expressions are well known and may be easily found in the literature (Li et al., 1998, Hartmann et al., 2011, and references therein).

The intermolecular potential: Reliable anisotropic potentials are now available for the CO₂+H₂ pair. In the present work, we have chosen the potential proposed by Li et al. (2010), which gave good predictions of the IR spectra of the complex. Its isotropic part can be easily determined through an “ad-hoc” averaging over the relative orientations.

The classical isotropic approximation (IA): In a classical approach, the pair distribution function is given by (Borysow & Moraldi, 1992):

$$ g(R,\Omega) = \exp(-V(R,\Omega)/k_BT) $$

where $V(R,\Omega)$ is the intermolecular potential, with $R$ the intermolecular distance and $\Omega$ indicating the relative orientation of the two molecules. In the IA, one assumes that the potential may be limited to its isotropic part $V_0(R)$.

The absorption coefficient: As the theory has been extensively presented in detail elsewhere (see for instance Boissoles et al., 1994), only a brief review is given here. Within the IA, the CIA coefficient (in cm⁻¹ amagat⁻¹) can be written as a sum of rotational components, each having a translational profile:

$$ \alpha_{iso}(\omega) = \frac{4\pi^2}{3\hbar c} n_0^2 \omega \left(1 - e^{-\hbar \omega/k_BT}\right) \sum_n \Gamma_n(T) G_n(\omega - \omega_n, T) $$

Where $n_0$ is the number density at normal temperature and pressure. Each component $n$ is specified by a set of quantum numbers, $n = \{j_1, j_2, j_1', j_2', \lambda_1, \lambda_2, \Lambda \land \Lambda\}$, in which $j_1$ designates the rotational quantum number of CO₂ (i=1), and H₂ (i=2); a prime indicates final states. $\Gamma_n(T)$ represents the strength of the rotational component while $\omega_n = \omega_{j_1j_1'} + \omega_{j_2j_2'}$ is its central frequency. Their expressions may be found in Boissoles et al. (1994).

The translational profile: In a fully quantum but isotropic approach, the product $\Gamma_n(T) G_n(\omega, T)$ can be directly calculated from the isotropic potential by solving a Schrödinger equation (see Karman et al., 2015). Here we preferred to use a more empirical lineshape. There have been many models proposed in the past. In the present work, we have chosen the so-called K2 lineshape to represent the translational profile (Hunt and Poll, 1978):

$$ G_n(\omega, T) = \frac{2}{3\pi n_0} \frac{1}{1 + e^{-\hbar \omega/k_BT}} \left(\frac{\omega}{\eta_n}\right)^2 K_2\left(\frac{\omega}{\eta_n}\right) $$
where $K_2$ is a modified Bessel function of the second kind. $\eta_w$ is a parameter of the same dimension as $\omega$. The main advantage of the K2 lineshape is that $\eta_w$ can be determined, for each temperature, from the only knowledge of the isotropic potential and the corresponding spectral moments. Details on how this can be done are available, for instance, in Leforestier et al. (2010).

Figure 4: Comparison between the experimental results and the theoretical calculations of the CO$_2$-H$_2$ CIA within the isotropic approximation.

Results in the isotropic approximation: Once the rotational strengths and translational profiles are available, the CIA coefficient at $T=296K$ can be calculated and compared with the experimental data. As shown in Fig. 4, this calculation does not provide sufficient spectral intensity to explain the measured absorption.

Of course, the present model is subject to many uncertainties. It was, therefore, of some interest to compare its predictions with a more “exact” calculation in order to determine its failures. As mentioned above, quantum calculations are now feasible for CO$_2$-H$_2$, within the isotropic and coupled states approximations, avoiding therefore the use of a classical pair distribution function (appearing in the rotational strengths) and empirical translational profiles. In Karman et al. (2015), this formalism has been applied to the N$_2$-N$_2$ CIA, leading to a good agreement with the measured data in a wide range of temperatures. By using the same isotropic potential and the same ID components as in our semi-empirical model, the “isotropic quantum” spectrum has been calculated at 296K and is compared with the more simple semi-empirical model results in Fig. 4. There is a very good agreement between the two theoretical calculations, thus validating the use of the semi-empirical approach, which is much easier to handle. However, both calculations disagree with the measured absorption, indicating that anisotropic effects may be important to take into account here.

Failure of the isotropic approximation: It appears more clearly that the validity of the isotropic approximation needs to be analyzed. A first indication on its accuracy can be obtained by examining the anisotropic potential of Li et al. (2010) which exhibits a strong dependence on the mutual orientation of the two colliding molecules. Based on a spectral moments analysis, the
inadequacy of the IA can then be easily demonstrated. Gruszka & Borysow (1996) have developed a formalism for the calculation of the zeroth order spectral moment and of the integrated intensity of the band, which fully accounts for the anisotropy of the potential. We have applied this formalism to the CO\textsubscript{2}-H\textsubscript{2} pair. The results, for some selected temperatures are given in Tables 1 and 2, and compared with those based on the IA. Even if spectral moments contain less information than spectral densities, this comparison provides a significant test of the inadequacy of the IA. Before going on, note that our results for the “anisotropic” 0\textsuperscript{th} order spectral moments are in reasonable agreement with those calculated by Wordsworth et al. (2017), which are equal to 1.6-1.8×10\textsuperscript{-4} cm\textsuperscript{-1} between 200-300K, respectively (see Fig. 1 in the Supporting Information of Wordsworth et al., 2017).

Table 1: Integrated intensity S (in 10\textsuperscript{-2} cm\textsuperscript{-2} amagat\textsuperscript{2}). As a reminder, \( S = \int_0^\infty d\omega \alpha(\omega) \) is the integral of the CIA binary coefficient \( \alpha(\omega) \) over wavenumber \( \omega \).

| T(K) | \( S_{iso}(T) \) | \( S_{aniso}(T) \) | ratio |
|------|-----------------|------------------|-------|
| 100  | 1.38            | 4.37             | 3.17  |
| 200  | 1.27            | 2.54             | 2     |
| 300  | 1.3             | 2.4              | 1.85  |
| 500  | 1.42            | 2.46             | 1.73  |

Table 2: Zeroth order moment (in 10\textsuperscript{-4} cm\textsuperscript{-1} amagat\textsuperscript{2}). As a reminder, \( M^{(0)} = \int_0^\infty d\omega \frac{\alpha(\omega)}{\omega} \frac{1}{\tanh\left(\frac{\hbar\omega}{2k_BT}\right)} \) is the zero\textsuperscript{th} order moment of the CIA binary coefficient \( \alpha(\omega) \).

| T(K) | \( M_{iso}^{(0)}(T) \) | \( M_{aniso}^{(0)}(T) \) | ratio |
|------|-------------------------|--------------------------|-------|
| 100  | 1.15                    | 4.03                     | 3.17  |
| 200  | 1.07                    | 2.16                     | 2.02  |
| 300  | 1.09                    | 2.01                     | 1.84  |
| 500  | 1.18                    | 2.05                     | 1.74  |

**Empirical correction of the isotropic spectral densities:** As mentioned above, accounting for the anisotropy of the intermolecular potential remains a challenge for fully quantum calculations with a heavy collision partner like CO\textsubscript{2}. Here we rather built on our semi-empirical model that we modified to account for anisotropic effects using the following procedure:

i. We assumed that the area-normalized absorption coefficient (i.e. the spectral shape) can be reasonably calculated within the IA, from eq. (A-2).

ii. We multiplied the normalized profile by the “true” anisotropic integrated intensity (provided in Table 2):

\[
\alpha_{aniso}(\omega, T) = \frac{s_{aniso}(T)}{s_{iso}(T)} \alpha_{iso}(\omega, T) \quad (A-4)
\]

Figure 5 shows that this procedure leads to a theoretical CIA coefficient that is in good agreement with the available experimental data at 296K. We then computed the CO\textsubscript{2}-H\textsubscript{2} CIA in a wide range of temperatures using the temperature dependencies of the parameters of our models. Results are provided in Figure 6. Note that, because the calculated zeroth order spectral moments are quasi-independent of temperature within the 200-300K range (which is the typical range of temperatures
expected in the atmosphere of early Mars) as seen in Table 2, our model should be reliable for early Mars applications.

**Figure 5:** Comparison between the experimental results (presented in Section 2) and the renormalized, anisotropic CO$_2$+H$_2$ collision-induced absorption coefficient.

**Figure 6:** Temperature dependence of the renormalized, anisotropic CO$_2$+H$_2$ collision-induced absorption coefficient.
A.2. CO$_2$-CH$_4$

Before considering the CO$_2$+CH$_4$ pair, let us recall the state of the art for a very similar system, N$_2$-CH$_4$, for which many comparisons between theory and measurements have been made. The most recent analysis has been proposed by Buser et al. (2004). Their main approximations were:

i. The isotropic approximation (IA), but using an “effective” isotropic potential, i.e. determined from fitting various scattering data. This effective isotropic potential may include part of the effects of the true anisotropic potential.

ii. The induced dipole (ID) limited to its long-range components (calculated with well-known molecular parameters requiring no adjustment).

For wavenumbers $\geq 175$ cm$^{-1}$, theory and measurements diverge more and more, reaching one order of magnitude around 1000 cm$^{-1}$ (Buser et al., 2004). To the best of our knowledge, no clear explanation of that discrepancy has been given yet. However, an alternative had been proposed by Borysow & Tang (1993) in order to reproduce all the existing measurements, in a wide range of temperature (70-296K) with the greatest possible accuracy (for support of the analysis of Titan’s atmosphere). Their alternative model consists in adding empirical short-range contributions to the $\lambda_1, \lambda_2, L$ ID components 203, 034, 045 and 067 ((1) stands for N$_2$ and (2) for CH$_4$). The corresponding parameters were adjusted through a fitting of all the available experimental spectra. Here we followed a similar procedure for the CO$_2$-CH$_4$ system.

Isotropic approximation and effective isotropic potential: A sophisticated anisotropic potential is now available for the CO$_2$+CH$_4$ pair (Hellman et al., 2016). As for CO$_2$-H$_2$ the analysis of the shape of this potential for various mutual orientations of the collisional partners rises some doubt about the validity of the “true” isotropic approximation. By “true” we mean using the “true” isotropic part of the anisotropic potential. For example, from Fig. 2 of Hellman et al. (2016), the distance between the two molecules at which the interaction potential reaches zero may vary from 3Å to about 4.5Å for different mutual orientations. However, less rigorous descriptions of static and dynamic properties for that pair have been made, using an effective isotropic potential adjusted to reproduce the corresponding data. In this work we have used a potential given by Bastien et al. (2010). They fitted viscosity data for binary mixtures and among different solutions proposed a Lennard-Jones 6-12 potential, with the following parameters: $\epsilon/k_B T = 203 K; \sigma = 3.735$ Å.

ID components: In a first step we have considered only the long-range components as given for instance in Borysow & Tang (1993). Here too, the needed molecular parameters are well known and easily found in the literature (Li et al., 1998, Hartmann et al., 2011, Zvereva-Loete et al., 2010, and references therein). In a second step and as stated above, we added an empirical short-range component following the approach of Borysow & Tang (1993).

Translational shape: Since the isotropic potential is known, we decided to use K2 lineshapes that were determined following the procedure already outlined for the CO$_2$+H$_2$ pair.
Figure 7: Comparison between the experimental data of Turbet et al. (2019) and the prediction of our semi-empirical model for the CO$_2$+CH$_4$ CIA spectrum. Here the induced dipole (ID) is limited to its long-range components.

Results: Figure 7 shows the result of our semi-empirical model when considering only the long-range components of the ID. We observe significant discrepancies between this first model and the experimental data of Turbet et al. (2019) and those presented in the Section 2. The situation is in fact rather similar to that observed for N$_2$-CH$_4$ at the same level of approximation.

Therefore, we have followed the method initially proposed by Borysow & Tang (1993), by adding short range contributions to the same $\lambda_1, \lambda_2, L$ ID components. Fitting the four corresponding parameters requires an adjustment on many experimental profiles measured in a wide range of temperatures, as was done for the N$_2$-CH$_4$ pair. However, such measurements are not available yet for the CO$_2$+CH$_4$ pair. We have therefore included the contribution of the short-range components of the CO$_2$+CH$_4$ pair by using the short-range component of the N$_2$+CH$_4$ pair multiplied by a constant (a factor 2) adjusted to fit the available experimental data. The result of this second semi-empirical model (including a parameterization of the short-range components) is presented in Figure 8.
Figure 8: Comparison between the experimental data and the optimized model for the CO$_2$+CH$_4$ CIA, after introducing short range components to the induced dipole. While “Previous measurements” refer to the work of Turbet et al. 2019, the “new experiment” refer to the work presented in Section 2 of this paper.

Figure 8 shows that we can obtain a reasonable agreement with the measured absorption at 296K. We then computed the CO$_2$-CH$_4$ CIA in a wide range of temperatures using the temperature dependencies of the parameters of our models. Results are provided in Figure 9.

Figure 9: Temperature dependence of the CO$_2$-CH$_4$ collision-induced absorption coefficient, as predicted by the optimized model.
Appendix B – Additional Figure on the calculations of early Mars surface temperature

Figure 10: Predicted surface temperature in CO$_2$-dominated atmospheres under early Mars condition (75% of present-day Mars insolation; surface albedo taken equal to 0.2) as a function of H$_2$ and CH$_4$ concentration (upper and lower panels, respectively) and for various surface pressures. Dashed lines show results using Wordsworth et al. (2017) CIAs while solid lines were computed using CIAs presented in the Section 3 of this paper. For reference, the horizontal dashed black lines indicate the melting temperature of water, i.e. 273.15K.