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New experimental measurements of the Collision Induced Absorptions of H₂-H₂ and H₂-He in the 3600-5500 cm⁻¹ spectral range from 120 to 500 K

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ABSTRACT

The Collision-Induced Absorption (CIA) fundamental band of H₂ has been studied in the 3600–5500 cm⁻¹ spectral range for temperatures ranging from 120 to 500 K for both a pure H₂ gas and a H₂-He mixture. We used a simulation chamber called PASSxS (Planetary Atmosphere System Simulation x Spectroscopy) developed at INAF/ISAC which contains a Multi-Pass cell interfaced with a Fourier Spectrometer, aligned to reach an optical path of 3.28 m. The H₂-H₂ and H₂-He binary absorption coefficients (BACs) have been derived for seven temperatures in the chosen range and provided in tabular form, including the unexplored high-temperature range above 300 K. We also calculated the integral of the H₂-H₂ and H₂-He experimental BACs in the reduced 4000–5000 cm⁻¹ spectral range, finding a linear trend with temperature in both cases. The integrals have also been computed with larger uncertainties for the whole band, in the total 3600–5500 cm⁻¹ spectral range including the band's wings, partially affected by the water vapor absorption. The integrals calculated over the whole and reduced spectral ranges are collected in tables. In addition, we performed measurements with a H₂-He mix for different mixing ratios to explore possible deviations from the linear combination of the BACs. The experimental BACs have been shown in comparison with Abel and Borysow's *ab initio* models for a temperature of about 400 K, resulting in a good agreement over almost the whole spectral range, with a maximum deviation around the main peak of the band. Data and models also show a good agreement in the linear trend of the integrated BACs with temperature, apart from the H₂-H₂ Borysow's BACs, which follow a quadratic trend. Finally, we resolved all the interference dips, which were not taken into account by the existing theoretical models.

1. Introduction

The Collision-Induced Absorption (CIA) bands are of primary importance for all the molecules, such as H₂, O₂, and N₂, that don't have a permanent nor a transient dipole moment, which could allow respectively rotational and ro-vibrational transitions. However, by colliding with another molecule, or an atom, they can acquire an induced dipole moment and generate the so-called CIA bands in various spectral ranges.

In this work, we have studied the CIA fundamental band of H₂, in the 3600–5500 cm⁻¹ spectral range, for both a pure H₂ gas and a H₂-He mixture in the 120–500 K temperature range. We assume the (H₂)₂ dimer absorption contribution to be negligible in our experimental

conditions. In other similar cases, it has been detected in the laboratory just at very low temperatures [1,2] and, thanks to the high sensitivity of the CRDS technique, at room temperature in the first overtone band of H₂ [3].

Previous experimental works have already studied this particular CIA band using those gaseous mixes, but only for a few selected temperatures below or at room temperature [4–9]. Furthermore, only a few studies provided binary absorption coefficients (BACs) and their errors in tabular form [7–9].

This work aims to determine the experimental BACs in the CIA fundamental band of H₂ for both the H₂-H₂ and H₂-He contributions in the 3600–5500 cm⁻¹ spectral range and for temperatures from 120 to 500 K, studying the hitherto unexplored high-temperature range above

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300 K, and to make them available in tabular form, along with their uncertainties, on the Zenodo¹ platform at the following link [10.5281/zenodo.13142015](https://zenodo.org/record/13142015).

Theoretical models, allowing to simulate the CIA fundamental band of H₂, are also available.

For temperatures up to 300 K, the H₂-H₂ and H₂-He theoretical BACs computed by Birnbaum et al. [10] are available in tabular form.

Moreover, two remarkable studies have been published by A. Borysov [11–13] and M. Abel [14,15] to calculate the BACs for both the H₂-H₂ and H₂-He contributions for temperatures ranging from 18 to 7000 K for the Borysov's models and from 200 to 9000 K for the Abel's ones. Borysov data can be found at <https://www.astro.ku.dk/~aborysov/programs/>, while Abel's BACs can be downloaded from the Hitran website (<https://hitran.org/cia/>) in the section dedicated to the CIA [16,17].

In this work, a comparison between our measured experimental BACs with Abel and Borysov's theoretical models, for both the H₂-H₂ and H₂-He contributions will be shown at about 400 K.

We want to point out that our data, reported in this paper, are also very important to support the remote sensing observations of the outer planets in our Solar system and giant exoplanets, all being primarily composed of H₂ and He, representing the main sources of IR opacity in their atmospheres.

2. Experimental details

Heatable and coolable cells have been constructed throughout the years to measure the spectra of different gaseous mixtures at various pressure and temperature conditions. The equipment used for the present work, called PASSxS (Planetary Atmosphere System Simulation x Spectroscopy) is specifically designed for these types of studies. It consists of a simulation chamber, developed at INAF/ISAC, containing a Multi-Pass (MP) cell interfaced with a Fourier Spectrometer. The MP cell has been aligned to reach an optical path of 3.28 m.

The chamber can be filled with the gaseous mixture of interest with pressures from 0.02 mbar up to 70 bar and it can be heated up to 550 K and cooled down to 100 K. Spectra can be acquired with a maximum resolution of 0.06 cm⁻¹. The experimental setup is equipped with three different pressure transducers, with full scales of 1, 20, and 100 bar. Their specified accuracy is defined as 0.06 % of the full scale. In addition, 6 thermocouples have been mounted in different parts of the internal chamber to measure the gas temperature, of which one probes directly the gas phase. Their accuracy is specified as 0.75% of the value, or ±1K, depending on which is larger. More details can be found in Snels et al. [18].

2.1. Experimental procedure

The present experimental setup allows to directly measure the spectral transmittance of a particular gaseous mixture by performing the ratio between the radiance I_ν , obtained with the chamber filled with the gas, and the background radiance I_0 , acquired with the empty cell.

Since in our experimental conditions emission can be neglected, the absorption coefficients can be estimated as the logarithm of the transmittance, divided by the optical path (L), as shown in Eq. (1).

$$k_\nu = -\frac{1}{L} \log \left(\frac{I_\nu}{I_0} \right) \quad (1)$$

To measure the radiance I_ν we adopted the following procedure.

We can directly select the type of gas we want to insert, specifying the pressure and temperature set points we want to reach in the chamber. Once the chamber has been filled up with the gaseous mixture of

interest, we wait enough time to let the gas thermalize before acquiring the radiance.

When performing the measurements for a pure H₂ gas, we can just select the pressure and temperature desired, to obtain a certain density, which can be calculated by using the NIST Chemistry book online tool².

A slightly different procedure is required to insert a two-gaseous mixture with a specific mixing ratio.

Starting from the total pressure we want to reach in the chamber at a specific temperature, and the percentage of the species we want to insert, we calculate the pressure of the two selected gases to obtain a certain mixing ratio. Then, we insert the right amount of the two gases one at a time.

Finally, we measure the background with the empty cell at the same temperature at which the sample radiance has been acquired.

Following this procedure, we performed two sets of measurements in the 120–500 K temperature range with a resolution of 1 cm⁻¹, first using a pure H₂ gas and second with a H₂-He mixture for different He concentrations. We considered the 1 cm⁻¹ more than adequate for the scope, since the CIA features studied here are rather spectrally broad.

For each temperature, we calculated the BACs associated with both the H₂-H₂ collisions, $k(\nu)_{\text{H}_2\text{-H}_2}$, and the derived H₂-He ones, $k(\nu)_{\text{H}_2\text{-He}}$.

In fact, according to the binary scattering theory, the CIA total absorption coefficients $k(\nu)^{\text{mix}}$ of a H₂-He mix depend on the two terms mentioned above through the following equation:

$$k(\nu)^{\text{mix}} = k(\nu)_{\text{H}_2\text{-H}_2} \rho_{\text{H}_2} \rho_{\text{H}_2} + k(\nu)_{\text{H}_2\text{-He}} \rho_{\text{H}_2} \rho_{\text{He}} \quad (2)$$

where ρ_{H_2} and ρ_{He} are respectively the H₂ and He gas densities.

To calculate the $k(\nu)_{\text{H}_2\text{-H}_2}$ term we divided the absorption coefficients measured with a pure H₂ sample for the H₂ density squared, and to obtain the $k(\nu)_{\text{H}_2\text{-He}}$ term the following equation has been used:

$$k(\nu)_{\text{H}_2\text{-He}} = \frac{k(\nu)^{\text{mix}}}{\rho_{\text{H}_2} \rho_{\text{He}}} - k(\nu)_{\text{H}_2\text{-H}_2} \frac{\rho_{\text{H}_2}}{\rho_{\text{He}}} \quad (3)$$

Where $k(\nu)^{\text{mix}}$ are the absorption coefficients acquired with the H₂-He mix, and $k(\nu)_{\text{H}_2\text{-H}_2}$ are the binary absorption coefficients for the pure H₂ case, both measured at the same temperature, ρ_{H_2} and ρ_{He} are respectively the H₂ and He densities used to perform the measurement with the mixture.

The errors in the BACs are calculated as the sum of the relative errors of the baseline³, the density, and the optical path of the internal MP cell.

The first one is related to the variation of the radiance signal over time which introduces a systematic error in the measurement. This fluctuation results in a variation of the baseline when performing the ratio between the background and the radiance acquired with the chamber filled with the gas. As a consequence, a baseline correction has been applied to the experimental data.

One important parameter that can be evaluated is the band's integral, calculated as shown in Eq. (4) for a specific spectral range.

$$I(\nu) = \int_{\nu_{\text{min}}}^{\nu_{\text{max}}} k(\nu) d\nu \quad (4)$$

Here $k(\nu)$ can be both the absorption coefficients or the binary absorption coefficients, and ν_{min} , ν_{max} represent the minimum and maximum frequencies between which the integral is calculated.

In the following sections, the measurements obtained and the results

² Online tool available at the <https://webbook.nist.gov/chemistry/> website, that provides users with easy access to chemical and physical property data for chemical species. It allows the calculation of the temperature, pressure, and density for a certain gaseous species, using the real gas equation

³ Spectral region that does not present any absorption feature. It corresponds to the value one for the transmittance, and zero for the absorbance or the absorption coefficients

¹ The platform can be found at <https://zenodo.org/>.

achieved will be presented in detail.

3. CIA measurements and results

3.1. CIA of a pure H₂ gas

Using a pure H₂ gas, with a purity of 99.9999%, we measured the absorption coefficients at seven temperatures, ranging from 120 to 500 K. For three of those temperatures, 200 K, 296 K, and 400 K, we performed measurements at different density conditions, to investigate the behavior of the absorption coefficients with respect to the density squared.

We chose three frequencies, namely 4200 cm⁻¹, 4600 cm⁻¹, and 5000 cm⁻¹, at which we calculated the absorption coefficients at a fixed temperature, and plotted them as a function of the H₂ density squared. Then, we performed a linear fit over the data, finding a good agreement inside the error bars for all three temperatures mentioned above. In Fig. 1 the room temperature case is displayed. As the experimental points follow a linear trend, we can confirm that at those density and temperature conditions, the binary scattering theory represents a good approximation for our data (see Eq. (2)).

As one can see, the points referred to the lowest density just marginally agree with the linear behavior. It may be due to the slight difference in temperature at which we performed this set of measurements.

The slopes related to the linear fits performed over the data at 4200 cm⁻¹, 4600 cm⁻¹ and 5000 cm⁻¹ are, respectively: $(3.70 \pm 0.06) \cdot 10^{-6} \text{cm}^{-1} \text{amagat}^{-2}$, $(1.92 \pm 0.07) \cdot 10^{-6} \text{cm}^{-1} \text{amagat}^{-2}$ and $(9.25 \pm 0.63) \cdot 10^{-7} \text{cm}^{-1} \text{amagat}^{-2}$.

Since we measured the absorption coefficients at seven different temperatures with the highest density and thus with the highest signal-to-noise ratio, we decided to use them to calculate the $k(\nu)_{\text{H}_2-\text{H}_2}$ binary absorption coefficients. A graphical representation of the coefficients thus obtained is shown in Fig. 2. A large water vapor absorption can be noticed on the band's wings, in the 3400–4000 cm⁻¹ and 5000–5500 cm⁻¹ spectral intervals. This absorption is due to the water vapor present in part of the absorption path which is external to the simulation chamber.

At 200 K, near 3900 cm⁻¹, water vapor seems to be in emission. This effect is due to the small variation of the water vapor concentration

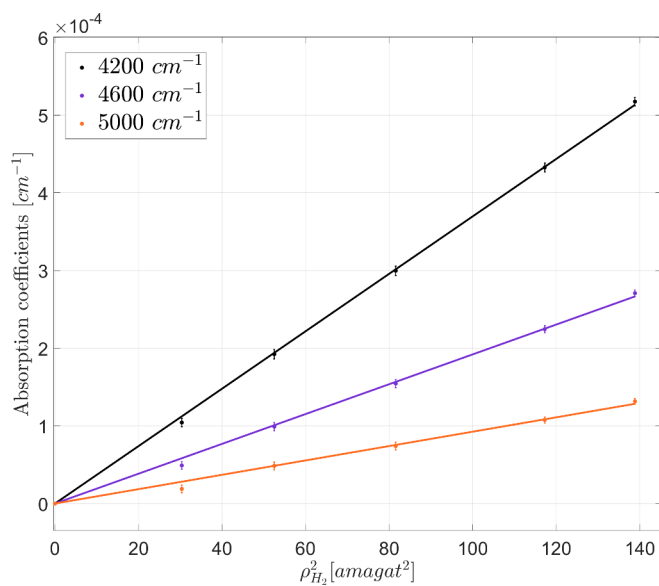


Fig. 1. Behavior of the absorption coefficients acquired with a pure H₂ gas at about 296 K with the H₂ density squared for three different frequencies. The straight lines represent the linear fits performed over the data.

between the recording of the background spectrum and the gas spectrum.

The experimental H₂-H₂ BACs have also been made available in tabular form on the Zenodo platform along with their uncertainties at the selected temperatures at the following link [10.5281/zenodo.13142015](https://zenodo.org/record/13142015).

From the lowest temperature, up to 294 K, the band shows three peaks. The first one, at the lowest wavenumbers, is related to the Q₁(J) transitions ($\Delta_J = 0, \nu = 1$), while the other two are generated by the S₁(J) transitions ($\Delta_J = +2, \nu = 1$), with J and ν being respectively the rotational and vibrational quantum numbers.

As the temperature increases, the H₂ molecules start to occupy higher energy levels, causing a mixing of the branches, which starts to overlap, making the peaks less and less recognizable.

The H₂ fundamental band is also composed of O₁(J) ($\Delta_J = -2, \nu = 1$) transitions, occurring for wavenumbers below 4000 cm⁻¹, which are very weak at room temperatures and mostly absent at lower temperatures [4].

The O₁(J) branch should be visible at 400 and 500 K but unfortunately, it falls in a frequency range where the water vapor absorption dominates, so we were not able to observe it.

Fig. 2 shows that, while the BACs around the first peak tend to increase with temperature, the other two peaks at higher wavenumbers don't show a similar trend.

Furthermore, some sharp features corresponding to single Q₁(J) and S₁(J) transitions are visible; they are called interference dips and will be discussed in Section 3.5.

To be noted, we didn't observe in our data any feature that can be attributed to the hydrogen dimer, even at the lowest temperatures achieved in our experiments.

The temperature and density conditions for the pure H₂ measurements used to calculate the H₂-H₂ binary absorption coefficients are listed in Table A.1.

To study the temperature trend, we calculated the integral of the experimental H₂-H₂ BACs following Eq. (4), in the 4000–5000 cm⁻¹ range and plotted them as a function of the temperature. The reduced spectral range has been used to lower the uncertainties, because of the presence of water vapor absorption in the above-mentioned spectral intervals. In Fig. 3 the behavior of the integrals versus temperature is shown.

The experimental values are well described by a linear trend, with a slope of $(3.64 \pm 0.13) \cdot 10^{-6} \text{cm}^{-2} \text{amagat}^{-2} \text{K}^{-1}$. Since it could be useful to report the integrals calculated over the whole band, we decided to determine the values using also the 3600–5500 cm⁻¹ total range. In Table A.2 the integrals obtained in the reduced and total range are collected. The values obtained for the whole band are slightly affected by the water vapor lines, so that they are less accurate.

While for the integrated H₂-H₂ BACs a linear behavior with temperature has been observed, unfortunately, it was not possible to retrieve any similar trend for the BACs at single frequencies.

In the following section, the results obtained by the mixture adding helium to the pure H₂ will be discussed.

3.2. CIA of a H₂-He mixing

Using a H₂-He mixture at various mixing ratios, we measured the absorption coefficients at the same seven temperatures chosen for the pure H₂ case.

For three selected temperatures, 200 K, 300 K, and 400 K, we performed measurements with the same helium mixing ratio of about 13.6% but different total densities, in order to study the behavior with density.

We chose the same previous three frequencies, 4200 cm⁻¹, 4600 cm⁻¹, and 5000 cm⁻¹, at which we calculated the absorption coefficients at a fixed temperature, and plotted them as a function of the product of the H₂ and He densities. We found a linear trend for all the

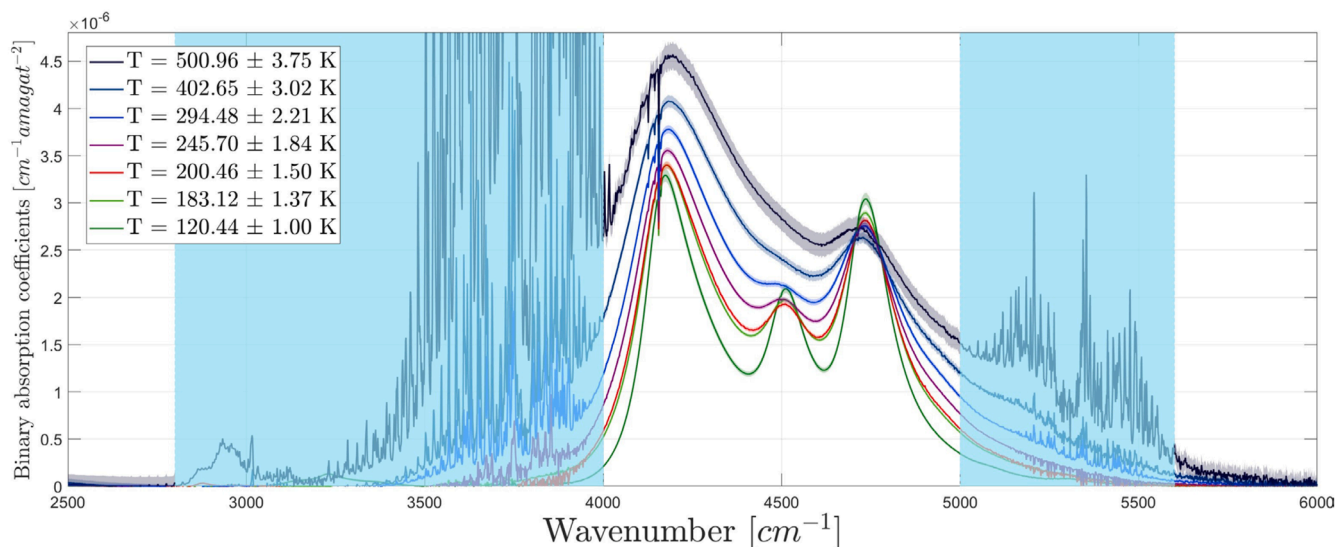


Fig. 2. H_2 - H_2 experimental binary absorption coefficients for temperatures between 120 and 500 K. The shaded envelopes on the experimental curves represent the errors associated with the values. The two light blue rectangular shaded regions represent the spectral ranges where the band was partially affected by water vapor absorption, in different amounts depending on the temperature.

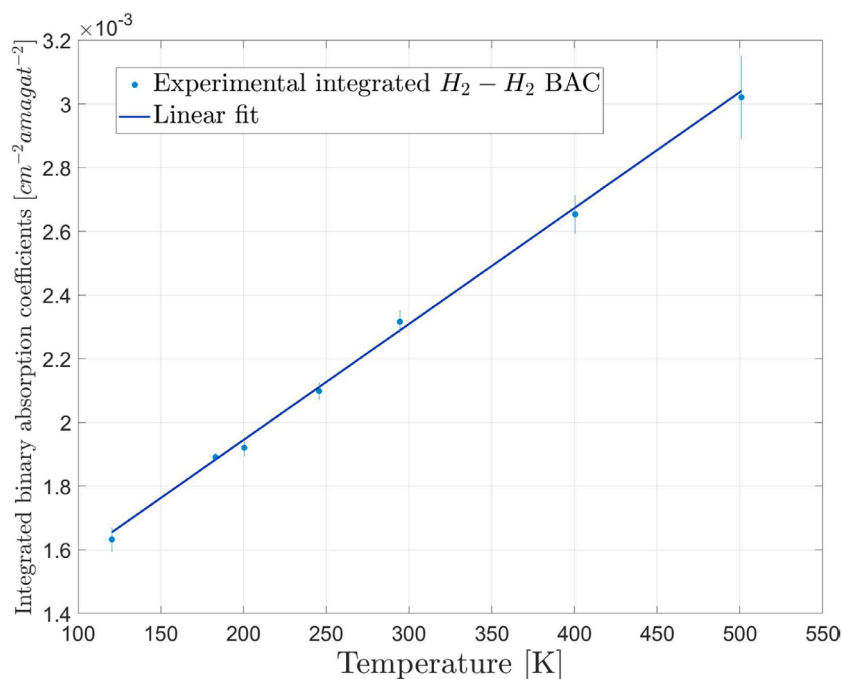


Fig. 3. Integral of the experimental H_2 - H_2 BACs in the reduced 4000–5000 cm^{-1} spectral range as a function of the temperature calculated from the experimental data (blue dots). The blue line represents the linear fit performed over the experimental values with an associated slope of $(3.64 \pm 0.13) \cdot 10^{-6} cm^{-2} amagat^{-2} K^{-1}$.

frequencies chosen, as shown in Fig. 4 for the room temperature case, confirming that, also for a H_2 -He mixture, at those temperature and density conditions, the binary scattering theory represents a very good approximation (see Eq. (2)).

The slopes of the linear fits performed over the data at 4200 cm^{-1} , 4600 cm^{-1} and 5000 cm^{-1} are respectively: $(2.70 \pm 0.08) \cdot 10^{-5} cm^{-1} amagat^{-2}$, $(1.31 \pm 0.10) \cdot 10^{-5} cm^{-1} amagat^{-2}$ and $(6.10 \pm 0.98) \cdot 10^{-6} cm^{-1} amagat^{-2}$.

For the seven chosen temperatures in the 120–500 K temperature range, we retrieved the H_2 -He BACs following Eq. (3), as shown in Fig. 5.

For 200 K, 296 K, and, 400 K, we added helium to a fixed H_2 density, varying the He concentration from a minimum of 13.6% to a maximum

of 90% and we found the same H_2 -He binary coefficients within the errors. We then decided to use the measurements with the highest total density, corresponding to the highest He volume mixing ratio because it provided the best accuracy for the values. The experimental H_2 -He BACs are available on Zenodo in tabular form, along with their errors, at the selected temperatures at the following link [10.5281/zenodo.13142015](https://zenodo.org/record/13142015). As shown in Fig. 5, the main contribution to the total H_2 -He binary absorption coefficients is located near the $Q_1(J)$ branch. Just for the temperatures below 296 K, the small contribution due to the $S_1(J)$ transitions is more and more visible for colder temperatures.

Also in the H_2 -He BACs a large water vapor absorption can be observed, with the same origin, as explained in the previous Section 3.1.

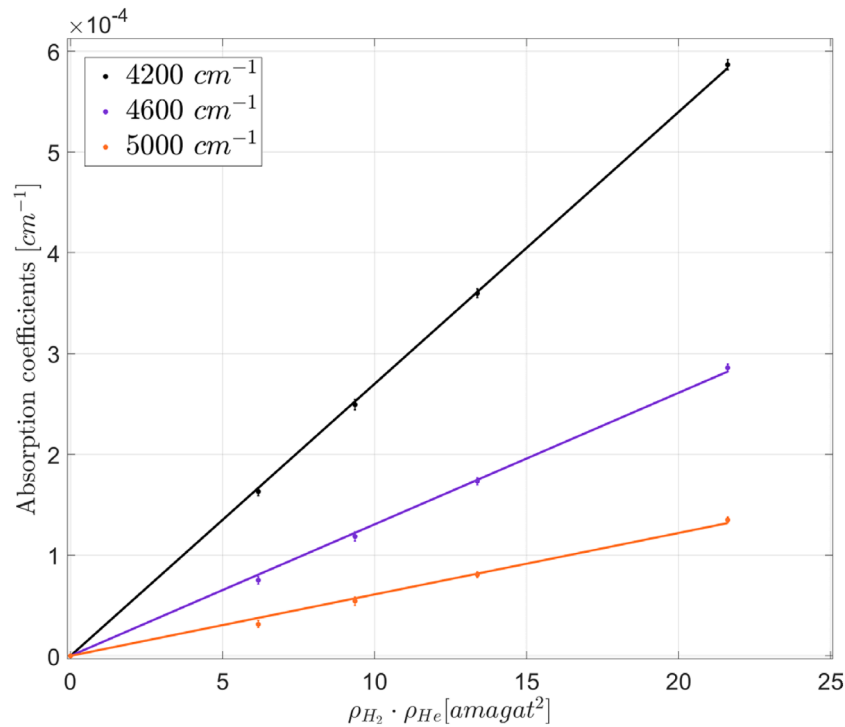


Fig. 4. The absorption coefficients acquired with a H₂-He mixing at about 300 K for a mixing ratio of about 13.6 % versus the product of the H₂ and He densities for three different frequencies. The straight lines represent the linear fits performed over the data.

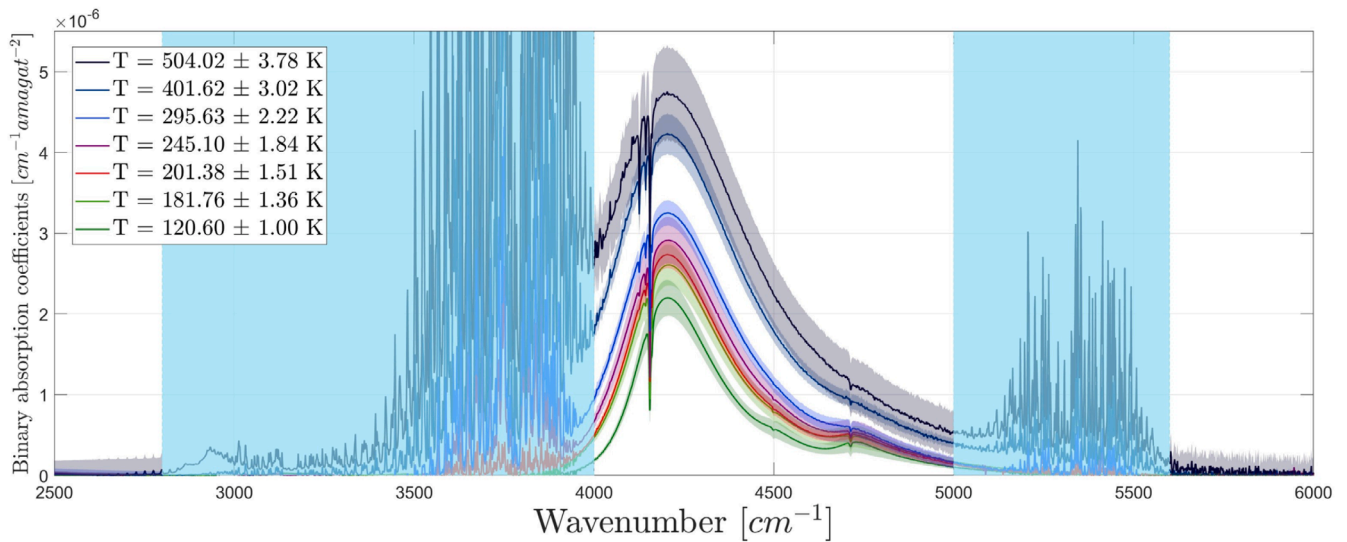


Fig. 5. H₂-He experimental BACs for temperatures between 120 and 500 K. The shaded envelopes along the data represent the errors associated with the experimental values. The two light blue rectangular shaded regions represent the spectral ranges where the band was partially affected by water vapor absorption, in different amounts depending on the temperature.

The temperature and density conditions for the measurements acquired with the mixing and used to calculate the H₂-He binary absorption coefficients are listed in Table A.3.

The BACs for both the H₂-H₂ and H₂-He contributions at the same temperature can be recombined by using Eq. (2) to obtain the total absorption for any desired He mixing ratio. This is of paramount importance, for example to study the IR optical opacity due to the hydrogen CIA fundamental band of every gaseous and icy giant's planet atmosphere, primarily composed of these two gases.

Fig. 6 shows the integrals of the H₂-He binary absorption coefficients in the 4000–5000 cm⁻¹ range for the experimental data as a function of

the temperature. Results from Fig. 6 that the experimental data follow a linear trend with a slope of $(4.22 \pm 0.29) 10^{-6} \text{cm}^{-2} \text{amagat}^{-2} \text{K}^{-1}$.

Also in this case, a reduced spectral range has been used, due to the presence of water vapor absorption on the band's wings. Despite being less accurate, we calculated the integrals also in the full 3600–5500 cm⁻¹ spectral range, since it could be useful for future works. The values obtained for both the reduced and the total spectral ranges are listed in Table A.4.

While for the integrated H₂-He BACs a linear behavior with temperature has been observed, unfortunately, it was not possible to retrieve any similar trend for the BACs at single frequencies.

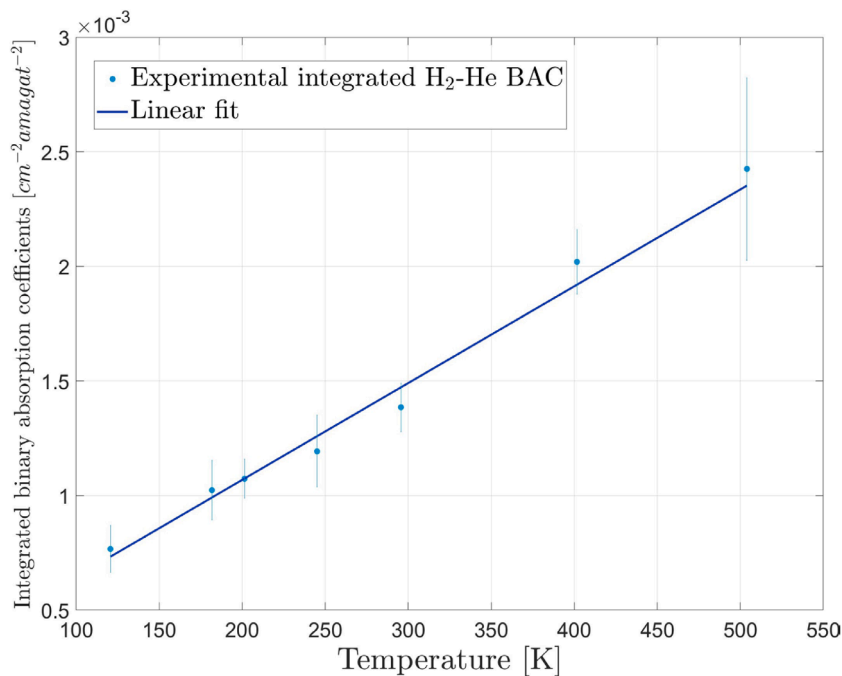


Fig. 6. Integrals of the H₂-He BACs in the reduced 4000–5000 cm⁻¹ spectral range as a function of the temperature calculated from the experimental data (blue dots). The blue straight line represents the linear fit performed over the experimental values, with an associated slope of $(4.22 \pm 0.29) \cdot 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2} \text{ K}^{-1}$.

For a temperature of 296 K, we acquired data with the same total pressure of about 20 bar by varying the amount of He in order to have the same total density but different mixing ratios. In Fig. 7 the absorption coefficients for a H₂-He mix for three different mixing ratios are shown. It results that increasing the amount of He, for a fixed total density, has the effect of decreasing the absorption coefficients, which is reasonable since H₂ represents the only absorbing species in the considered mixture.

Moreover, it is easy to notice that increasing the He concentration results in a highest contribution of the Q₁(J) branch with respect to the

S₁(J) branch to the total absorption coefficients.

3.3. Comparison with other experimental works

To the best of our knowledge, the CIA fundamental band of H₂ has not been experimentally studied for temperatures above 300 K. For those previous experimental works that provided data in tabular form [7,8,9], a comparison with our H₂-H₂ and H₂-He binary absorption coefficients has been made.

Moreover, a recent measurement of the BAC at about 4917 cm⁻¹

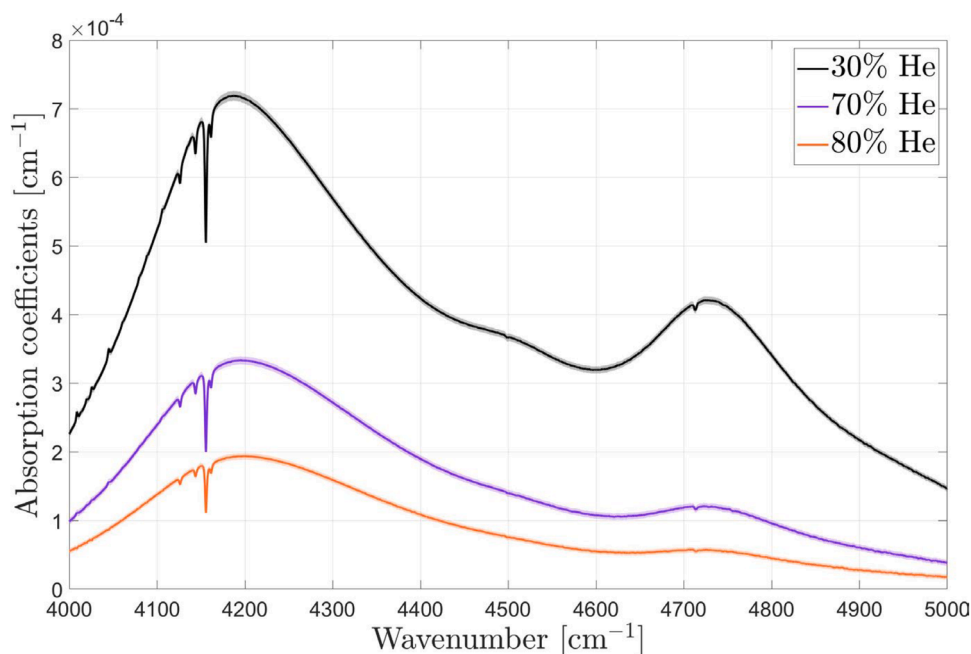


Fig. 7. Experimental absorption coefficients for a H₂-He mixture for three different mixing ratios and the same total density. The shaded envelopes represent the errors associated with the data.

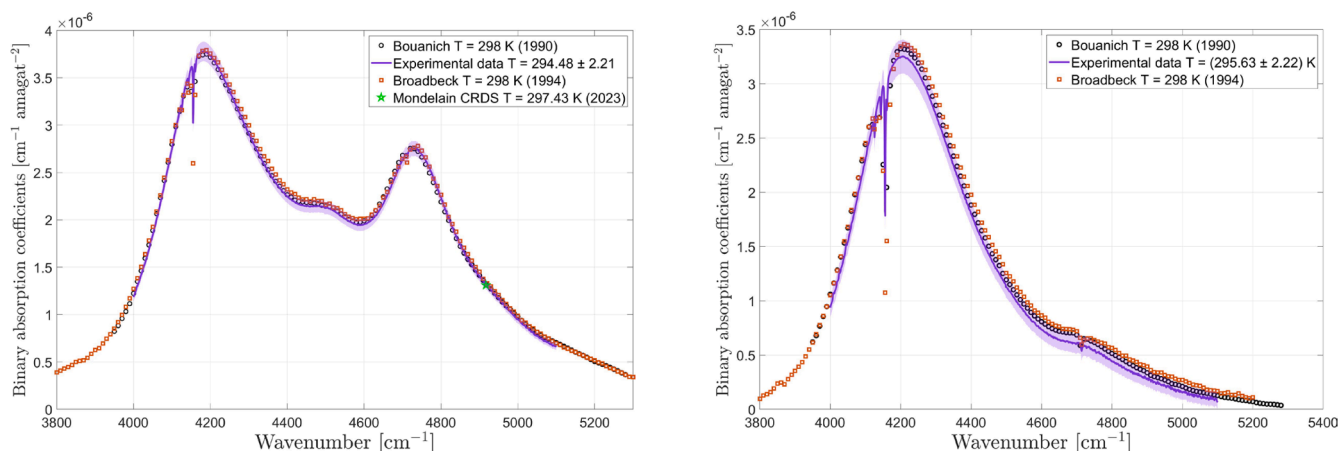


Fig. 8. Left plot shows the comparison between our H₂-H₂ experimental BACs (violet solid curve), with the existing experimental measurements of Bouanich et al. (1990) [7] (black circles), Broadbeck et al. (1994) [8] (orange squares), and Mondelain et al. [19] (green star) at room temperature. Right plot shows the comparison between our H₂-He experimental BACs (violet solid curve), with the existing experimental measurements of Bouanich et al. [7] (black circles), and Broadbeck et al. (1995) [9] (orange squares) at room temperature.

using a CRDS setup has been made by Mondelain et al. [19] which has been compared to our data.

The left and right plots of Fig. 8 compare our experimental H₂-H₂ and H₂-He BACs with previous measurements taken at room temperature.

A good agreement can be noted over the whole band for both the contributions, apart from a deviation of both H₂-H₂ and H₂-He BACs measured by Broadbeck et al. [8,9] at about 4155 cm⁻¹ which could be due to a different spectral resolution used for the measurements.

3.4. Comparison with the models

CIA of H₂ is important not only for the planetary atmospheres but also for the stellar environment. The latter account for very high temperatures, reaching thousands of Kelvin, conditions that can't be reproduced in a terrestrial laboratory. As a consequence, theoretical models have been implemented throughout the years, calculating separately the BACs for the H₂-H₂ and H₂-He collisions for temperatures ranging from hundreds to thousands of Kelvin.

As far as we know, just two models are reproducing the CIA fundamental band of H₂ for temperatures above 300 K available in the literature. The first one has been computed from A. Borysov [11–13], whose data for both the H₂-H₂ and H₂-He contribution can be found at <https://www.astro.ku.dk/~aborysov/programs/>. The second one, which is also the most recent, has been implemented by M. Abel [14,15], whose data can be downloaded from the Hitran website at <https://hitran.org/cia/> in the section dedicated to the CIA [16,17].

Considering the linear trend of the experimental H₂-H₂ and H₂-He integrated BACs versus temperature, as shown in Figs. 3 and 6, we tested the trend for Abel and Borysov's models. The integrated BACs obtained in the reduced 4000–5000 cm⁻¹ spectral range for both models are reported in Fig. 9 compared with our experimental results.

From the plots, it clearly results a linear trend for both the H₂-H₂ and H₂-He Abel's integrated BACs, very consistent with the experimental data, with the slopes being respectively $4.06 \cdot 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2} \text{ K}^{-1}$ for the pure H₂ case, and $4.39 \cdot 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2} \text{ K}^{-1}$ for the H₂-He contribution.

On the other hand, Borysov's integrated BACs show a quadratic trend for the H₂-H₂ case, and a linear trend for the H₂-He contribution, with a slope of $4.62 \cdot 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2} \text{ K}^{-1}$.

Furthermore, we compared our experimental H₂-H₂ and H₂-He BACs with both Abel and Borysov's models for a temperature of about 400 K, as shown in Fig. 10. It is worth to notice that the data presented here at this temperature are the only existing experimental available data for the CIA fundamental band.

The comparison for the H₂-H₂ contribution in the left plot of Fig. 10 shows a maximum deviation of the models from the data on the main peak of the band around 4200 cm⁻¹, where Borysov's model presents the larger absorption. In the other part of the band, a better agreement is noted, with a marginal deviation of the models in the central region, around 4500 cm⁻¹.

For the H₂-He contribution (right plot of Fig. 10) we have generally a better agreement over the whole range, although due to the larger uncertainties in the data, except for a marginal deviation of Abel's model in the 4400–4800 cm⁻¹ range.

It is important to mention that these models do not take into account the so-called *interference dips*, which have been observed at this temperature for both pure H₂ and H₂-He mix contributions on the main peak of the band. Those features will be discussed in more detail in the following section.

3.5. Interference dips

Figs. 2, 5, 7, and 10 show the presence of some sharp features, called interference dips.

In the spectral range interested in the CIA fundamental band of H₂, they are observed in the proximity of the Q₁(3), Q₁(2), Q₁(1), Q₁(0), S₁(0) and S₁(1) transitions, respectively at 4126 cm⁻¹, 4143 cm⁻¹, 4155 cm⁻¹, 4161 cm⁻¹, 4498 cm⁻¹ and 4713 cm⁻¹ [5].

They have been observed in our experimental measurements at all the temperatures considered, in both the H₂-H₂ and H₂-He BACs. At room temperature, we can spectrally resolve in our data all four interference dips on the H₂-H₂ binary absorption coefficients, while on the H₂-He contribution the S₁(0) one is barely visible, as shown in Fig. 11, where the dashed vertical green lines indicate the six frequencies where we may expect the dips from the work of S. Paddi Reddy et al. [5].

It is also noticeable from Figs. 10 and 11 that the dips in the H₂-He binary absorption coefficients are deeper than for H₂-H₂.

These dips are caused by the interference of induced dipoles between consecutive collisions, which can cause this sharp lack of absorption near the frequencies of specific H₂ ro-vibrational transitions, according to van Kranendonk [20].

In the last decades, different experimental works observed those features in their spectra acquired at temperatures below or equal to the room temperature case. The experimental works of Bouanich et al. [7], Poll et al. [21], and McKellar et al. [22] studied the properties of the interference dips with density and temperature by fitting them with the line profile given by van Kranendonk [20]. The work by Kelley and Bragg [23] instead used a line profile developed by the authors, similar

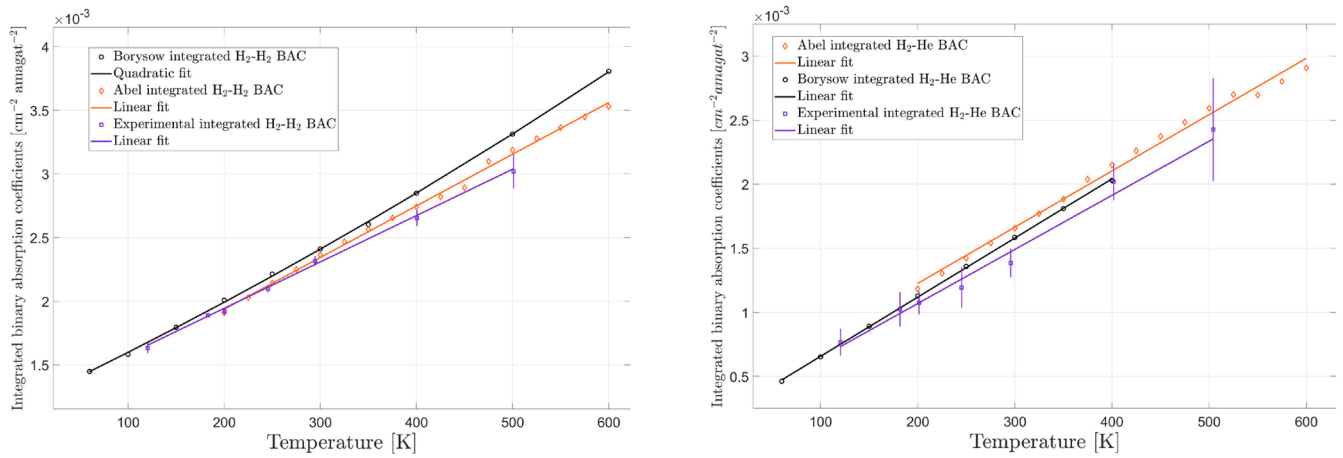


Fig. 9. Left plot shows the integrated H₂-H₂ BACs calculated from Borysow's models (black circles) [11], Abel's models (orange diamonds) [14], and the experimental data (violet squares). The orange and violet lines represent the linear fits performed respectively on Abel's data and the experimental results, while the black curve reproduces the quadratic fit performed over Borysow's data. Right plot shows the integrated H₂-He BACs calculated from Borysow's models (black circles) [12, 13], Abel's models (orange diamonds) [15], and the experimental data (violet squares). Here the three straight lines represent the linear fits performed over Borysow's data (black line), Abel's data (orange line), and experimental data (violet line).

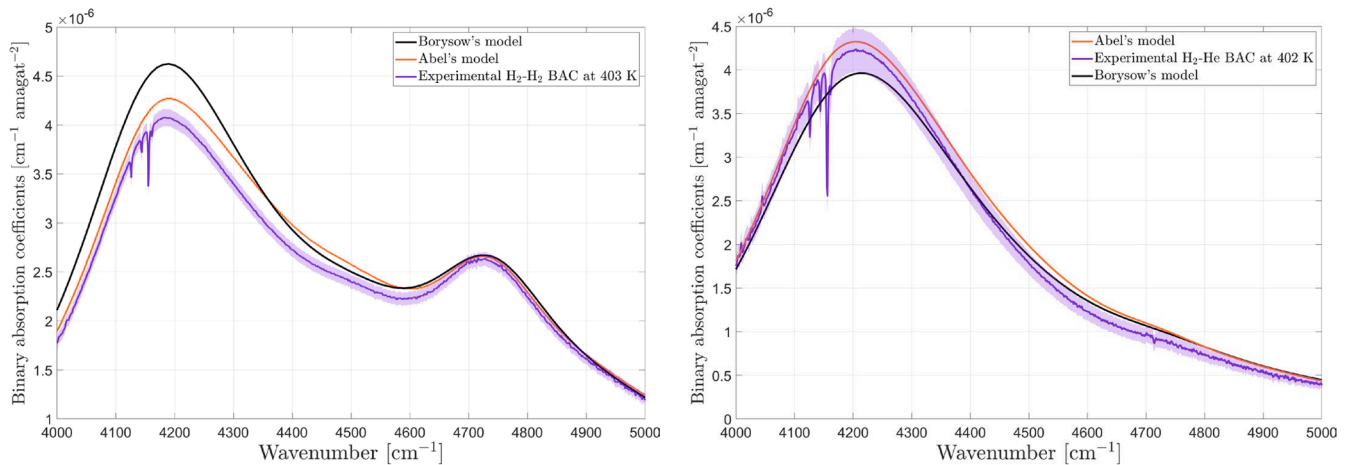


Fig. 10. Left plot shows the comparison between measured H₂-H₂ BACs (violet line), Abel's model (orange line) [14], and Borysow's model (black line) [11] for a temperature of about 400 K. Right plot shows the comparison between measured H₂-He BACs (violet line), Abel's model (orange line) [15], and Borysow's model (black line) [12,13] for a temperature of about 400 K. The sharp features observable in the experimental data represent the interference dips.

to the van Kranendonk one, to study the observed asymmetry of the dips.

To be noticed that the positions of the Q₁(1) and S₁(1) dips calculated by Bouanich et al. (1990) and the Q₁(1), Q₁(2) and S₁(0) dips positions observed by Kelley et al. [23] are in agreement with the position of the dips observed in our measurements.

The experimental properties of the dips resolved in our spectra will be part of future studies.

4. Conclusions and final remarks

The PASSxS experimental setup used for this work allowed us to perform high signal-to-noise ratio measurements of the CIA fundamental band of hydrogen using a pure H₂ and an H₂-He mixture.

We derived experimentally the H₂-H₂ and H₂-He BACs for seven temperatures between 120 and 500 K, studying a high-temperature range not yet explored from an experimental work.

The BACs can be recombined to obtain the total absorption coefficients for a desired mixing ratio, very important for studying the atmospheric opacity in the IR of the gaseous and icy giant's planets whose atmosphere is primarily composed of hydrogen and helium.

We showed the linear behavior of the pure H₂ and the H₂-He

absorption coefficients, for a mixing ratio of about 13.6 %, at three different frequencies as an example, 4200 cm⁻¹, 4600 cm⁻¹, and 5000 cm⁻¹, respectively with the H₂ density squared and the product of the H₂ and He densities, confirming that the binary scattering theory, at those temperature and density conditions, represents a very good approximation.

We calculated the integrals of the H₂-H₂ and H₂-He experimental BACs in the reduced 4000–5000 cm⁻¹ spectral range versus temperature, comparing them with Borysow [11–13] and Abel's [14,15] theoretical models.

We found a linear trend for the experimental integrated BACs versus temperature, with a slope of $(3.64 \pm 0.13) \cdot 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2}$ for the H₂-H₂ case, and $(4.22 \pm 0.29) \cdot 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2}$ for the H₂-He contribution. The integrated BACs calculated from Abel's theoretical data resulted to follow a linear trend, with a slope of $4.06 \cdot 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2}$ for the H₂-H₂ case and $4.39 \cdot 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2}$ for the H₂-He contribution, consistent with the experimental data.

On the other hand, Borysow's models show a quadratic trend with the temperature of the H₂-H₂ integrated BACs, and a linear behavior for the H₂-He contribution, with a slope of $4.62 \cdot 10^{-6} \text{ cm}^{-2} \text{ amagat}^{-2} \text{ K}^{-1}$.

While for the experimental integrated BACs a linear behavior with

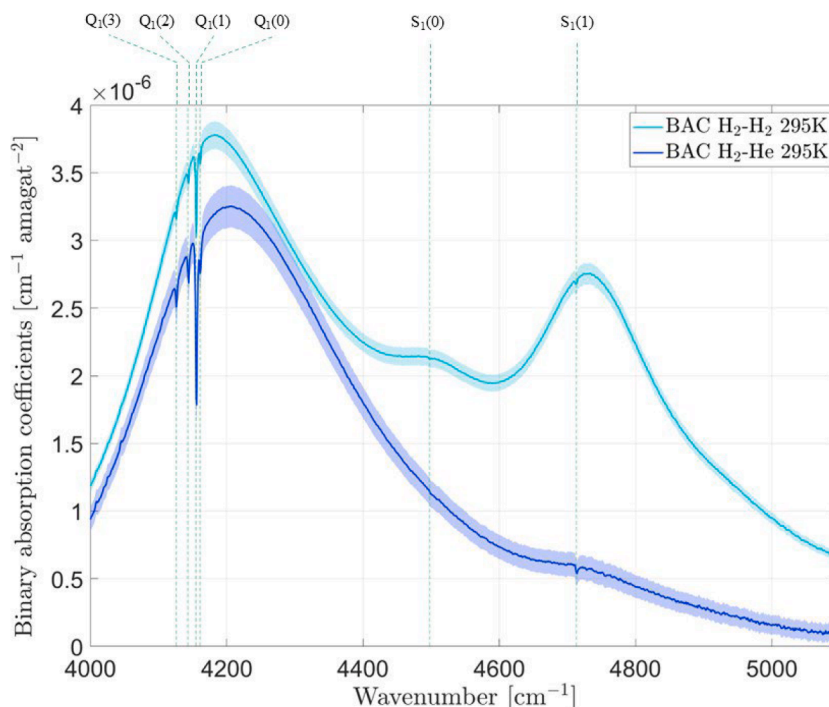


Fig. 11. H₂-H₂ (light blue line) and H₂-He (blue line) BACs acquired at room temperature. The vertical dashed green lines indicate the frequency positions of the Q₁(3), Q₁(2), Q₁(1), Q₁(0), S₁(0) and S₁(1) interference dips [5]. While all the dips are resolved in the H₂-H₂ case, in the H₂-He case the S₁(0) is barely visible.

temperature has been observed, it was not possible to retrieve any similar trend for the BACs at single frequencies in our data.

A comparison between our measurements and previous experimental works has been made at room temperature, resulting in an excellent agreement, apart from a marginal deviation of both the H₂-H₂ and H₂-He binary absorption coefficients measured by Broadbeck et al. [8,9] at about 4155 cm⁻¹ which could be due to a different spectral resolution used for the measurements.

In addition, we found a generally good agreement between experimental H₂-H₂ and H₂-He BACs and the two models considered at about 400 K, apart from some specific areas, where the models show a deviation from the experimental data, most of all in the main peak of the H₂-H₂ BACs, to a larger extent for the Borysow's model.

Furthermore, for three selected temperatures, 200 K, 296 K, and 400 K, we found that the H₂-He BACs don't depend on the mixing ratio, and that for a fixed total density and the same temperature, increasing the amount of helium results in a decrease of the total absorption coefficients, consistent with H₂ being the only absorbing species in the considered mixture.

To be noted that for all the explored temperatures, the existing models do not take into account the interference dips, observed on both the H₂-H₂ and H₂-He experimental BACs.

In conclusion, new studies with new experimental data have been made on the CIA fundamental band of H₂, and H₂-He mix, helpful not only for future experimental and theoretical works but also for those space missions whose primary scope is to investigate the atmospheres, mainly composed of H₂ and He, of the gaseous and icy giant planets of

our solar system and beyond.

All the experimental data are available on the Zenodo website with their errors.

CRediT authorship contribution statement

Francesca Vitali: Writing – original draft, Visualization, Validation, Software, Resources, Investigation, Data curation, Conceptualization. **Stefania Stefani:** Writing – review & editing, Validation, Investigation, Data curation, Conceptualization. **Giuseppe Piccioni:** Writing – review & editing, Validation, Resources, Investigation, Funding acquisition, Conceptualization. **Marcel Snels:** Writing – review & editing, Resources. **Davide Grassi:** Writing – review & editing. **David Biondi:** Software, Conceptualization. **Angelo Boccaccini:** Software, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Data and errors

Table A.1

The Table contains the values of temperature and density of the measurements made with a pure H₂ gas used to retrieve the H₂-H₂ binary absorption coefficients with the associated errors. Here, σ refers to the statistical errors, while ε represents the systematic errors.

T [K]	σ_T [K]	ε_T [K]	ρ_{H_2} [amagat]	$\sigma_{\rho_{H_2}}$ [amagat]	$\varepsilon_{\rho_{H_2}}$ [amagat]
120.44	0.46	1.00	22.786	0.170	0.216
183.12	0.14	1.37	19.063	0.025	0.160
200.46	0.21	1.50	13.874	0.037	0.120
245.70	0.17	1.84	14.135	0.012	0.119
294.48	0.07	2.21	11.784	0.005	0.099
402.65	0.18	3.02	8.835	0.002	0.029
500.96	0.45	3.75	8.615	0.012	0.070

Table A.2

Integrals of the H₂-H₂ binary absorption coefficients calculated over the reduced 4000-5000 cm⁻¹ spectral range (second column), and the whole band (third column). The uncertainties associated to the temperature are the systematic errors.

T \pm ε_T [K]	$I(\nu)[\text{cm}^{-2}\text{amagat}^2]$ (4000-5000 cm ⁻¹)	$I(\nu)[\text{cm}^{-2}\text{amagat}^2]$ (3600-5500 cm ⁻¹)
120.44 \pm 1.00	(1.63 \pm 0.04) $\cdot 10^{-3}$	(1.70 \pm 0.04) $\cdot 10^{-3}$
183.12 \pm 1.37	(1.89 \pm 0.01) $\cdot 10^{-3}$	(2.04 \pm 0.03) $\cdot 10^{-3}$
200.46 \pm 1.50	(1.92 \pm 0.03) $\cdot 10^{-3}$	(2.04 \pm 0.03) $\cdot 10^{-3}$
245.70 \pm 1.84	(2.10 \pm 0.03) $\cdot 10^{-3}$	(2.36 \pm 0.04) $\cdot 10^{-3}$
294.48 \pm 2.21	(2.32 \pm 0.03) $\cdot 10^{-3}$	(2.86 \pm 0.06) $\cdot 10^{-3}$
402.65 \pm 3.02	(2.65 \pm 0.06) $\cdot 10^{-3}$	(4.13 \pm 0.11) $\cdot 10^{-3}$
500.96 \pm 3.75	(3.02 \pm 0.13) $\cdot 10^{-3}$	(6.24 \pm 0.25) $\cdot 10^{-3}$

Table A.3

The Table contains the values of temperature and density of the measurements made with a H₂-He mixing used to retrieve the H₂-He binary absorption coefficients with the associated errors. Here, σ refers to the statistical errors, while ε represents the systematic errors.

T [K]	σ_T [K]	ε_T [K]	ρ_{H_2} [amagat]	$\sigma_{\rho_{H_2}}$ [amagat]	$\varepsilon_{\rho_{H_2}}$ [amagat]	ρ_{He} [amagat]	$\sigma_{\rho_{He}}$ [amagat]	$\varepsilon_{\rho_{He}}$ [amagat]
120.60	0.52	1.00	23.790	0.038	0.200	22.300	0.085	0.549
181.76	0.39	1.36	20.400	0.038	0.172	19.309	0.060	0.471
201.38	0.42	1.51	8.332	0.007	0.080	24.346	0.118	0.202
245.10	0.19	1.84	13.981	0.015	0.119	13.548	0.049	0.329
295.63	0.08	2.22	5.459	0.001	0.052	12.580	0.008	0.187
401.62	0.05	3.01	4.026	0.002	0.038	11.963	0.009	0.131
504.02	0.05	3.78	8.679	0.003	0.073	8.674	0.009	0.209

Table A.4

Integrals of the H₂-He binary absorption coefficients calculated over the reduced 4000-5000 cm⁻¹ spectral range (second column), and the whole band (third column). The uncertainties associated to the temperature are the systematic errors

T \pm ε_T [K]	$I(\nu)[\text{cm}^{-2}\text{amagat}^2]$ (4000-5000 cm ⁻¹)	$I(\nu)[\text{cm}^{-2}\text{amagat}^2]$ (3600-5500 cm ⁻¹)
120.60 \pm 1.00	(0.77 \pm 0.10) $\cdot 10^{-3}$	(0.75 \pm 0.14) $\cdot 10^{-3}$
181.76 \pm 1.36	(1.02 \pm 0.13) $\cdot 10^{-3}$	(1.07 \pm 0.20) $\cdot 10^{-3}$
201.38 \pm 1.51	(1.07 \pm 0.09) $\cdot 10^{-3}$	(1.16 \pm 0.20) $\cdot 10^{-3}$
245.10 \pm 1.84	(1.19 \pm 0.16) $\cdot 10^{-3}$	(1.49 \pm 0.50) $\cdot 10^{-3}$
295.63 \pm 2.22	(1.39 \pm 0.11) $\cdot 10^{-3}$	(1.89 \pm 0.68) $\cdot 10^{-3}$
401.62 \pm 3.01	(2.02 \pm 0.14) $\cdot 10^{-3}$	(3.38 \pm 1.60) $\cdot 10^{-3}$
504.02 \pm 3.78	(2.43 \pm 0.40) $\cdot 10^{-3}$	(5.30 \pm 3.71) $\cdot 10^{-3}$

Data availability

Data are available on the Zenodo platform at the following link [10.5281/zenodo.13142015](https://zenodo.org/record/13142015).

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