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Room temperature measurements of the collision-induced absorption by H₂+CO₂ mixtures near 2.4 μm

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Abstract: Using a 101 m absorption path-length cell, Fourier transform spectra of H₂+CO₂ mixtures have been recorded at room temperature in the region around 2.4 μm. This enables to quantify the absorption induced, by collisions with CO₂, in the central part of the fundamental band of H₂. These measurements, which cover 3950-4350 cm⁻¹ range, validate previous fully independent computations.

1. Introduction

Studying the collision-induced absorption (CIA) spectra of H₂+CO₂ mixtures is relevant for studies of radiative exchanges in past or present CO₂-rich atmospheres of planets, including that of Early Mars. This context has motivated both Fourier transform measurements in the far infrared spectral region [1, 2] and Cavity Ring Down Spectroscopy data for a few spectral points around 2.23 μm [3]. Computations have also been made [2,3], in order to fill the gaps between measurements, but the quality of their predictions over the intense central (Q branch) peak of the fundamental band of H₂ had not been tested so far, which is the subject of the present study. To overcome this, experiments using a multi-pass cell aligned for a 101 m absorption path length and associated to a Fourier transform spectrometer have been performed, providing values of the binary H₂+CO₂ CIA between 3950-4400 cm⁻¹.

2. Experiments

Spectra have been recorded at the AILES beamline of the Soleil synchrotron facility using a Bruker IFS 125HR Fourier transform spectrometer (FTS) and a 2.5 m long multi-pass cell equipped with diamond windows. The global source inside the FTS was used, together with a

KBr beam splitter and a liquid nitrogen cooled photovoltaic HgCdTe detector. Recordings were performed at room temperature (≈ 295 K) for an absorption path length of 101.3 m, and with an unapodized spectral resolution of 0.5 cm^{-1} . No optical filter was used, leading to a spectral interval within which reliable values are collected ranging from 700 to 4600 cm^{-1} . Spectra, obtained by averaging 1000 scans, were collected with an empty cell before and after a series of successive recordings involving gas samples (with 48.5% H_2 and 51.5% CO_2) at 8 different total pressures P_{Tot} , from 208 to 949 hPa (measured with a 0-1000 mb Pfeiffer model CMR361 capacitive gauge which has an accuracy of 0.2%). For this, after recording an empty cell spectrum, 489 mb of CO_2 were injected into the cell and complemented by adding 460 mb of H_2 . According to the above mentioned pressure measurement accuracy, this leads to a mixture with partial pressures known within better than 1%. After waiting 30 mn for the mixture to homogenize, a first spectrum was collected. Then the pressure was reduced, by pumping, down to 851 mb and a second recording was made. This procedure was repeated, progressively reducing the total pressure down to 208 mb, and this sequence was ended by a recording of a second empty cell spectrum. The associated transmissions around the center of the H_2 fundamental band, obtained by dividing the gas-sample spectra by the empty cell ones, are shown in Fig. 1. Besides the H_2+CO_2 CIA, responsible by the broad feature peaking at around 4160 cm^{-1} , absorption by H_2O traces in the gas sample (with relative amounts of $2.6 \cdot 10^{-5}$ determined by fitting some water lines) can be seen on the low frequency side of the plot, with some weak local contributions by CO_2 around 4025 cm^{-1} . Note that a slight non-linearity of the detector response results in the presence, at wavenumber σ , of a (very) small contribution of the square of the true signal at wavenumber $\sigma/2$. This explains the small structures superimposed on the H_2+CO_2 CIA, which are "ghosts" of the lines of the $\nu_1+\nu_2$ band of $^{12}\text{CO}_2$ band centered around 2078 cm^{-1} .

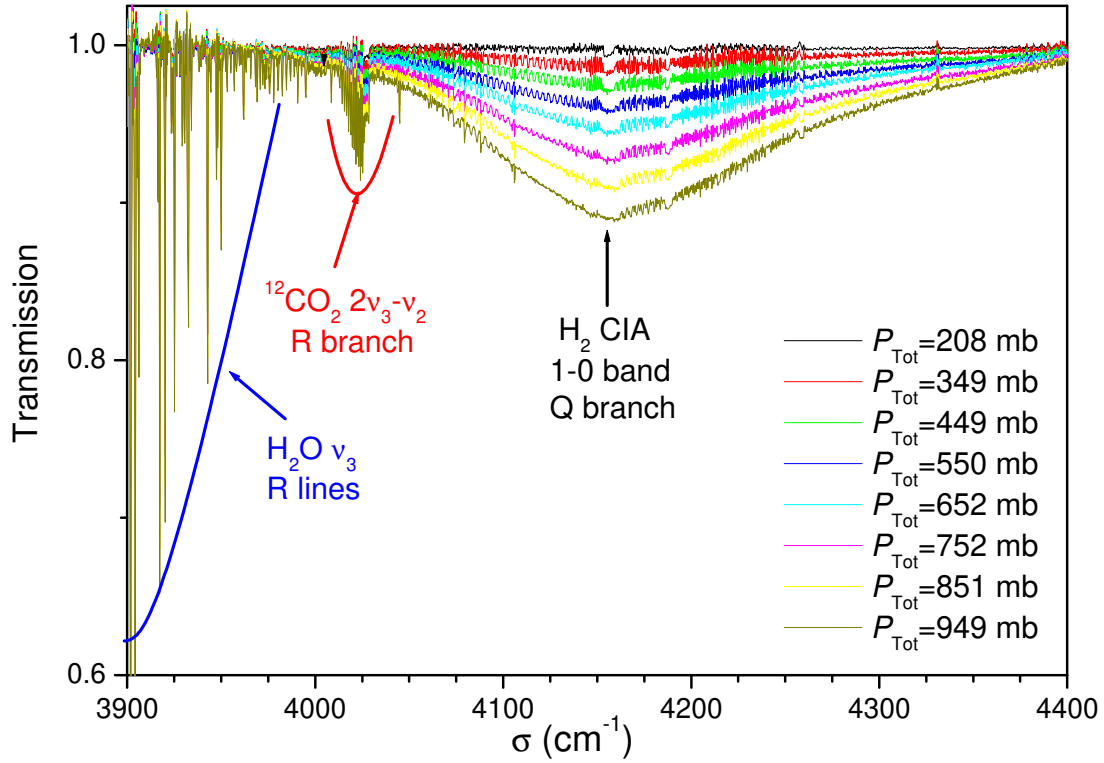


Fig. 1: Transmission spectra measured at room temperature and for various total pressure conditions, with an optical path of 101.3 m and a spectral resolution of 0.5 cm⁻¹.

3. Spectra treatment

In order to retrieve the binary H₂+CO₂ CIA from the measured spectra, a procedure involving the following six steps was used.

(1): The contribution of CO₂ lines was calculated for the known partial pressures (see preceding section) using spectroscopic data from the HITRAN2020 [4] database and Voigt profiles. Note that the H₂-broadening coefficients were assumed to be the same as the air-broadening ones, an approximation of negligible consequences considering the spectral resolution and the fact that CO₂ contributions in the considered spectral range are small. Furthermore, the absorption by CO₂ being weak in the considered spectral region (see Fig. 1), the associated continuum contribution is fully negligible and it was thus disregarded.

(2): The same procedure was applied to compute the contribution of H₂O, after adjusting the (unknown) water-vapor partial pressure (found to be about $2.6 \cdot 10^{-5} P_{\text{Tot}}$) for an optimal removal.

(3): The measured transmissions were divided by those computed taking CO₂ and H₂O into account after convolution by the instrument function. This leaves a remaining absorption which is entirely due to the CIA by the H₂+CO₂ mixture. Note that the absorption by the H₂

monomer, whose Q(2) and Q(3) quadrupolar lines fall within the 3950-4400 cm^{-1} final range [4], was not removed since it is completely negligible under our experimental conditions.

(4): The associated absorption coefficients $\alpha(\sigma, P_{\text{Tot}})$ for the different spectra were derived by taking the natural logarithm and dividing by the path length.

(5): For each wavenumber, these absorption coefficients were then fitted assuming (which is the case for CIA), that they are proportional to the squared density, i.e. writing $\alpha(\sigma_i, P_{\text{Tot}}) = \alpha_{\text{H}_2+\text{CO}_2}^0(\sigma_i, T) d^2(P_{\text{Tot}}, T)$, $d(P_{\text{Tot}}, T) = P_{\text{Tot}}(\text{atm}) \times 273.15/T(\text{K})$ being the sample density in amagat units (1 amagat corresponding to $2.687 \cdot 10^{19} \text{ molec.cm}^{-3}$). Typical results of this fitting exercise are displayed in Fig. 2, showing that the measured values do well follow the proportionality to the squared density and that the slope is determined with a small uncertainty (typically below 5% in the central part of the band).

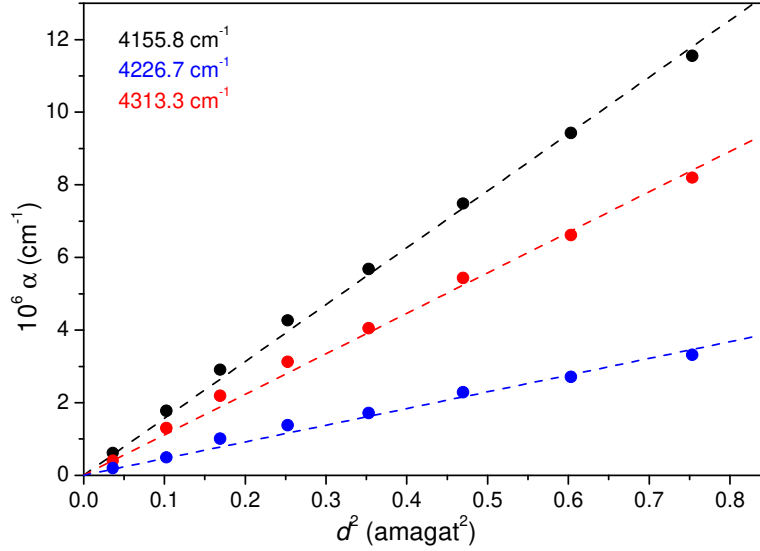


Fig. 2: Measured collision-induced absorption coefficients of the 48.5% H₂+51.5% CO₂ mixture versus the squared sample density for selected wave numbers (symbols) and their fits assuming a proportionality law (dashed lines).

(6): Finally, the pure H₂ density-normalized absorption induced by interactions between pairs of H₂ molecules, $\alpha_{\text{H}_2-\text{H}_2}^0(\sigma_i, T)$, computed in [5] and provided in [6], was removed from $\alpha_{\text{H}_2+\text{CO}_2}^0(\sigma_i, T)$, yielding the H₂-CO₂ binary CIA contribution, $\alpha_{\text{H}_2-\text{CO}_2}^0(\sigma_i, T)$, using the expression: $\alpha_{\text{H}_2-\text{CO}_2}^0(\sigma_i, T) = [\alpha_{\text{H}_2+\text{CO}_2}^0(\sigma_i, T) - x_{\text{H}_2}^2 \alpha_{\text{H}_2-\text{H}_2}^0(\sigma_i, T)] / (x_{\text{H}_2} x_{\text{CO}_2})$, when x_S denotes the mole fraction of species S. Note that removing the pure CO₂ continuum (due to CIA an far line wings) is here unnecessary because its contribution in the investigated spectral range is totally negligible.

4. Results and discussion

The density-normalized binary absorption coefficients obtained as explained above are compared to previously published experimental and theoretical values in Fig. 3. Only the region around the central peak (Q branch) of the CIA band is displayed since reliable values could not be retrieved outside the range of Fig. 3, because of a significantly weaker $\alpha_{\text{H}_2+\text{CO}_2}^0(\sigma_i, T)$ and of a poorer base-line stability. Note that the uncertainty on the slopes retrieved from the fit of the density dependences (e.g. Fig. 2), shown by the red error bars in Fig. 3, is relatively small. For "safety" they have been increased in order to take uncertainties on the amplitude of the FTS spectra (including the 100% transmission base line), which were estimated to be around 0.75% from analysis of the differences between various empty cell spectra. Note that at such variations may likely be explained by changes of the glowbar temperature, since a change of only +2K is sufficient to increase the radiance of a blackbody at 1000 K by 1%. This leads to the final uncertainties denoted by the blue error bars in Fig. 3. As can be seen, our measurements agree quite well with the previous CRDS ones [3] (for which a conservative uncertainty of 6.5% was estimated), and they validate the theoretical values. This is a noticeable success for predictions which have been made without adjustment of any parameter. Note that measurements at various temperatures and if possible at significantly different values from the ambient, would be of great interest, for both planetary applications and further tests of the predictions. Finally, the comparison between the H₂-CO₂ and H₂-H₂ CIAs displayed in Fig. 3 demonstrates the great enhancement, with respect to the pure H₂ case, of the interaction-induced dipole when collisions with CO₂ are considered. This shows that, for the 50%H₂+50%CO₂ mixtures investigated in this study, the pure H₂ CIA relative contribution is small and that uncertainties on its knowledge have negligible consequences on the retrieved H₂-CO₂ CIA.

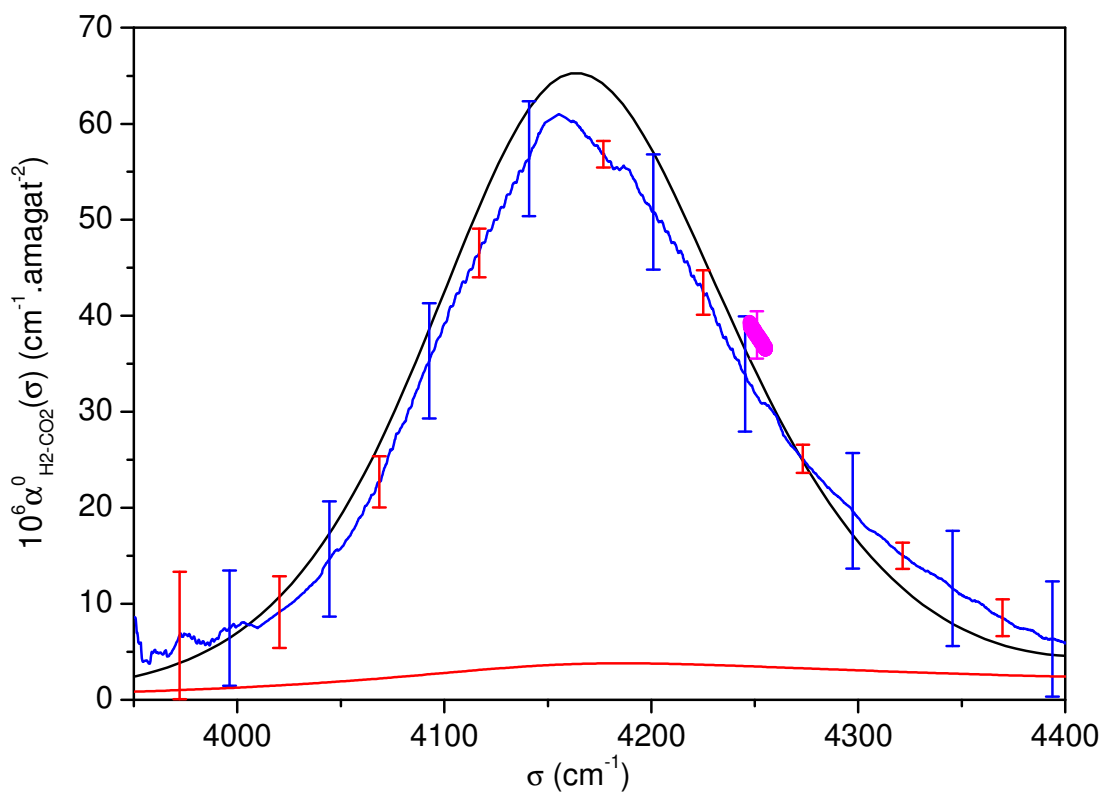


Fig. 3: Binary collision-induced absorption coefficients $\alpha_{\text{H}_2\text{-CO}_2}^0(\sigma_i, T)$. The blue line denotes the present measurements where the red error bars are those from the fits exemplified in Fig. 2 while the blue ones indicate the final uncertainty taking base-line errors into account. The magenta circles are experimental results obtained by CRDS [3]. The black line represents the values calculated in [3]. For comparison, the red line shows the pure H₂ CIA $\alpha_{\text{H}_2\text{-H}_2}^0(\sigma_i, T)$ taken from [6].

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Data availability

A table of the measured values of the H₂-CO₂ CIA displayed in Fig. 3 is available on request to the corresponding author.

Declaration of Competing Interest

The authors declare no conflicts of interest.

CRedit authorship contribution statement

Wissam Fakhardji: Investigation, Formal analysis, Validation, review & editing. **Ha Tran:** Conceptualization, review & editing. **Olivier Pirali:** Investigation, review & editing. **Jean-Michel Hartmann:** Conceptualization, Writing

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