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**The CW-Cavity Ring Down Spectrum of CH<sub>4</sub> has been recorded in the 1.55  $\mu\text{m}$  transparency window with a very high sensitivity**

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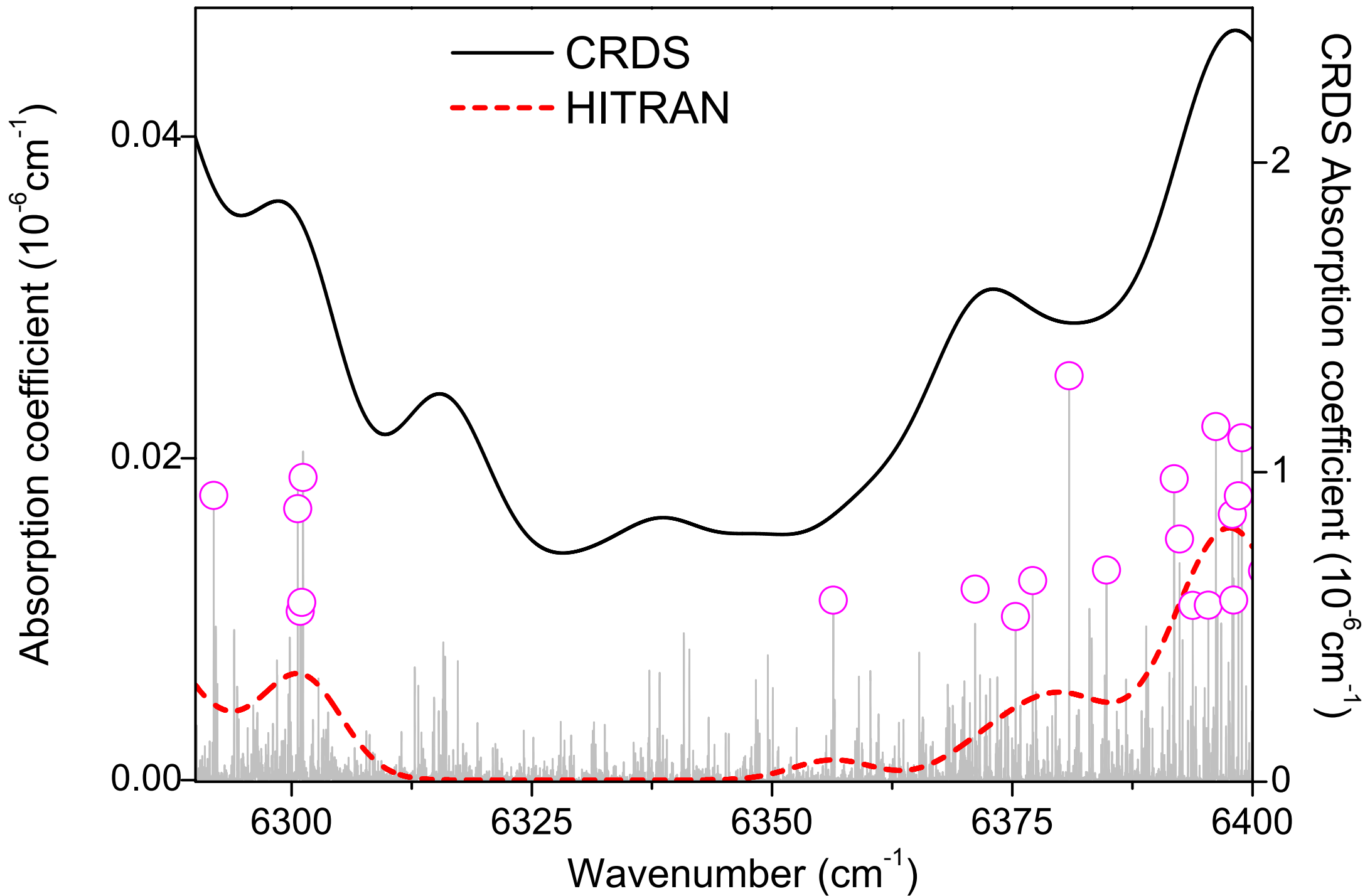
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## \* Response to Reviews

We thank the referee for the minor corrections he noted. They have been taken into account in the revised version

Regards,  
Alain Campargue

## High Sensitivity *CW*-Cavity Ring Down Spectroscopy of CH<sub>4</sub> in the 1.55 μm transparency window

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### *Abstract*

The high resolution absorption spectrum of methane has been recorded at room temperature by high sensitivity CW-Cavity Ring Down Spectroscopy between 1.50 and 1.60  $\mu\text{m}$  (6250-6680  $\text{cm}^{-1}$ ). This spectral region has a low opacity and is then of particular interest for the spectral analysis of the outer planets and Titan.

The recordings were performed with a sensitivity corresponding to a noise equivalent absorption of  $\alpha_{min} \sim 5 \times 10^{-10} \text{ cm}^{-1}$  and allowed for the detection of lines with an intensity smaller than  $10^{-28} \text{ cm/molecule}$  far beyond the weakest lines provided by the HITRAN database. The spectrum exhibits a highly complex and congested structure with a kind of “fractal” character and a density of transitions of a few tens per  $\text{cm}^{-1}$ . The impact of the weak newly observed transitions on the total absorption in the region is discussed.

## 1. INTRODUCTION

The quality of the analysis of the near infrared spectrum of the giant outer planets and Titan is strongly dependant on the knowledge of the methane absorption spectrum in the experimental conditions existing on these planets (see for instance Ref. [1]). Despite considerable progress achieved on the theoretical modelling of the CH<sub>4</sub> absorption spectrum [2], individual line parameters cannot presently be satisfactorily modelled or predicted below 1.7  $\mu\text{m}$ . As a consequence, the modelling of the spectrum of the above planetary atmospheres relies on band models which are extrapolation from laboratory measurements performed at higher temperatures and/or shorter path lengths. In particular, the actual CH<sub>4</sub> absorption in the low opacity spectral regions is of first importance to investigate the deeper atmosphere and determine the surface reflectivity (with implications on its composition). However, as recently discussed in Ref. [3], the methane band models have a limited accuracy in these “transparency windows” corresponding to very weak absorption of methane.

Empirical line by line spectroscopic parameters is the alternative to the band models. But the present situation of databases such as HITRAN [4] or GEISA [5] are far from fulfilling the needs in the case of methane. For instance, above 5000  $\text{cm}^{-1}$ , HITRAN is limited to empirical line parameters which were obtained at room temperature by high resolution Fourier Transform Spectroscopy (FTS) with path lengths up to 433 meters [6]. In absence of rovibrational assignments or at least of the determination of the lower energy of the transitions, the line intensity cannot be extrapolated at low temperature and are then of limited use in planetology. Another drawback of these data in particular, in the transparency windows, is their sensitivity which is too limited to account for the methane spectrum with kilometric atmospheric scale heights. To our knowledge, apart from the FTS results of Ref. [6], the only previous report devoted to the high resolution and high sensitivity spectrum of methane near 1.55  $\mu\text{m}$ , is the very recent contribution of Deng *et al* [7]. These authors used a Distributed Feed-Back (DFB) diode near 1.51  $\mu\text{m}$  and a 1159 meters path length (obtained with a 7.7 meters base cell) to record a 17  $\text{cm}^{-1}$  wide spectral section around 6620  $\text{cm}^{-1}$  by direct absorption spectroscopy.

As a contribution to the characterization of the methane absorption spectrum in spectral regions of very weak absorption, we have investigated the whole 1.60-1.50  $\mu\text{m}$  transparency window by high sensitivity CW-Cavity Ring Down Spectroscopy (CW-CRDS). After a brief description of the spectrometer used in the next section, the obtained spectra will be presented. The high sensitivity of our experimental set up has allowed for the observation



of a considerable number of new transitions and revealed an impressive complexity and congestion of the spectrum. The impact of the newly observed transitions to the total absorption in the considered region will be discussed.

## 2. EXPERIMENT

We have developed a fibered CW-CRDS spectrometer using DFB diode lasers dedicated to the characterization of the important 1.5  $\mu\text{m}$  atmospheric window of transparency. The typical achieved sensitivity of  $2\text{-}5 \times 10^{-10} \text{ cm}^{-1}$  and the 4 to 5 decades dynamic range on the intensity scale, have allowed for a significant improvement of the knowledge of the absorption spectrum of species of major atmospheric interest:  $\text{H}_2\text{O}$  [8, 9],  $^{12}\text{CO}_2$  [10],  $^{13}\text{CO}_2$  [11, 12],  $\text{N}_2\text{O}$  [13] and ozone [14, 15]. The set up has been described in Ref. [16] and its application for routine spectroscopic measurements has been described in Ref. [11]. Briefly, a single-mode fibre delivers laser radiation to one end of a vacuum-tight ringdown cell, made of a stainless steel tube. The fibered laser diode (NEL 20 mW butterfly mounted) was slowly temperature tuned from  $-10$  to  $60^\circ\text{C}$  in order to cover a  $30 \text{ cm}^{-1}$  spectral region within about 70 minutes. The cavity mirrors ( $R= 1 \text{ m}$ ) are mounted on tilt stages, one of which includes a piezoelectric tube that modulates the cavity length by slightly more than  $\lambda/2$ . This makes the cavity modes oscillate by more than one Free Spectral Range thus producing a passage through resonance with the laser line, twice per modulation cycle. The cavity output was focused on an amplified InGaAs photodiode. The cavity losses at each laser wavelength were obtained by averaging the results of exponential fits to 70 ring-down events, thus giving one data point in the spectrum. The absorption coefficient,  $\alpha \text{ (cm}^{-1}\text{)}$ , was then directly calculated from the decrease of the cavity ring-down time  $\tau$  (in s) induced by the molecular absorption:

$$\alpha c = 1/\tau - 1/\tau_0 \quad (1)$$

where  $c$  is the light velocity and  $\tau_0$  is the ring-down time of the empty cell (on the order of 60 ms) depending of the mirror losses

The ringdown cell temperature (typical value 298 K) and the gas pressure, measured by a capacitance gauge (MKS Baratron, 10 Torr range) are monitored during the spectrum acquisition. Two series of recordings were performed at 2.5 and 10 Torr. In these pressure conditions, the collisional broadening ( $9.0 \times 10^{-4} \text{ cm}^{-1}$  HWHM at 10 Torr [4]) is significantly weaker than the Doppler width (HWHM  $9.8 \times 10^{-3} \text{ cm}^{-1}$ ). As the DFB linewidth is about one thousandth of the Doppler broadening, the observed line profile is mostly Gaussian.

Each  $30 \text{ cm}^{-1}$  wide spectrum was calibrated independently on the basis of the wavelength values provided by the Michelson-type wavemeter (Burleigh WA-1650, 60 MHz resolution and 100 MHz accuracy at this wavelength). The calibration was further refined by stretching the whole spectrum in order to match accurate positions of reference lines. For this purpose, we used  $\text{CH}_4$  line positions measured by L. Brown [6] and adopted in the HITRAN database. The standard deviation error of the differences between CRDS and HITRAN line positions was minimized (typical *rms* values are less than  $10^{-3} \text{ cm}^{-1}$ ). A maximum deviation of  $2 \times 10^{-3} \text{ cm}^{-1}$  was observed for a few reference lines which is then claimed here to be the maximum position error.

### 3. RESULTS AND DISCUSSION

The whole investigated region which extends from  $6250 \text{ cm}^{-1}$  ( $1.60 \mu\text{m}$ ) to  $6680 \text{ cm}^{-1}$  ( $1.50 \mu\text{m}$ ), was recorded by the help of 22 DFB diodes. An overview of the central part of the CW-CRDS spectrum is presented in Fig. 1. The high sensitivity and high dynamics achieved with our CW-CRDS spectrometer is illustrated in Fig. 2: five successive zooms reveal the considerable complexity of the room temperature spectrum of methane in the considered region. The  $\text{CH}_4$  transitions present in the HITRAN database has been marked with an open circle on Fig. 2. The HITRAN database provides line parameters of 684 transitions in the  $6250\text{-}6680 \text{ cm}^{-1}$  region, with minimum line intensity of  $3.7 \times 10^{-26} \text{ cm/molecule}$ . A gain of sensitivity of about 3 orders of magnitude is obtained by CW-CRDS allowing for the measurements of intensity values smaller than  $10^{-28} \text{ cm/molecule}$ . However a major difficulty arises when estimating the minimum measurable intensity value: as illustrated on the different plots of Fig. 2 where the intensity scale has been expanded from  $10^{-5}$  to  $4 \times 10^{-8} \text{ cm}^{-1}$ , it seems impossible to localize a spectral section free of absorption lines and then difficult to evaluate the zero absorption level. We have estimated the density of lines detected in the  $6600 - 6630 \text{ cm}^{-1}$  section and obtained a value of about  $20 \text{ lines/cm}^{-1}$  which leads to an extrapolated value of about 9000 transitions for the whole  $6250 - 6680 \text{ cm}^{-1}$  region ...

The considered region of weak opacity lies between two strongly absorbing regions corresponding to the tetradecad (14) and the icosad (20) of vibrational states. Interactions connecting the different upper rovibrational levels are expected to be so strong and numerous that an accurate theoretical treatment is probably intractable. The observed spectral congestion is then the result of the superposition of (i) transitions from highly excited rotational levels reaching these strongly interacting rovibrational levels, (ii) hot bands arising from the first dyad near  $1500 \text{ cm}^{-1}$  and (iii) transitions due to minor isotopologues present in

natural abundance in our sample. It is worth noting that, as a consequence of the isotopic shift of the band centers, the minor isotopologues may have a relative contribution in the transparency windows which largely exceeds their respective abundance. Interestingly, the appearance of the observed spectrum show similarities with the high resolution spectrum of methane recorded at much higher energies in the visible range [17, 18].

As spectra of planetary atmospheres are generally obtained at low resolution (several  $\text{cm}^{-1}$  or more), it is interesting to estimate the importance of the newly observed transitions on the integrated absorption in the region. For this purpose, a “low resolution CW-CRDS spectrum” was simulated by convolution with a  $10 \text{ cm}^{-1}$  wide (FWHM) Gaussian function. The resulting spectrum is displayed on Fig. 3 and compared to a “low resolution HITRAN spectrum” obtained by affecting the same normalized Gaussian profile function to each transition provided by HITRAN for methane. The obtained curve multiplied by the molecular density (at 10.0 Torr) gives the absorption coefficient allowing for a quantitative comparison with the low resolution CRDS spectrum. The spectra displayed in Fig. 3 show that an additional absorbance ranging between  $1.4 \cdot 10^{-8}$  and  $10^{-7} \text{ cm}^{-1}$  is induced by the newly detected lines. ((Note that we estimate to less than  $10^{-9} \text{ cm}^{-1}$  uncertainty on the base line of the CRDS spectrum). This absorption depends smoothly on the wavelength and could be interpreted as a “continuum” in absence of our high resolution spectrum.

As expected, the relative impact of the newly detected transitions is much higher in the regions of lower opacities. The additional absorbance represents 100 % of the CRDS absorption near  $6325 \text{ cm}^{-1}$  and about 25 % in the low and high energy regions. Fig. 4 shows the region of highest transparency: While the HITRAN absorption is nonexistent between  $6310$  and  $6350 \text{ cm}^{-1}$ , the CRDS absorption is always larger than  $1.4 \times 10^{-8} \text{ cm}^{-1}$ . On the other hand, the low and high energy regions are dominated by stronger transitions which have a dominant contribution to the absorption, leading to a better agreement between CRDS and HITRAN.

We have calculated the sum of the line intensities reported in Ref. [7] from high sensitivity direct absorption spectroscopy between  $6607.9$  and  $6624.6 \text{ cm}^{-1}$ . The obtained value is  $9.23 \times 10^{-24} \text{ cm/molecule}$  which exceeds by 15 % the integrated intensity value calculated from the HITRAN database ( $7.14 \times 10^{-24} \text{ cm/molecule}$ ). For comparison, the CRDS absorption exceeds by about 35 % HITRAN absorption in this particular region.

#### 4. CONCLUSION

The highly sensitive absorption spectrum of methane has been recorded at Doppler limited resolution between 6250 and 6680  $\text{cm}^{-1}$  corresponding to the full coverage of the 1.55  $\mu\text{m}$  transparency window. The achieved experimental sensitivity has evidenced a highly complex and congested structure with a density of transitions on the order of 20 per  $\text{cm}^{-1}$ . The high dynamics on the line intensities allowed by the CW-CRDS technique reveals a kind of “fractal” character with no region free of absorption lines. The total number of observed transitions is estimated to be about 9000 while 684 lines are included in the HITRAN database. From simulations at low resolution (10  $\text{cm}^{-1}$  FWHM), it has been found that the impact of the newly detected transitions is considerable in the centre of the region (near 1.57  $\mu\text{m}$ ) corresponding to the highest transparency.

Unfortunately the present results will be of little benefit to interpret the methane opacities in the low temperature conditions existing in the outer planets or Titan. In absence of determination of the lower energy level of the observed transitions, the room temperature spectrum cannot be extrapolated at temperatures different from 295 K. This is why we are planning to combine our CW-CRDS spectrometer with a cell cooled at liquid nitrogen. Such combination of high sensitive laser absorption techniques with low temperature cells has been applied to methane for photoacoustic spectroscopy [17] and Intracavity Laser Absorption spectroscopy (ICLAS) [19]. The combination with CW-CRDS is more challenging as the use of optical windows is excluded. Even if the spectral congestion and line width will be drastically reduced at 77 K, we anticipate a considerable task for the line by line retrieval of the intensities.

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## **Figure Captions**

**Figure 1.** Overview of the room temperature spectrum of methane recorded by CW-CRDS between 6250 and 6680  $\text{cm}^{-1}$ . The whole spectral region was covered by the help of 22 DFB diode lasers which correspond to the alternated colors. The gas pressure was 10.0 Torr.

**Figure 2.** Five successive enlargements of the CW-CRDS spectrum of methane revealing a “fractal” structure of the highly congested spectrum of methane in the 1.55  $\mu\text{m}$  transparency window. The pressure was 10.0 Torr. The open circles mark the lines included in the HITRAN database corresponding to the right hand intensity scale. Note the high dynamics of the CW-CRDS spectrometer allowing for the measurement of absorption coefficient differing by four orders of magnitude.

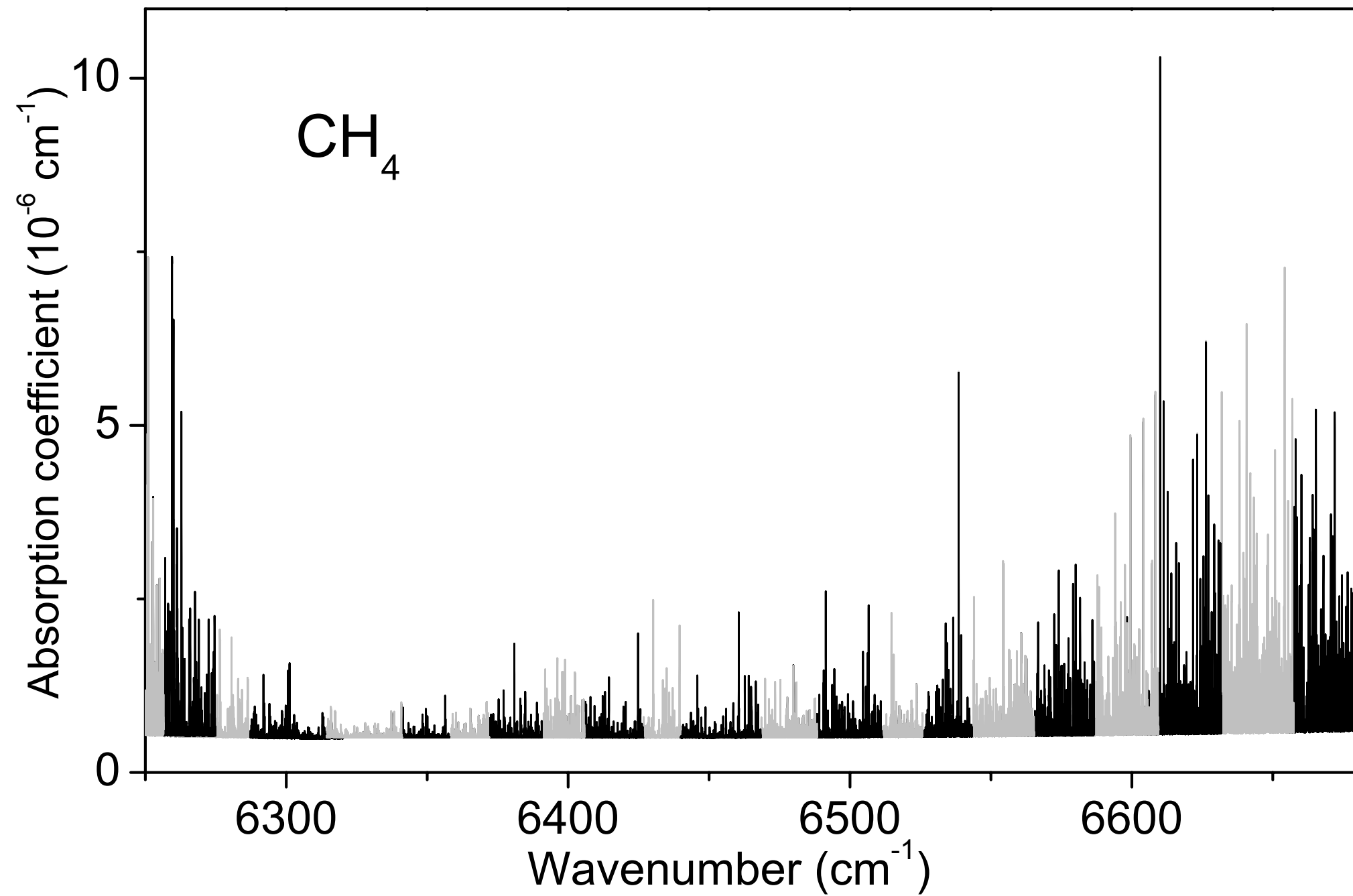
**Figure 3.** Comparison of the “low resolution” absorption spectrum of methane ( $p = 10.0$  Torr) simulated from the CW-CRDS spectrum (solid line) and from the HITRAN database (dashed line). The spectra were obtained by convolution with a normalized Gaussian function ( $\text{FWHM} = 10.0 \text{ cm}^{-1}$ ) modeling the apparatus function of a low resolution spectrometer. The intensity given on the right hand scale corresponds to the recorded CW-CRDS spectrum displayed on the background plot.

**Figure 4.** Same as Fig. 3 for the 6300-6400  $\text{cm}^{-1}$  high transparency region. The open circles mark the lines included in the HITRAN database. Their vertical position corresponds to the HITRAN intensity values which have been scaled to match the CW-CRDS spectrum.

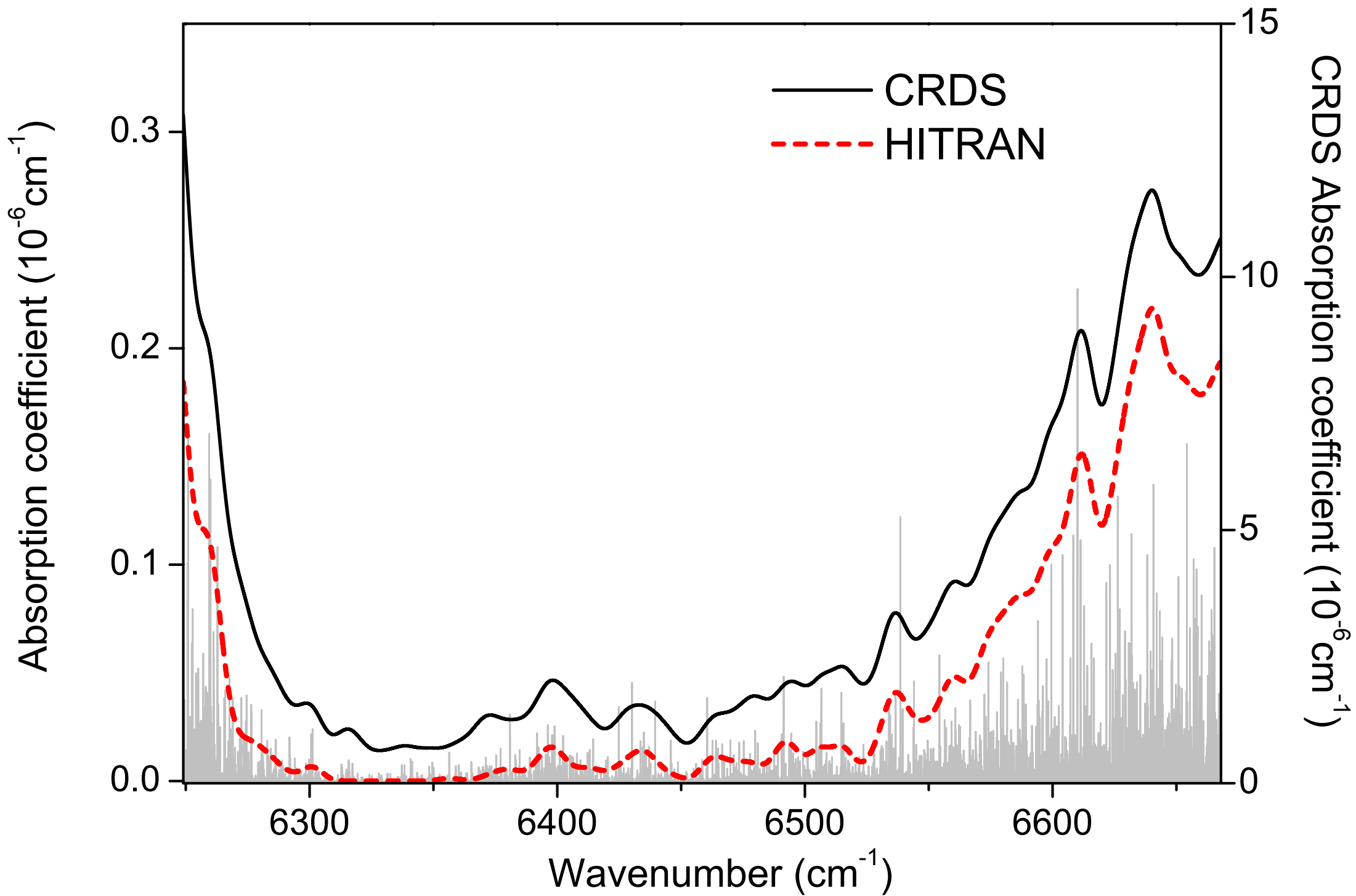
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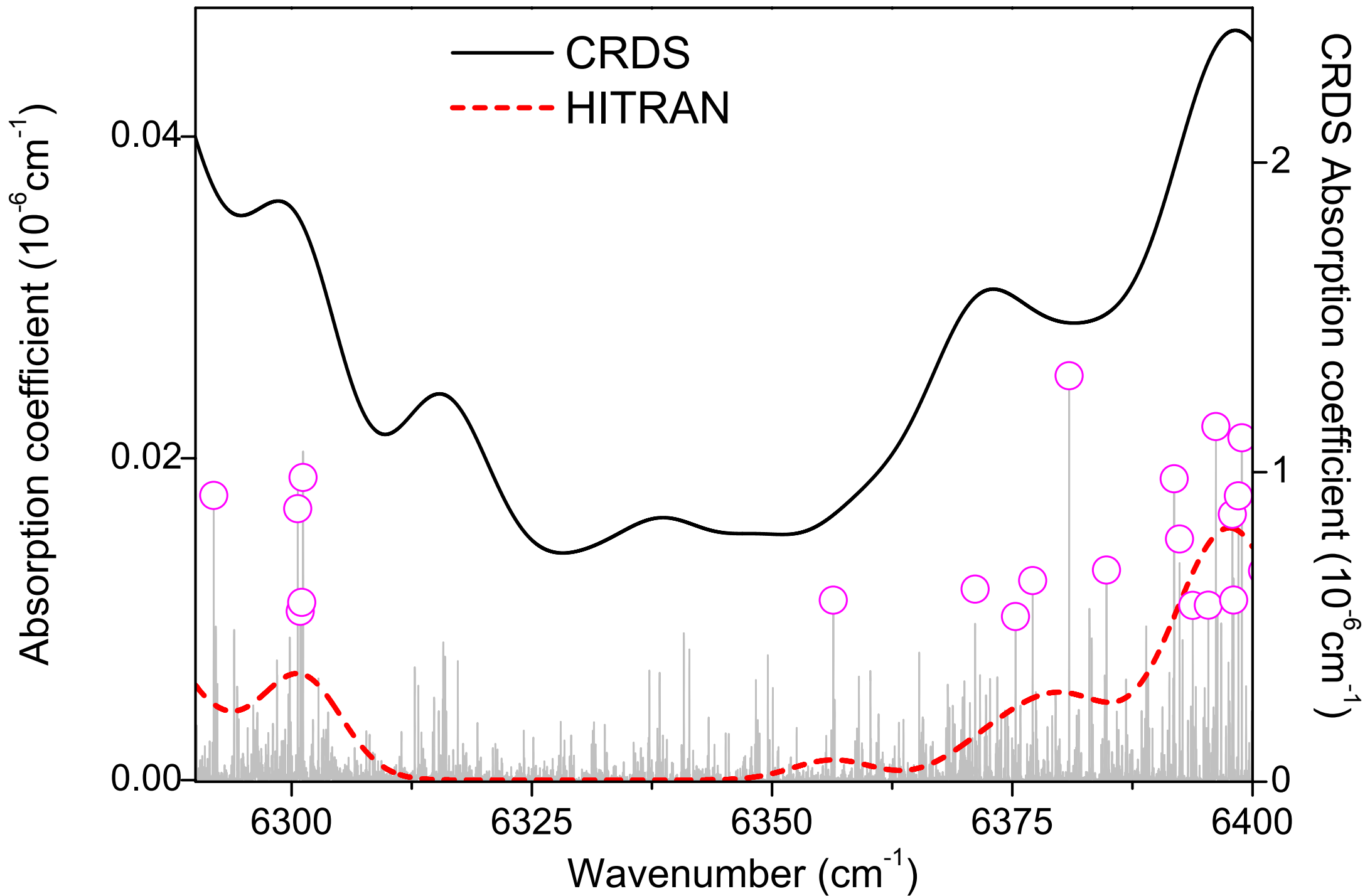
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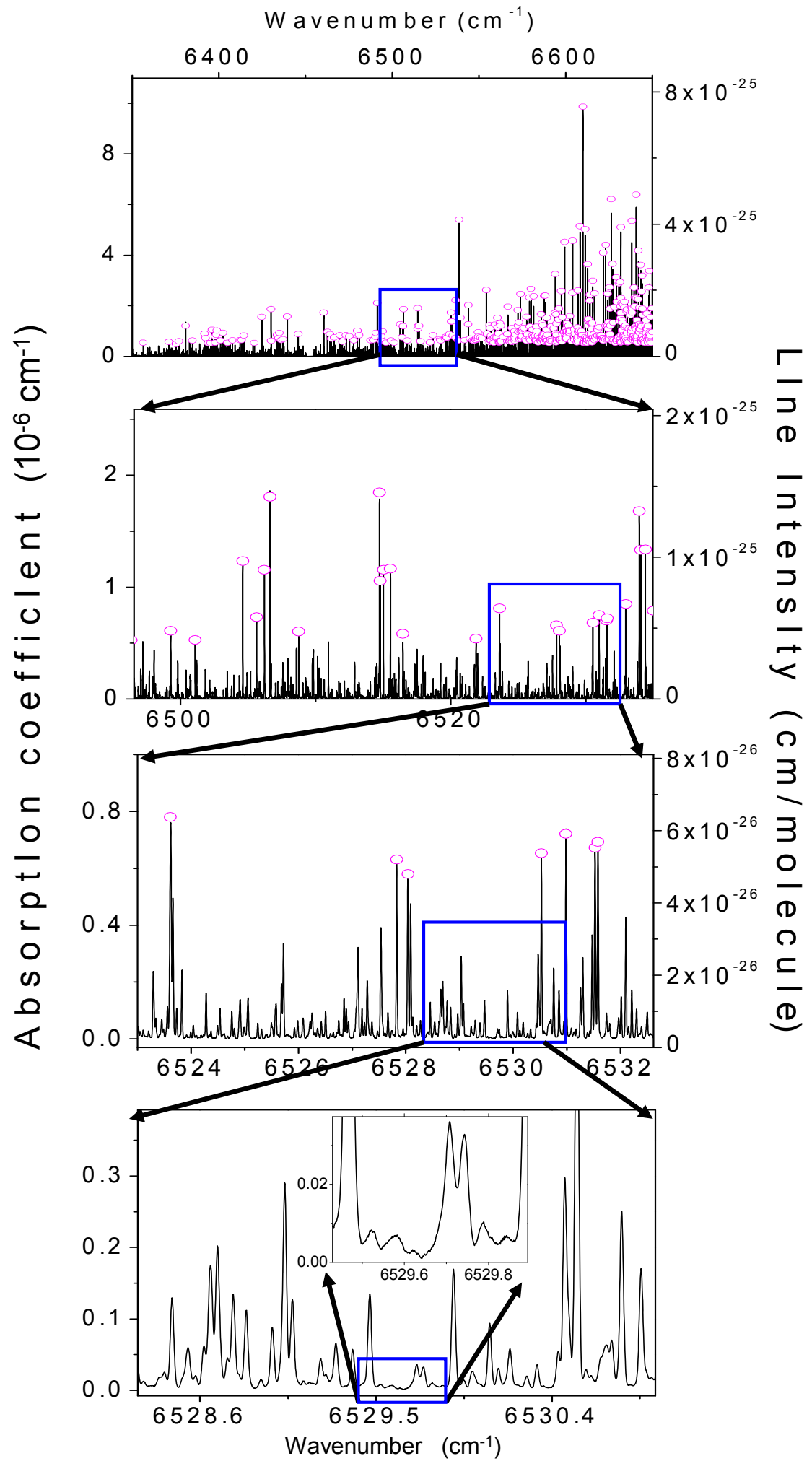








Figure



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