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journal homepage: www.elsevier.com/locate/pssRevised infrared bending mode intensities for diacetylene (C₄H₂): Application to TitanA. Jolly^{a,*}, L. Manceron^{b,c}, F. Kwabia-Tchana^a, Y. Benilan^a, M.-C. Gazeau^a^a Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583 du CNRS, Universités Paris Diderot et Paris-Est Créteil, Institut Pierre Simon Laplace (IPSL), Créteil, France^b Synchrotron SOLEIL, L'orme des Merisiers, Saint-Aubin-BP 48, 91192 Gif-sur-Yvette Cedex, France^c LADIR, CNRS-U. Paris 6, 4, Place Jussieu, 75252, France

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ABSTRACT

Diacetylene (C₄H₂) has been observed in various astrophysical environments in the infrared range through the bending modes ν_8 at 628.0 and ν_9 at 220.1 cm⁻¹. Accurate intensity measurements of both modes are necessary to obtain precise abundance determination. Laboratory spectra covering both bending modes have been recorded with a pure diacetylene sample. Precise band intensities have been measured showing large discrepancies compared to previous studies, reaching a factor 2.3 for the ν_9 band and a smaller difference of 20% for the ν_8 band. Consequences on the determination of abundances of diacetylene in Titan's atmosphere are discussed.

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1. Introduction

Diacetylene (C₄H₂) was first identified in Titan's atmosphere in 1981 by the Voyager IRIS spectrometer (Kunde et al., 1981) and later in the atmospheres of all four giant planets: Saturn in 1997 (de Graauw et al., 1997), Jupiter in 2004 (Kunde et al., 2004), Uranus in 2006 (Burgdorf et al., 2006) and Neptune in 2008 (Meadows et al., 2008). All detections were made through the strong ν_8 bending mode at 628.0 cm⁻¹, while the weaker bending mode ν_9 at 220 cm⁻¹ has only been observed on Titan (Kunde et al., 1981). Outside the solar system, diacetylene has been detected in two carbon rich protoplanetary nebulae, CRL 618 and CRL 2688 (Cernicharo et al., 2001) through the bending mode ν_8 , but the strong combination band $\nu_6 + \nu_8$ at 1241 cm⁻¹ could also be identified (Cernicharo et al., 2001). The molecule has even been detected outside the galaxy in the Large Magellanic cloud (Bernard-Salas et al., 2006).

At the time of the first detection of C₄H₂ (Kunde et al., 1981), accurate band intensity measurements were not available. Laboratory experiments were thus performed by Kunde et al. (1981) to confirm the detection of diacetylene on Titan but only a rough estimate of the diacetylene mole fraction in Titan's atmosphere could be derived from those experiments. More accurate band intensities were later measured (Koops et al., 1984) and used in a

radiative transfer model by Coustenis et al. (1989) to determine, using the ν_8 band, the first precise abundance of diacetylene in Titan's atmosphere.

While most observers have used Koops' values to determine the abundance of diacetylene (Coustenis et al., 1989), others (Cernicharo et al., 2001) have used more recent band intensity measurements (Khelifi et al., 1995). As can be seen in Table 1, the measured band intensity for ν_8 published by Khelifi et al., 1995 is 1.6 times lower than Koops' value. Khelifi's study of diacetylene is very similar in terms of method and resolution (4 cm⁻¹) to the study of cyanoacetylene (HC₃N) by the same authors (Khelifi et al., 1992). Intensity results for the strong bending modes of HC₃N where found to be in error due to saturation according to Jolly et al. (2007) and it is very likely that the ν_8 band intensity of diacetylene is also underestimated. Recent line lists included in the GEISA (Jacquinot-Husson et al., 2009) and the HITRAN (Rothman et al., 2013) databases use Koops' measured intensities for the ν_8 band, as well as for the weaker bending mode ν_9 at 220 cm⁻¹. The latter has only been measured once by Koops et al. (1984). To reach the far infrared domain, they had to use a different apparatus (lower resolution and lower broadening pressure) resulting in deviation from linearity in Beer's law plots as shown in Figure 6 of their paper. The absolute intensity of the ν_9 band was obtained by Koops from the derivative at zero sample pressure. No other experiment has since confirmed this result as it was out of reach of Khelifi's apparatus. The ν_9 bending mode intensity value of Koops et al. (1984) was used to determine a new

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Table 1
Absolute intensities for the main absorption bands of diacetylene compared to previous studies.

Absolute intensity ($\text{cm}^{-2} \text{atm}^{-1}$) at 298 K					
Mode	Vibration	Position (cm^{-1})	This work	Koops et al. (1984) ^a	Khelifi et al. (1995) ^b
ν_4	CH stretch.	3332.8	476	556 ± 24	491 ± 12
ν_5	CC stretch.	2019.8	7.1	7.6 ± 0.4	7.4 ± 0.2
$\nu_6 + \nu_8$	Comb.	1240.7	169.0	–	172.1 ± 4
$\nu_7 + \nu_9$	Comb.	701.0	10.3	–	11.6 ± 0.4
ν_8	CCH bend.	628.0	563.2 ± 23	703.6 ± 49	439.9 ± 11
ν_9	CCC bend.	220.1	60.7 ± 2.7	25.3 ± 1.2	–

^a Converted from km/mol to $\text{cm}^{-2} \text{atm}^{-1}$ at 298 K.

^b Converted from $T=300 \text{ K}$ to $T=298 \text{ K}$.

abundance of diacetylene in Titan's atmosphere through the far infrared observation of the CIRS instrument on board the CASSINI spacecraft (Teany et al., 2009).

In this paper, we intended to remove the remaining uncertainties on the diacetylene band intensities by taking special care of the purity of the sample and avoiding all saturation problems. The intensities of both bending modes ν_8 and ν_9 have been measured using a unique apparatus at a resolution of 0.1 or 0.5 cm^{-1} in the range between 50 and 650 cm^{-1} . In addition, we have used another apparatus to study the spectra of diacetylene between 500 and 4000 cm^{-1} .

2. Experimental

C_4H_2 was synthesized according to Khelifi et al. (1995) by the reaction of dehydrochlorination of 1,4-dichloro-2-butyne ($\text{C}_4\text{H}_4\text{Cl}_2$). The latter is placed in a 40% aqueous sodium hydroxide solution. The mixture is heated at 110 °C while tetraethylenediethylether is slowly added for deshydrochlorination. C_4H_2 thus gradually formed is carried away in a stream of nitrogen, dried over calcium chloride and is trapped in an acetone/liquid nitrogen slush (–25 to –30 °C).

A crucial issue for band intensity measurements is, of course, the sample purity. During the first experiments, absorption was observed near 328 cm^{-1} , which could be assigned to trace impurity of $\text{C}_4\text{H}_3\text{Cl}$, a well-known byproduct of the synthesis (Smith et al., 1998). Thanks to an important difference in vapor pressure at low temperature, this impurity could be eliminated during alternating freeze–thaw and pump cycles. The purity of the sample was controlled by testing a small fraction of the gas through mass spectrometry. Small peaks at masses 86 and 88, characteristic for $\text{C}_4\text{H}_3\text{Cl}$, were sometimes observed and removed, as explained above, before injecting in the cell. The absence of characteristic masses also ensured that non-IR absorbing gases such as N_2 or O_2 were totally absent of the sample. As can be seen in Fig. 1, main peak mass 50 and fragment masses 49, 48, 37, 25 and 12 are observed, in agreement with the National Institute for Standards and Technology standard ionization mass spectra of C_4H_2 (NIST, 2013). According to the intensity ratio in the mass spectra between the main peak and the residual impurities level of about 100, sample purity close to 99% is expected.

Diacetylene absorption spectra were recorded between 40 and 670 cm^{-1} at the French synchrotron radiation facility SOLEIL (Saint-Aubin, France) using a Fourier Transform InfraRed (FTIR) spectrometer (Bruker IFS125HR) at the Advanced Infrared Line Exploited for Spectroscopy (AILES) beam line. Spectra were recorded at

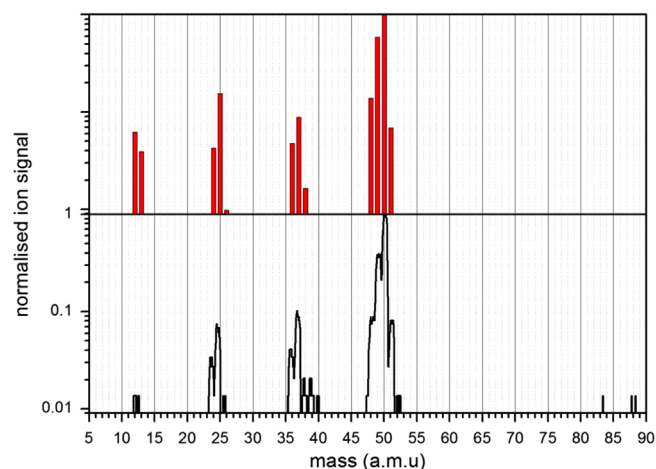


Fig. 1. Comparison between the sample mass spectra (lower panel in black) and the NIST standard ionization mass spectra (upper panel in red). Slight differences in ion relative intensities are due to differences in the mass spectrometers. Note, however, the similarity in mass patterns and the absence of significant impurity peaks at 86 and 88 ($\text{C}_4\text{H}_3\text{Cl}$) and 28 and 32 (air). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

0.1 and 0.5 cm^{-1} resolution in the 670–40 cm^{-1} region, 3.8 cm/s scanner velocity, a 6 μm Si/Myar beamsplitter and a 4 K-cooled Si composite bolometer with a 1.5 ms rise time and a cold, 670 cm^{-1} low-pass filter. Four hundred interferograms were averaged and processed with “boxcar apodization” (defining that no mathematical post-treatment was applied to the data) against a background of the empty cell taken at the same temperature and resolutions. All spectra were recorded with the internal Globar source, an aperture diameter of 6.3 mm, and taken at room temperature (298 K) using a multipass cell equipped with polypropylene windows, for a total optical path of 84.9 cm. A total of six pressures were measured using 0.1 and 10 mbar range thermostated capacitive gauges (Pfeiffer, Germany), directly connected to the gas cell, with stated accuracies of 0.5% and 0.2% respectively. The buffer gas pressure was measured with a 1000 mbar capacitive gauge connected to the vacuum line, with an accuracy of 0.2%.

Spectra with the same sample were also recorded at 0.5 cm^{-1} resolution between 500 and 3500 cm^{-1} at LISA in Créteil using an FTIR spectrometer (Bruker, Equinox 55) equipped with a KBr/Ge beamsplitter and a DTGS detector. The gas samples were placed in a White multipass cell (10.6 m total path length) equipped with KBr windows. Sample pressures were measured with two MKS Baratron covering the 1 bar to 10^{-4} mbar pressure range. The gas samples were transferred from the tubes where they are stored in solid phase at liquid nitrogen temperature, to the cell via a vacuum line pumped below 10^{-7} mbar with a turbo pump (Pfeiffer TMH 065).

3. Far infrared intensity measurements

Spectra in the far infrared (50–650 cm^{-1}) were recorded at resolutions of 0.1 and 0.5 cm^{-1} for nine different pressures between 0.05 and 4 mbar. Adding a broadening gas is commonly used to avoid saturation effects as observed in our previous studies with HC_3N (Jolly et al., 2007) and C_2N_2 (Fayt et al., 2012). Strong saturation of the band intensities was also observed in the present study and 1000 mbar of N_2 has been systematically added to the samples. After addition of the broadening gas to the sample, we observed a strong decrease of the intensities of the studied bands, followed by a slow increase until a stable level was reached after

about 1 h. This was also observed in our study on C_2N_2 (Fayt et al., 2012) and our interpretation is that the homogenization of the mixture takes a long time, due to the slow diffusion of the diacetylene molecules in the molecular nitrogen background. For each measured sample, the spectrum at 0.5 cm^{-1} resolution was recorded for more than 1 h after adding nitrogen. Subsequently, the spectrum at 0.1 cm^{-1} resolution was recorded about 15 min later with the same sample. No significant differences in the integrated absorbance were observed when changing the resolution. We therefore rule out any saturation or homogenization problems.

Fig. 2 shows two transmission spectra taken at 0.8 mbar and 0.053 mbar mixed with 1 bar of N_2 , at room temperature and at a resolution of 0.5 cm^{-1} . The strong Q-branch at 628.0 cm^{-1} (ν_8) reaches zero transmission in the higher partial pressure spectrum while the weaker Q-branch at 220.1 cm^{-1} (ν_9) stops at about 0.45. In the low partial pressure spectrum, the ν_9 Q-branch transmission reduces to 0.95 while the ν_8 Q-branch is still strong, reaching about 0.4. An approximate band intensity ratio $S(\nu_8)/S(\nu_9)$ of 15 can be graphically derived by taking into account the pressure ratio of about 15 between the two spectra shown in Fig. 2 and the relatively close transmission values for the ν_9 Q-branch in the high pressure spectrum and the ν_8 Q-branch in the low pressure spectrum. This ratio is expected to be reduced by the broadness of the ν_9 band compared to the ν_8 band which changes the surface ratio in favor of ν_9 . This estimated value is in strong disagreement with the band intensity ratio $S(\nu_8)/S(\nu_9)$ derived from Koops' measurements which is equal to 27.8 (see Table 1).

In this study, absorption coefficients for both bands have been determined for all spectra and both resolutions. Absolute band intensities in $\text{cm}^{-2}\text{ atm}^{-1}$ (S_{band}) are calculated as the integral over the wavenumber ν

$$S_{\text{band}} = \frac{1}{pl} \int_{\text{band}} \ln\left(\frac{I_0}{I}\right) d\nu \quad (1)$$

where I_0 is the incident intensity, I is the transmitted intensity with the sample at the pressure p (atm) and l is the path length (cm). Results reported in Table 1 have been obtained by averaging absorption coefficients from all spectra up to 0.8 mbar for the strong ν_8 bending modes and from 0.25 up to 4 mbar for the weaker ν_9 band. The goal of this selection is to eliminate small uncertain absorption values, as well as transmission values close to zero. Averaging absorption coefficients has the advantage of giving

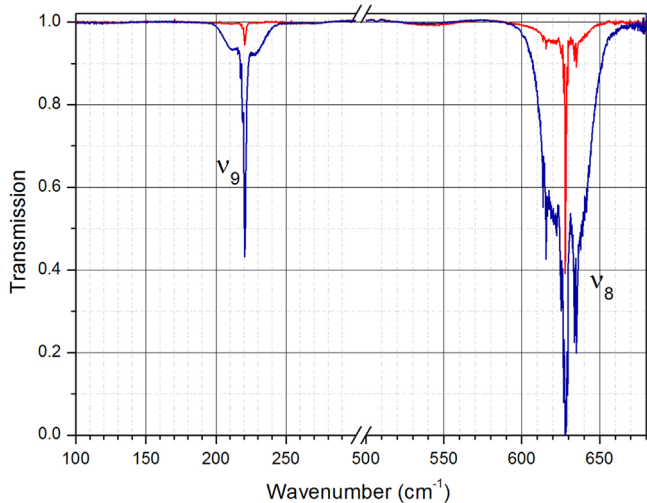


Fig. 2. Far infrared spectra of C_4H_2 mixed with 1 bar of N_2 at room temperature and a resolution of 0.5 cm^{-1} : partial pressure of 0.8 mbar in blue and 0.053 mbar in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the same weight to all selected measurements. As can be seen in Fig. 3, the dispersion of the individual values is not larger than $\pm 5\%$ compared to the average value.

As can be seen in Table 1, our results do not agree with previous results by Koops et al. (1984) and Khlifi et al. (1995), even if we take into account the uncertainties. We found the ν_8 band intensity to be 20% weaker than expected from Koops' result and 28% stronger compared to Khlifi's result. The strongest disagreement concerns the ν_9 band, where we find an absolute intensity larger by a factor 2.4 compared to the only previous measurement (Koops et al., 1984). The difference with Khlifi's result for the ν_8 band was expected, since saturation problems due to low resolution and strong absorbance reduce the measured value. On the contrary, the difference with Koops' values is surprising and not explained at this stage. Using the same experimental setup in a previous study, we determined the absolute intensity of the ν_5 band of C_2N_2 at 230 cm^{-1} and found a perfect agreement with three other studies (see Fayt et al., 2012).

4. Mid-infrared complementary measurements

In order to test our diacetylene sample, we used another infrared spectrometer between 500 and 3500 cm^{-1} to compare our results for other fundamental and combination bands of diacetylene with Khlifi and Koops. We used the Bruker Equinox 55 described above at the best resolution of 0.5 cm^{-1} to record two spectra at partial pressures 0.071 and 0.97 mbar. The spectral overlap of both studies makes the comparison only possible for the ν_8 band. Using the spectra at 0.071 mbar recorded in Créteil (and a path length of 1040 cm), we find a band intensity for ν_8 9% lower than our value reported in Table 1. A slight saturation of the Q-branch could be responsible for this discrepancy as was observed in our far infrared spectra at 0.8 mbar and a path length of 84.9 cm. As presented in Fig. 4, both spectra have very close absorbance values, in agreement with their respective (pl) values obtained from the product of the path length and the pressure which differ only by 6%. Band intensities deduced from both spectra are also very close and only differ by 5%, within the announced uncertainties. Nevertheless, intensities of the other stretching and combination bands can be compared with Khlifi's values without fearing any saturation since weaker parallel bands will not saturate as quickly as a strong perpendicular bands. This comparison is quite satisfactory since, as can be seen in Table 1,

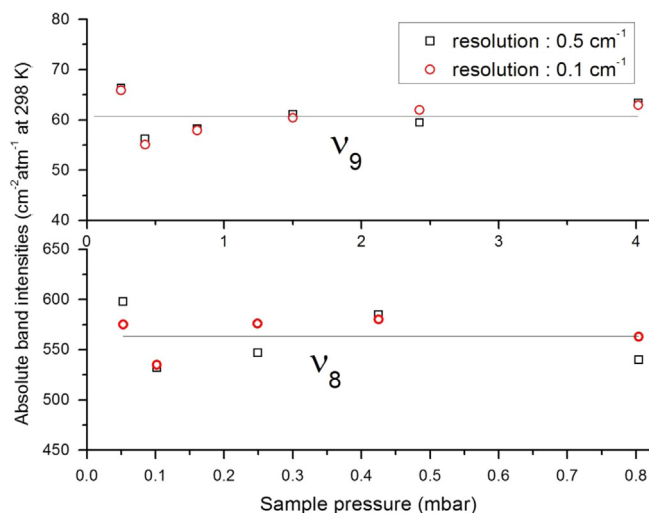


Fig. 3. Band intensities for ν_8 and ν_9 for various sample pressures and both resolutions.

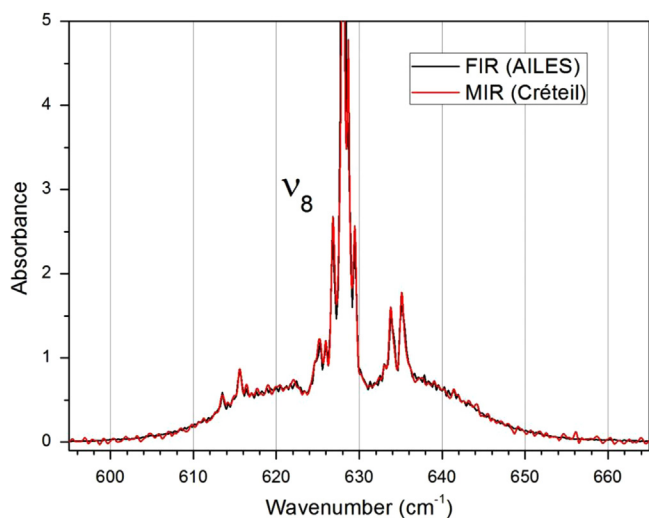


Fig. 4. Comparison of the absorbance of the ν_8 band of C_4H_2 recorded with the far infrared AILES apparatus and the mid-infrared Créteil instrument, in both cases at room temperature and a resolution of 0.5 cm^{-1} : partial pressures are 0.8 mbar in black (path length is 84.9 cm) and 0.071 mbar in red (path length is 1040 cm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the differences with Khlifi's values are below 5% for ν_4 , ν_5 and $\nu_6 + \nu_8$. A larger difference is observed for the small combination band at 701 cm^{-1} , which can be due to the difficulty of resolving, at low resolution and large absorbance, this band from the very strong ν_8 band. Apart from the two bending modes, Koops et al. (1984) also measured the fundamental stretching modes ν_4 and ν_5 . Similarly to the ν_8 band, our values are lower by 17% for ν_4 and 6% for ν_5 .

5. Discussion

To summarize, we believe that the intensity of the ν_9 band is in reality much stronger than determined from Koop's study. In the present work, we have measured both bending modes in the same experimental conditions and are able to measure a very precise intensity ratio which is in strong disagreement with Koop's measurements. Therefore, we believe that the measurement of the ν_9 band by Koop's is in error and propose to reevaluate the intensity of the ν_9 line lists available from the GEISA and HITRAN databases by a factor of 2.4.

For the ν_8 band, the situation is different. Our result for the intensity of this band is in between the two previous measurements by Khlifi and Koops. Saturation explains without doubt the lower value found by Khlifi for ν_8 . For the weaker bands, which do not suffer from saturation, we have a good agreement with Khlifi's results. Overall, our measurements are therefore very consistent with Khlifi's. On the contrary, Koop's value for ν_8 is 20% higher than ours and a similar difference is observed for ν_4 . Such a difference cannot be due to saturation since a perpendicular and a parallel band would not saturate the same way. This difference could be due to a systematic error, for instance to an impurity in the sample or a false pressure reading. In the case of an impurity, the band intensity is underestimated. In our case, we have checked the purity of our sample using a mass spectrometer which is able to detect very small amounts of molecules. Concerning the reading of the pressure, the consistency between our two sets of data and with Khlifi's values does not show any significant systematic trend, which makes us relatively confident about our determination. In conclusion, we propose, in addition to the reevaluation of the ν_9 band intensity, a change of the ν_8 band intensity by a factor of

0.8 should be applied to the line lists available in the GEISA and HITRAN databases.

6. Applications to Titan's atmosphere

Twenty percent weaker ν_8 band intensity could lead to a 20% reevaluation of the retrieved abundances in all astrophysical environments, where diacetylene has been detected through the strong ν_8 band. Nevertheless, this is only true in the case of a linear dependence of the abundances with respect to the apparent band intensity. The non-linear dependence occurring in some laboratory measurements, in particular in the absence of any broadening gas, can also occur in astrophysical environments where column densities of diacetylene can be strong (Vinatier et al., 2010).

A 2.4 times stronger ν_9 band should, on the contrary, lead to a significantly weaker abundance of diacetylene, but this band at 220 cm^{-1} has only been detected on Titan. It has not been used very often to determine abundances of diacetylene, since the ν_8 band at 628 cm^{-1} is much stronger and more easily reachable by most infrared spectrometers. However, abundances in the far infrared range have been retrieved in Titan's atmosphere for C_4H_2 (using the ν_9 band at 220 cm^{-1}), as well as for C_2N_2 and C_3H_4 , which also have detectable bands in that wavelength range (Teanyby et al., 2009). The far infrared values have been compared for various latitudes with results obtained in the mid-infrared domain (using the ν_8 band at 628 cm^{-1}). Diacetylene abundances turned out to be consistent around equatorial latitudes and diverging above 45°N . The interpretation of the authors was that higher stratopause temperature at northern latitudes was causing an extra peak at higher altitude in the mid-IR contribution function. Because of the positive gradient of the abundance profile, a stronger abundance is observed in the mid-IR compared to the far IR. The agreement at equatorial latitudes was interpreted as the result of mid-IR and far IR sounding the same altitude and also as a consequence of a consistent band intensity ratio between mid and far IR. The authors were using new line lists by Jolly et al. (2010), where band intensities by Koops et al. (1984) were included. In the light of the revised diacetylene band intensities described in the present paper, the comparison between abundances should rather result, at all latitudes, in lower abundances in the far IR than in the mid-IR. It is interesting to note that the same situation is observed for another molecule, C_3H_4 , where the far infrared abundances are, for all altitudes, lower than in the mid-infrared (Teanyby et al., 2009). For both molecules, the different abundances should thus be interpreted as a consequence of varying abundance profiles and sounding different atmospheric levels at different temperatures in far and mid-infrared. A reanalysis of the observations could be performed to confirm this hypothesis.

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