Carbon Chemistry in IRC+10216: Infrared Detection of Diacetylene

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Abstract

We present the detection of C₄H₂ for first time in the envelope of the C-rich AGB star IRC+10216, based on high spectral resolution mid-infrared observations carried out with the Texas Echelon-cross-Echelle Spectrograph mounted on the Infrared Telescope Facility. The obtained spectrum contains 24 narrow absorption features above the detection limit, identified as lines of the ro-vibrational C₄H₂ band ν₄ + ν₆(σᵣᵣ'). The analysis of these lines through a ro-vibrational diagram indicates that the column density of C₄H₂ is (2.4 ± 1.5) × 10¹⁶ cm⁻². Diacetylene is distributed in two excitation populations accounting for 20% and 80% of the total column density and with rotational temperatures of 47 ± 7 and 420 ± 120 K, respectively. This two-folded rotational temperature suggests that the absorbing gas is located beyond ∼0″4 ∼ 20 R_*, from the star, with a noticeable cold contribution outwards from ∼10″ ∼ 500 R_. This outer shell matches up with the place where cyanoacetylenes and carbon chains are known to form due to the action of the Galactic dissociating radiation field on the neutral gas coming from the inner layers of the envelope.

Key words: circumstellar matter – line: identification – stars: abundances – stars: AGB and post-AGB – stars: individual (IRC+10216) – surveys

1. Introduction

Evolved stars are known to develop a circumstellar envelope surrounding their central objects. Around a third of the total number of molecules discovered in space are present in the envelope of this kind of star (e.g., Guélin et al. 1978, 1987; Hinkle et al. 1988; Bernath et al. 1989; Ohishi et al. 1989; Bell et al. 1993; Cernicharo & Guélin 1996; Cernicharo et al. 2000, 2015; Agúndez et al. 2014a, 2014b; Anderson & Ziyurs 2014). Most of these molecules are formed in the outer shells of the envelopes due to the active chemistry triggered by the radicals and ions that arise after the dissociation of neutral molecules by the external ultraviolet (UV) radiation field (Millar & Herbst 1994; Millar et al. 2000; Cernicharo 2004; Agúndez et al. 2017). In particular, the abundances of polyynes (CₙH₂) and cyanopolyynes (HCₙ₊₁N) that have been observed only in the C-rich proto-planetary nebula CRL618 to date can be explained by a photochemical model in which these molecules are formed by chemical reactions involving the radicals C₂H and C₂n+1N, giving raise to a polymerization mechanism that produces carbon-chain molecules (Woods et al. 2003; Cernicharo 2004). The abundance of these molecules decreases as their number of atoms increases, strongly depending on the temperature and the density of the gas (Cernicharo 2004).

To date, several members of the cyanopolyne family have been detected in several evolved stars, including the very well known Asymptotic Giant Branch star IRC+10216 (HC₂n+₁N, n = 0, ..., 4; Winnewisser & Walmsley 1978; Henkel et al. 1985; Matthews et al. 1985; Guélin & Cernicharo 1991). Regarding the polyyne family, no member has been detected so far in this source, apart from C₂H₂, which was observed with a column density of ∼10¹⁹ cm⁻² (Cernicharo et al. 1999; Fonfría et al. 2008). This non-detection suggests low column densities for other polyynes (≤10¹⁶ cm⁻²), contrary to what happens in CRL618. Cernicharo et al. (2001) and Fonfría et al. (2011) clearly detected the C₂H₂ and C₆H₂ features produced in the photodissociation shells of the envelope of this proto-planetary nebula, with column densities ∼10¹⁷ cm⁻², similar to that of C₂H₂. This remarkable difference is an effect of the gas density in the photochemical evolution of the envelopes of evolved stars and the photopolymerization of C₂H₂ and HCN (Cernicharo 2004).

In this paper, we present the first detection of the spectrum of C₄H₂ toward the C-rich AGB star IRC+10216. The observations are described in Section 2. Section 3 contains the results of the data analysis. A discussion about them and their implications in the current chemical scenario of IRC+10216 can be found in Section 4. A brief summary of our work and the final conclusions are in Section 5.

2. Observations

The observations were carried out with the Texas Echelon-cross-Echelle Spectrograph (TEXES, Lacy et al. 2002) mounted on the 3 m Infrared Telescope Facility (IRTF) on 2008 May. TEXES was used in its HighMedium mode with a resolving power of R ≈ 85,000, which provides us with a spectral resolution of ∼3–4 km s⁻¹. IRC+10216 was nodded along the slit to allow for a better sky subtraction and an efficient on-source integration. The observations were corrected from the atmosphere with a blackbody-sky difference. The data were reduced with the standard TEXES pipeline. The baseline of each order was removed with an up to 10th order polynomial fit, taking care of excluding all the features in the spectrum in this process. The total spectrum was composed of 150 different segments that almost completely cover the spectral range of 7.9–9.1 μm. The part of the spectrum where the C₄H₂ lines are found roughly ranges from...
8.0 to 8.1 μm (Figure 1). The noise rms is estimated to be ±0.2% of the continuum.

The spectrum was not corrected from telluric contamination since IRC+10216 is much brighter at 8 μm than any available calibrator. The telluric feature identification has been performed by comparing the observations with the Atmospheric TRANsmission (ATRAN) model (Lord 1992). The identification of the features coming from IRC+10216 has been performed with the aid of the data in the last version of the HIgh-resolution TRANsmission molecular absorption Database (HITRAN, Rothman et al. 2013). The Doppler shift affecting these lines was accurately removed by fitting the strong CS and SiO lines in the observed data. The analysis of the spectra of these molecules will be published elsewhere.

3. Results

C4H2 is a molecule with five stretching modes and four doubly-degenerated bending modes. Only the fundamental modes ν4(σ_u), ν5(σ_u) (stretching bands at ≈3.0 and 5.0 μm), and the symmetric C≡C−H and C−C≡C bending modes ν6(π_u) and ν7(π_u) (bending bands at ≈15.9 and 45 μm) are infrared active, i.e., the rotational levels in the corresponding excited vibrational states are radiatively connected in the infrared with those of the vibrational ground state by electric dipole transitions. The anti-symmetric C≡C−H and C−C≡C bending modes ν6(π_g) and ν7(π_g) are inactive in the infrared. Vibrational modes ν6 and ν8 play the same role in C4H2 that ν4 and ν5 play in C2H2. The infrared spectrum of C4H2 comprises additional combination bands, such as ν6 + ν8 (Khliifi et al. 1995). ν8 is blocked by the strong telluric ozone band around 15 μm and is unavailable from the ground (but was detected from space by Cernicharo et al. 2001). ν4 is highly overlapped with strong bands of C2H2 and HCN, which are very abundant in IRC+10216 (Fonfría et al. 2008), and other hydrocarbons, such as C3H6, that are also present in the atmosphere. Thus, looking for the lines of band ν6 + ν8 from the ground is a very good choice in order to detect C4H2, in spite of the absence of the prominent Q branch.

Figure 1. Observed spectrum of IRC+10216 around ≈1241 cm⁻¹ against rest frequency (black histogram) containing the R and P branches of the band ν6 + ν8 of C4H2 (see the text for a definition) and a rough model of the C4H2 spectrum (red; see Section 4). The telluric transmission is plotted in gray. The thickness of the arrows indicates the statistical weight of the line (thick: o-C4H2; thin: p-C4H2). The red arrows point at the identified C4H2 lines. The pink ones show the C4H2 lines fully blended with other molecular features.
C$_2$H$_2$ abundance is expected to be low, so we can consider the observed lines as optically thin. Thus, the following formula holds for each line:

$$\ln \left[ \frac{8\pi u^2 c I}{A_{ul} g_u N_{col,0}} \right] \simeq \ln \left[ \frac{N_{col}}{N_{col,0} Z \theta^2 + \theta^2_b} \right] - \frac{hc E_{low}}{k_B T_{rot}} \tag{1}$$

where $\nu$ is the rest frequency (cm$^{-1}$), $I$ is the integrated absorption, $A_{ul}$ is the A-Einstein coefficient (s$^{-1}$), $g_u$ is the degeneracy of the upper level, $Z$ is the total partition function, $N_{col}$ is the column density (cm$^{-2}$), $E_{low}$ is the energy of the lower ro-vibrational level (cm$^{-1}$), and $T_{rot}$ is the rotational temperature (K). The integrated absorption was estimated by means of a Gaussian fit that chose the proper baseline. This baseline was the continuum emission for isolated C$_2$H$_2$ lines and the profile of a molecular feature around the C$_2$H$_2$ line if it took part of a blending. The total partition function was calculated by direct summation over all the available ro-vibrational levels. The lack of hot bands and of an emission component in the detected lines prevents us from deriving the vibrational temperature of C$_2$H$_2$, which is necessary to calculate the partition function and thus the column density.

We have then assumed the vibrational temperature for C$_2$H$_2$ equals that of the C$_2$H$_2$ band $\nu_4 + \nu_5$($\nu'_4$) (Fonfría et al. 2008). $N_{col,0} = 10^{15}$ cm$^{-2}$ is a fixed column density included for convenience to get dimensionless arguments for the logarithms. The factor $\theta^2/\left(\theta^2_b + \theta^2_b\right)$ is the Point Spread Function (PSF) filling factor, where $\theta_b$ is the angular size of the C$_2$H$_2$ absorption, and $\theta_b$ results from the quadratic addition of the telescope half power beam width and the atmospheric seeing. It was $\sim 0.09$ at $8\mu$m during our observing run. The size of the C$_2$H$_2$ absorption can be roughly estimated with our radiative transfer code (Fonfría et al. 2008, 2014), assuming the rotational temperature derived from the ro-vibrational diagram. Thus, $\theta_b = 0.63 \pm 0.19$, and $\theta^2_b/\left(\theta^2 + \theta^2_b\right) = 0.33 \pm 0.13$. The uncertainties have been calculated, propagating the noise rms of the observed spectrum.

From this diagram, we derive the existence of two different C$_2$H$_2$ populations (cold and hot), with rotational temperatures of $47 \pm 7$ and $420 \pm 120$ K and column densities of $(4.5 \pm 2.9) \times 10^{15}$ and $(19.1 \pm 1.2) \times 10^{16}$ cm$^{-2}$, respectively. The total diacetylene column density is $(2.4 \pm 1.5) \times 10^{16}$ cm$^{-2}$. This low column density, distributed into rotational levels with energies spanning along several hundred of K, implies the weakness of the observed lines in the mid-infrared.

The lack of a permanent dipole moment of C$_2$H$_2$ prevents it to have a rotational spectrum. Therefore, it is rotationally under LTE, or very close to it in high density environments, but the population of the rotational levels can be significantly affected by the infrared continuum in low density ones. This effect is difficult to quantify so, to a first approximation, we can place the shell where the observed lines are formed using the kinetic temperature radial profile recently derived by Guélin et al. (2017) from high spatial resolution data of $^{12}$CO ($T_k \simeq 257(r/0.8)^{0.657}$ K, if $r \lesssim 15''$ and $T_k \simeq 35$ K beyond). Hence, the cold population of C$_2$H$_2$ is at $10.0^{+5.7}_{-1.8}$ arcsec from the star ($500^{+40}_{-30} R_k = (1.8^{+0.3}_{-0.2}) \times 10^{16}$ cm, if $R_k = 0^{+0.02}_{-0.02} = 3.7 \times 10^{13}$ cm; Ridgway & Keady 1988; Fonfría et al. 2017), while the hot population arises at $0.40^{+0.14}_{-0.14} = 1.4^{+0.5}_{-0.4} = 3.7 \times 10^{14}$ cm. We estimate the C$_2$H$_2$ abundance, with respect to H$_2$ to be $6 \times 10^{-7}$ and

Figure 2. Ro-vibrational diagram of C$_2$H$_2$. The data set can be divided into two different groups with different rotational temperatures (red triangles and blue dots for hot and cold lines, respectively). The green box contains the lines between both populations (transition lines). The blue and red solid straight lines are the fits to the corresponding data sets calculated by assuming a weight equal to $1/\sigma^2$, where $\sigma$ is the data uncertainty. The magenta curves are derived from two synthetic spectra assuming that C$_4$H$_2$ is distributed in two isolated shells (solid) and in one thick shell (dashed; see Section 4).
and red
formed at
around 20
beyond 20
few km
scaled. The cold and hot stacks involve lines with
gas expansion velocity. The lines comprising each stack have been previously
planetary nebulae CRL618 in low- and high spectral resolution
Bruget 1991; Shindo et al. 2001
also centered around 8
(ν
with respect to the rms noise, and a covered spectral range that
most probable reasons for this failure are the too weak lines,
Combination bands of molecules, such as C6H2 or C8H2, are
polyynes C4H2 and C6H2 were already found in the proto-
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1; e.g., Fonfría et al. 2015
8 \times 10^{-6}, for the hot and cold populations, respectively, with an
3.1. Searching for Other Polyynes
Polyynes C4H2 and C6H2 were already found in the proto-
Combination bands of molecules, such as C6H2 or C8H2, are
also centered around 8 μm (ν
10 + ν
14 at \approx 1229.6 cm^{-1}, respectively; McNaughton &
compared with the diacetylene abundance distribution derived in Section 3 to explore how
its variation affects the ro-vibrational diagram: (1) C4H2 is distributed in two isolated shells ranging from 15 to 20 Rs, and from 400 to 1000 Rs, and (2) C6H2 is formed at 15 Rs, with a constant abundance up to 400 Rs, adopting another constant value beyond. We chose a distance of 15 Rs as the inner radius of the abundance distribution because a value of 20 Rs results in ro-vibrational diagrams with significantly steeper slopes at high \( E_{\text{low}} \) than the observed data suggest. Noticeable emission components arose in the synthetic lines after assuming shorter distances, which was something unobserved in our spectrum. The results are plotted in Figure 2 as the solid and dashed magenta curves. Both models are compatible with the observational ro-vibrational diagram, but the data seems to be better reproduced with model 1 (plotted in Figure 1). However, the transition lines (\( E_{\text{low}} \approx 100-200 \text{ K} \)) can also be slightly influenced by a low-abundance C4H2 contribution with a rotational temperature of a few hundred K located between \( \approx 20 \) and 400 Rs.

The photochemical models for the outer envelope reproduce reasonably well the abundances of the molecules formed in the shells of C-rich evolved stars, such as IRC+10216 irradiated by dissociating radiation, in particular cyanopolyynes \( \text{HC}_2n+1 \text{N} \) (Millar & Herbst 1994; Millar et al. 2000; Cernicharo 2004; Agúndez et al. 2010, 2017). These models predict that C4H2 (and larger polyynes) arises mostly due to the reaction C2H2+C2H→C4H2+H that can happen after the formation of C2H, which results from the photodissociation of C2H2 (Figure 4). This polymerization process produces polyynes of an increasing length, as can be seen in Figure 5, where we show the radial abundance profiles calculated with the photochemical model of Agúndez et al. (2017). Briefly, this model calculates the chemical evolution of the isotropically expanding gas around a cold star starting at \( \approx 5 \text{ Rs} \) from its center, where the considered parent molecules (H2, CO, C2H2, CH4, C2H4, H2O, N2, HCN, NH3, CS, H2S, SiS, SiO, SiH4, PH3, and HCP) were supposed to be already formed. To reproduce their Atacama Large Millimeter/submillimeter Array observations of carbon chains in IRC+10216, the authors assumed a smooth envelope externally illuminated by the local UV radiation field of Draine (1978) and a ratio

4. Discussion
The preliminary results derived from the ro-vibrational diagram (Section 3) suggest that the C4H2 hot population with a rotational temperature of \( \approx 400 \text{ K} \) arises from regions located around 20 Rs, the star, which is similar to the case of C2H2 (Fonfría et al. 2017). The gas in this region of the envelope could expand at a lower velocity than the rotational velocity (\( \approx 11 \text{ km s}^{-1} \)), although this is still under debate (e.g., Decin et al. 2015; Fonfría et al. 2015). By adopting this gas expansion velocity field in the dust formation zone, the lines formed at \( r \lesssim 20 \text{ Rs} \) are expected to show a velocity shift of a few km s^{-1} compared to those that formed in the outer shells of the envelope. To explore this effect, we have divided the observed lines into three different groups; cold (\( E_{\text{low}} \lesssim 40 \text{ K} \)), hot (\( E_{\text{low}} \gtrsim 240 \text{ K} \)), and transition (40 K \( \lesssim E_{\text{low}} \lesssim 240 \text{ K} \)), stacking the previously scaled lines of each group to improve the signal-to-noise ratio and reduce the random shift of the absorption peak due to the spectral noise and the wavelength calibration uncertainties (Figure 3). The peak absorption of the cold stack, comprised of lines formed in the outer envelope, is shifted \( \approx 1 \text{ km s}^{-1} \) with respect to the hot stack, which was formed by averaging the lines that are supposed to arise in the dust formation zone. The absorption peak of the transition stack, which is composed of the lines mostly formed around the acceleration shell at 20 Rs, is placed between both. This scenario supports the chosen gas expansion velocity profile and the formation of C4H2 in the dust formation zone, which is something unpredicted by the most commonly accepted photochemical models (Millar & Herbst 1994; Millar et al. 2000; Agúndez et al. 2017).

The observed C6H2 lines can be roughly modeled with the code employed by Fonfría et al. (2017) to model the C2H2 spectrum toward IRC+10216. In this model, we adopted (1) the same kinetic and vibrational temperatures used during the analysis of the observational ro-vibrational diagram (Figure 2), (2) a mass-loss rate of \( 2.7 \times 10^{-5} \text{ M}_\odot \text{ yr}^{-1} \) (Guélin et al. 2017), (3) a distance of 123 pc (Groenewegen et al. 2012), and (4) the gas expansion velocity proposed by Fonfría et al. (2015), i.e., \( 1 + 2.5(r/R_\ast - 1) \text{ km s}^{-1} \) if \( 1 \leq r/R_\ast < 5 \), 11 km s^{-1} if \( 5 \leq r/R_\ast < 20 \), and 14.5 km s^{-1} if \( r/R_\ast \geq 20 \). We considered two different models that are compatible with the diacetylene abundance distribution derived in Section 3 to explore how its variation affects the ro-vibrational diagram: (1) C6H2 is distributed in two isolated shells ranging from 15 to 20 Rs, and from 400 to 1000 Rs, and (2) C6H2 is formed at 15 Rs with a constant abundance up to 400 Rs, adopting another constant value beyond. We chose a distance of 15 Rs as the inner radius of the abundance distribution because a value of 20 Rs results in ro-vibrational diagrams with significantly steeper slopes at high \( E_{\text{low}} \) than the observed data suggest. Noticeable emission components arose in the synthetic lines after assuming shorter distances, which was something unobserved in our spectrum. The results are plotted in Figure 2 as the solid and dashed magenta curves. Both models are compatible with the observational ro-vibrational diagram, but the data seems to be better reproduced with model 1 (plotted in Figure 1). However, the transition lines (\( E_{\text{low}} \approx 100-200 \text{ K} \)) can also be slightly influenced by a low-abundance C4H2 contribution with a rotational temperature of a few hundred K located between \( \approx 20 \) and 400 Rs.

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8 \times 10^{-6}, for the hot and cold populations, respectively, with an uncertainty of roughly a factor of 2.
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5. Summary and Conclusions

In this paper, we have presented for first time 24 features of the C$_2$H fundamental band $\nu_8 + \nu_9 (\sigma_u^+)$ observed with a high spectral resolution ($R \approx 85,000$) toward the C-rich star IRC+10216 with the TEXES spectrograph mounted on the 3 m telescope IRTF. From the analysis of this spectrum, we conclude that:

1. There are two C$_2$H$_2$ populations with different rotational temperatures ($420 \pm 120$ and $47 \pm 7$ K). We estimate that these rotational temperatures are typical of shells at $\approx 0.4 \times 20 R_* \approx 7 \times 10^{14}$ cm and $\approx 0.5 \times 500 R_* \approx 1.8 \times 10^{16}$ cm from the central star.

2. The total C$_2$H$_2$ column density is $(2.4 \pm 1.5) \times 10^{16}$ cm$^{-2}$. Only about 20% of it is located at the outer envelope, where the external dissociating radiation field is able to dissociate parent molecules coming from the inner layers of the infrared. The model also fairly well predicts the position of the shell where C$_4$H$_2$ arises and its abundance, which is compatible with our estimate regarding the cold population within a factor of 2. Nevertheless, this does not occur with the abundance of the hot population, which is several orders of magnitude higher than the model prediction in the shell where C$_4$H$_2$ forms. It is noteworthy that, contrary to what occurs with the column density, which is lower for the cold C$_4$H$_2$ population with respect to the hot one, the abundance (with respect to H$_2$ shown in Figure 5) is higher in the outer envelope than in the inner envelope. This apparent incompatibility is explained by the fact that the gas density in the outer shells ($\approx 500 R_*$) is well below its value at $\approx 20 R_*$ from the star.

The disagreement in the abundance of the hot population found between the observations and the model results can be explained in two different ways. First, the high excitation C$_4$H$_2$ lines in the spectrum could be blended with stronger, unidentified lines. However, the intensity of these lines is compatible with the lower excitation lines (Figure 2), which is something that would not happen if they were from other molecules. This leads us to the second way, which suggests that the photochemistry model underestimates the abundance of C$_4$H$_2$ in the inner envelope. This would be in line with the idea that the dissociating external radiation field can reach shells that are significantly closer to the star than what is usually accepted. It is observationally supported by the works based on data acquired in the visible and the far-UV by Leão et al. (2006), Kim et al. (2015), and Matthews et al. (2015). Since the bulk opacity for this external dissociating radiation field is the dusty component of the envelope, dissociating photons can go deeper into the envelope if dust grains are inhomogeneously distributed in clumpy shells. Several authors have demonstrated that the circumstellar chemistry can be significantly modified if a higher density, higher temperature photochemistry and clumpiness are considered (Redman et al. 2003; Woods et al. 2003; Cernicharo 2004; Agúndez et al. 2010). In this scenario, the abundance of C$_3$H is naturally explained at the same time as the existence of H$_2$O in the envelope of a C-rich star (Melnick et al. 2001; Agúndez & Cernicharo 2006; Agúndez et al. 2010; Neufeld et al. 2013) and the discovery of vibrationally excited C$_4$H and C$_2$H$_2$, which are as close to the star as $\approx 10 R_*$ (Yamamoto et al. 1987; Cooksy et al. 2015; Fonfría et al. 2017).

The predicted column density associated to the cold population ($\approx 1.7 \times 10^{15}$ cm$^{-2}$) compared to our estimate ($4.5 \pm 2.9) \times 10^{15}$ cm$^{-2}$) is particularly satisfactory, lying inside the 1σ error interval. This means that the predicted column density of C$_4$H$_2$, which is about half the C$_4$H$_2$ column density, is well estimated, and its spectrum could be detected in

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Diagram showing the reaction network involved in the polymerization of polynes from the dissociation of C$_2$H$_2$ (Agúndez et al. 2017). The solid arrows indicate reactions involving the molecules at the beginning of the arrows and by the arrows (with the same color) that give the products at their ends (e.g., C$_2$H$_2$+C$_2$H=C$_4$H$_2$+H in blue). The dashed arrows mean that the molecules at their beginnings are involved in the processes to which the arrows point at (e.g., C$_4$H$_2$+C$_2$H=C$_6$H$_3$+H). All the reactions in this diagram give a free H atom as a product.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Abundances with respect to H$_2$ of polynes (C$_2$H$_2$) and carbon chains (C$_2$H) in the outer envelope of IRC+10216. The abundance of C$_2$H derived in the current work is included as two horizontal arrows for the detected populations (hot in red and cold in blue) to highlight that we know where the shells with different population start, but we ignore where they end. The coordinate in the vertical axis of these arrows is the C$_4$H$_2$ abundance in each shell. The vertical lines at the beginning of each arrow indicate the positions of the inner boundaries of the shells with the inferred C$_4$H$_2$ populations. The solid and dashed curves are molecular abundances calculated by Agúndez et al. (2017). The hatched regions indicate the uncertainties of the position of the inner boundaries of the C$_4$H$_2$ shells and of its abundance in them.}
\end{figure}

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the envelope. The rest (80%) corresponds to C4H2 formed in the dust formation zone ($r \lesssim 20 R_\star$).

3. The underestimation of the C4H2 abundance predicted by our photochemical model suggests that the molecules in the envelope are photodissociated in shells closer to the star than is commonly assumed. The easiest scenario in which this could happen would involve a clumpy outer envelope where the dust grains density undergoes significant variations between different places.

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References

Agúndez, M., & Cernicharo, J. 2006, ApJ, 650, 374
Agúndez, M., Cernicharo, J., Decin, L., Encarnaz, P., & Teyssier, D. 2014a, ApJL, 790, L27
Agúndez, M., Cernicharo, J., & Güelín, M. 2010, ApJL, 724, L133
Agúndez, M., Cernicharo, J., & Güelín, M. 2014b, A&A, 570, A45
Agúndez, M., Cernicharo, J., Quintana-Lacaci, G., et al. 2017, A&A, 601, 4
Anderson, J. K., & Ziurys, L. M. 2014, ApJL, 795, L1
Bell, M. B., Avery, L. W., & Feldman, P. A. 1993, ApJL, 417, L37
Bernath, P. F., Hinkle, K. W., & Keady, J. J. 1989, Sci, 244, 562
Bohlin, R. C., Savage, B. D., & Drake, J. F. 1978, ApJS, 224, 132
Cernicharo, J. 2004, ApJL, 608, L41
Cernicharo, J., & Güelín, M. 1996, A&A, 309, L27
Cernicharo, J., Güelín, M., & Kahane, C. 2000, A&AS, 142, 181
Cernicharo, J., Heras, A. M., Tiellens, A. G. G. M., et al. 2001, ApJL, 546, L121
Cernicharo, J., McCarthy, M. C., Gottlieb, C. A., et al. 2015, ApJL, 806, L3
Cernicharo, J., Yamamura, I., González-Alfonso, E., et al. 1999, ApJL, 526, L41
Cooksy, A. L., Gottlieb, C. A., Killian, T. C., et al. 2015, ApJS, 216, 30
Decin, L., Richards, A. M. S., Neufeld, D., et al. 2015, A&A, 574, A5
Draine, B. T. 1978, ApJS, 36, 595
Fonfría, J. P., Cernicharo, J., Richter, M. J., et al. 2015, MNRAS, 453, 439
Fonfría, J. P., Cernicharo, J., Richter, M. J., & Lacy, J. H. 2008, ApJ, 673, 445
Fonfría, J. P., Cernicharo, J., Richter, M. J., & Lacy, J. H. 2011, ApJ, 728, 43
Fonfría, J. P., Fernández-López, M., Agúndez, M., et al. 2014, MNRAS, 445, 3289
Fonfría, J. P., Hinkle, K. H., Cernicharo, J., et al. 2017, ApJL, 835, 196
Gredel, R., Lepp, S., Dalgarno, A., & Herbst, E. 1989, ApJL, 347, 289
Groeneewegen, M. A. T., Barlow, M. J., Blommaert, J. D. A. L., et al. 2012, A&A, 543, L8
Güelín, M., & Cernicharo, J. 1991, A&A, 244, L21
Güelín, M., Cernicharo, J., Kahane, C., Gómez-González, J., & Walmsley, C. M. 1987, A&A, 175, L5
Güelín, M., Green, S., & Thaddeus, P. 1978, ApJL, 224, L27
Güelín, M., Patel, N. A., Bremer, M., et al. 2017, arXiv:1709.04738v1
Henkel, C., Matthews, H. E., Morris, M., Terebey, S., & Fich, M. 1985, A&A, 147, 143
Hinkle, K. W., Keady, J. J., & Bernath, P. F. 1988, Sci, 241, 1319
Hillen, M., Paillous, P., Delpech, C., et al. 1995, JMoSp, 174, 116
Kim, H., Lee, H.-G., Mauron, N., & Chu, Y.-H. 2015, ApJL, 804, L10
Lacy, J. H., Richter, M. J., Greathouse, T. K., Jaffe, D. T., & Zhu, Q. 2002, PASP, 114, 153
Leão, I. C., de Laverny, P., Mékarnia, D., De Medeiros, J. R., & Vandame, B. 2006, A&A, 455, 187
Lord, S. D. 1992, NASA Technical Memorandum, 103957
Matthews, H. E., Frielberg, P., & Irvine, W. M. 1985, ApJ, 290, 609
Matthews, L. D., Gérard, E., & Le Bertre, T. 2015, MNRAS, 449, 220
McElroy, D., Walsh, C., Markwick, A. J., et al. 2013, A&A, 550, A36
McNaughton, D., & Bruget, D. N. 1991, JMoSp, 147, 143
McElroy, D., Walsh, C., Markwick, A. J., et al. 2013, A&A, 550, A36
McNaughton, D., & Bruget, D. N. 1991, JMoSp, 150, 620
Melnick, G. J., Neufeld, D. A., Saavik Ford, K. E., Hollebach, D. J., & Asby, M. L. N. 2001, Natur, 412, 160
Millar, T. J., & Herbst, E. 1994, A&A, 288, 561
Millar, T. J., Herbst, E., & Bettens, R. P. A. 2000, MNRAS, 316, 195
Neufeld, D. A., Tolls, V., Agúndez, M., et al. 2013, ApJL, 767, L3
Ohishi, M., Kaifu, N., Kawaguchi, K., et al. 1989, ApJL, 345, L83
Redman, M. P., Viti, S., Cau, P., & Williams, D. A. 2003, MNRAS, 345, 1291
Ridgway, S. T., & Keady, J. J. 1988, ApJ, 326, 843
Rodhain, E. S., Gordon, I. E., Babivok, Y., et al. 2013, JQSRT, 130, 4
Shindo, F., Bénilan, Y., Chaquin, P., et al. 2001, JMoSp, 210, 191
Wakelam, V., Loison, J.-C., Herbst, E., et al. 2015, ApJS, 217, 20
Winnewisser, G., & Walmsley, C. M. 1978, A&A, 70, L37
Woods, P. M., Millar, T. J., Herbst, E., & Zijlstra, A. A. 2003, A&A, 402, 189
Yamamoto, S., Saito, S., Güelín, M., et al. 1987, ApJL, 323, L149

Fonfría et al.