Molecular Gas in 21 and 30 $\mu$m Sources: The 2mm and 1.3mm Spectra of IRAS 21318+5631 and 22272+5435

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Abstract

The carriers of the 21 and 30 $\mu$m emission features in infrared spectra of circumstellar envelopes are a longstanding enigma. In this paper, we present the results of molecular line observations toward two circumstellar envelopes exhibiting the 21 and/or 30 $\mu$m features, IRAS 21318+5631 and 22272+5435. We investigate whether they have unusual gas-phase chemistry and search for a possible gas-phase precursor of the carriers of the two dust features. The spectra cover several discrete frequency ranges of 130–164 GHz and 216.5–273 GHz, resulting in a detection of 13 molecular species and isotopologues in each object. A rotation-diagram analysis is carried out to determine the molecular abundances, column densities, and excitation temperatures. We did not discover any molecular species that would be unexpected in a normal C-rich star. Nevertheless, there exists subtle differences between their molecular abundances. IRAS 22272+5435 shows stronger SiC$_2$ and HC$_3$N lines and weaker SiS lines than IRAS 21318+5631, suggesting that this 21 $\mu$m source is more carbon-rich and has experienced more efficient dust formation. We discuss the potential implications of the results for the carriers of the 21 $\mu$m and 30 $\mu$m features.

Unified Astronomy Thesaurus concepts: Spectral line identification (2073); Circumstellar matter (241); Interstellar molecules (849); Asymptotic giant branch (108); Post-asymptotic giant branch (1287)

Supporting material: extended figures

1. Introduction

Circumstellar envelopes (CSEs) surrounding low- and intermediate-mass evolved stars are a major engine driving the material cycle in the Galaxy. The evolution of CSEs can be divided into three stages: asymptotic giant branch (AGB), protoplanetary nebula (PPN), and planetary nebula (PN), during which atoms and molecules ejected from stellar surface are processed into larger molecules and dust, and disperse into the ISM. With advances in observational techniques, over 70 different gas-phase molecules have been unambiguously detected in CSEs so far (Cernicharo et al. 2011; McGuire 2018). However, the full picture of circumstellar chemistry during AGB–PPN–PN evolution is still far from complete. One challenge is to identify infrared emission features, such as those at 21 and 30 $\mu$m. The two features may contribute to up to 10% and 30% of the total infrared luminosity of CSEs (Volk et al. 2000; Mishra et al. 2015), respectively. Their carriers likely contain essential information on chemical processes in circumstellar environments.

The 21 $\mu$m band, first discovered by Kwok et al. (1989), is a rare feature that has been detected in less than three dozen C-rich PPNs (Hrivnak et al. 2009; Volk et al. 2010; Mishra et al. 2016; Gladkowski et al. 2019). In different sources this feature exhibits an identical peak wavelength (~20.1 $\mu$m) and a remarkably similar profile (Volk et al. 1999). Its central wavelength was measured to be 20.47 ± 0.10 $\mu$m (Sloan et al. 2014). A variety of candidates have been proposed as its carrier, such as SiS$_2$, FeO, TiC, hydrogenated fullerenes, polycyclic aromatic hydrocarbons, hydrogenated amorphous carbon, and nanodiamonds (see, e.g., Posch et al. 2004; Speck & Hofmeister 2004, and references therein), but no consensus has been reached. Some carrier candidates were examined by Zhang et al. (2009c), who found that all of them except FeO are not abundant enough to account for the strong 21 $\mu$m emission, or would produce some sub-features that have never been found in 21 $\mu$m sources. Subsequently, Koike et al. (2017) showed that FeO particles are sensitively affected by oxygen fugacity and temperature, and its laboratory spectra vary depending on defects and disorders, suggesting that FeO is unlikely to be the carrier of the 21 $\mu$m feature. As PPNs represent a very short-lived phase between the AGB and PN stages, the carrier of this feature is presumably associated with a rapid chemical process, or alternatively, is formed in the AGB phase but not excited until the post-AGB phase (Mishra et al. 2016).

The 30 $\mu$m feature is more commonly detected than the 21 $\mu$m one. It has been discovered in C-rich AGB stars, PPNs, and PNs (Forrest et al. 1981; Volk et al. 2002). Although all 21 $\mu$m emitters also exhibit the 30 $\mu$m feature, there is no correlation between their strengths (Omont et al. 1995; Mishra et al. 2015). A statistic study shows that the strengths of the 30 $\mu$m feature correlate with the dust temperature and the metallicity of the host galaxy (Gladkowski et al. 2019). Though several candidate carriers have been discussed (Nuth et al. 1985), solid magnesium sulfide (MgS) is the mostly widely accepted one (Goebel & Moseley 1985). Large variations in the profiles of the 30 $\mu$m feature have been revealed in different sources by Hony et al. (2002), who suggested that this is due to changes in the MgS dust temperature. However, based on energetic and abundance arguments, Zhang et al. (2009d) showed that MgS dust is unlikely to be responsible for the observed feature strength. Their results are supported by a detailed study of the shape and position of the 30 $\mu$m feature (Messenger et al. 2013).

Since 21 and 30 $\mu$m features are detected only in C-rich environments, their carriers are likely associated with carbon
chemistry. Presumably, the routes of gas-phase chemistry and dust formation greatly rely on the physical conditions and evolutionary stages of CSEs. Studying gas-phase molecules in the 21 and 30 μm sources might provide useful clues for the accurate identification of the infrared features. Previous radio observations of these sources mainly focused on strong lines such as CO lines (e.g., Woodworth et al. 1990; Nakashima et al. 2012). In this paper, we report new radio spectra of the gas-phase molecules toward two CSEs, IRAS 21318+5631 and 22272+5435, covering a wide frequency range. These data allow us to investigate the chemical processes in the environments favoring the origin of the two features. IRAS 21318+5631 is an extreme carbon star that reaches the optically obscured supernova phase and is about to leave the AGB stage. Kwok et al. (1999) discovered the 30 μm feature in this object. They also reported the detection of an extremely weak feature resembling the 21 μm feature. This, however, was not confirmed in further measurements (Clément et al. 2005). We therefore do not consider IRAS 21318+5631 a 21 μm source. IRAS 22272+5435 is a PPN exhibiting relatively strong 21 and 30 μm features (Szczcerba et al. 1997). An extremely high C/O ratio (∼12) has been obtained from its optical spectrum (Zacs et al. 1995). The difference in chemical compositions between IRAS 21318+5631 and 22272+5435 might reflect the chemical processes in the short transition phase from AGB to PPN.

This paper is apart of a series of studies of molecular lines in CSEs (He et al. 2008; Zhang et al. 2008, 2009a, 2009b, 2013, 2020; Chau et al. 2012). Here we mainly attempt to investigate the relationship between gas-phase chemistry and unusual infrared behaviors in the post-AGB phase. These studies, combined with the molecular observations of evolved stars by other authors (e.g., Cernicharo et al. 2000; Pardo et al. 2007; Tenenbaum et al. 2010; Edwards et al. 2014, and the reference therein), can provide a more complete picture of circumstellar chemistry during the AGB–PPN–PN transitions. The paper is organized as follows. In Section 2 the 2 mm and 1.3 mm radio spectra toward IRAS 21318+5631 and 22272+5435 are presented. The detected molecules and derived abundances are shown in Section 3. Section 4 contains a comparison of the molecular compositions in different sources and the subsequent chemical implications. The main conclusions are summarized in Section 5.

2. Observations and Data Reduction

The observations at the 2 mm and 1.3 mm windows were carried out in 2009 January and 2014 April with the Arizona Radio Observatory (ARO) 12 m telescope at Kitt Peak and the Heinrich Hertz Submillimeter Telescope (SMT) 10 m telescope at Mt. Graham. The beam-switching mode was used with an azimuth beam throw of 2°. Pointing and focus were checked every 1–2 hr using nearby planets, and typically the pointing offsets were less than 10″. The dual-channel SIS receivers were employed, operated in single-sideband dual polarization mode. The image rejection ratio is typically better than 18 dB. The system noise temperatures were typically 250 K and 400 K for the 2 mm and 1.3 mm bands, respectively. The integration times per tuning step were 2–4 hr. The half power beam widths \( b_h \) of the 12 m telescope and the SMT are about 40″ and 30″ at the observed frequency ranges, respectively. For the 2 mm observations, the spectrometer backends employed are two 256-channel filter banks (FBs) with a channel width of 1 MHz and a millimeter autocorrelator (MAC) with 3072 channels and a 195 kHz resolution. For the 1.3 mm observations, the 2048-channel acousto–optical spectrometer and the 1024-channel Forbes Filterbanks were used simultaneously with a channel width of 500 kHz and 1 MHz, respectively. The temperature scales of the 2 mm and 1.3 mm are given in terms of \( T_R \) and \( T_A \), respectively. The main beam temperature \( T_R \) then was derived by \( T_R = T_{R/\mu}_m \) and \( T_A = T_{A/\mu}_m \), where the corrected beam efficiency \( T_{R/\mu} = 0.8 \) and the main beam efficiency \( T_{A/\mu} = 0.7 \).

The observed frequency range is from 130–164 GHz and 216.5–273 GHz. Our original proposal was to perform an unbiased line surveys at the two windows. However, because of limited observation time and occasional poor weather conditions, we were not able to observe the whole frequency range and there remained several gaps in the observed windows. We prioritized observing the frequency ranges where we previously observed strong lines in other sources (e.g., IRC+10216; He et al. 2008). The strengths of the molecular lines in the two IRAS sources are intrinsically much fainter than those in IRC+10216. The CO (\( J = 2–1 \)) line strengths in the two sources are lower than that in IRC+10216 by two orders of magnitude. If assuming that all the line strengths follow the same scale, we speculate that those lying within the unobserved spectral gaps should be below our detection sensitivity.

The data reductions were done using the CLASS software package in GILDAS\(^1\) following the standard procedure. Discarding the scans due to bad atmospheric conditions and receiver instabilities, we coadded the calibrated spectral data using the rms noise of each spectrum as weights. The spectral regions. The 2 mm and 1.3 mm spectra were smoothed and rebinned to a frequency resolution of 1 MHz and 3 MHz, resulting in typical rms noise levels of ∼5 mK in main beam temperature units.

3. Results
3.1. The Overall Observations

The obtained 2 mm and 1.3 mm spectra, along with line identifications, are presented in Figures 1 and 2, respectively. The features above 3σ noise levels are considered real detections. Although some extremely weak features have peak strengths lower than the 3σ noise level, they are regarded as positive detections if other transitions from the same species are clearly detected. The line identifications are carried out using the archives of molecular line frequencies derived from the theoretical calculations of the JPL catalog (Pickett et al. 1998)\(^2\) and the Cologne database for molecular spectroscopy (CDMS, Müller et al. 2001, 2005).\(^3\) We discover ten molecular species and 3 isotopologues in each source. Positively detected species in both sources include \( \text{C}_2\text{H}, \text{CH}_3, \text{H}_2\text{C} = \text{N}, \text{SiC}_2, \text{CS}, \text{C}^{13}\text{S}, \text{CO}, \text{C}^{13}\text{O}, \text{CN}, \text{HCN}, \text{H}^{13}\text{CN}, \) and HNC. For the first time, \( \text{CH}_3\text{CN} \) is detected in IRAS 22272+5435, confirming its extreme C-rich rich nature.

The overall spectral properties of the two sources are consistent with their C-rich nature. At first glance, there is no essential difference between their spectra and that of the

\(^1\) GILDAS is developed and distributed by the Observatorie de Grenoble and IRAM.
\(^2\) http://spec.jpl.nasa.gov
\(^3\) http://www.ph1.uni-koeln.de/vorhersagen/
prototypical carbon star IRC+10216 obtained by He et al. (2008) and Tenenbaum et al. (2010). But we did not detect SiO and HC$_{15}$N, two molecules with strong transitions in the spectrum of IRC+10216 within the same frequency range. Table 1 shows a full list of line identifications and measurements; columns 1–3 respectively give the frequencies, identified species, and transitions, and the remaining columns list the rms noise levels, the peak and integrated intensities, and the line widths (FWHM) obtained by fitting Gaussian line profiles. For nondetected lines, the upper limits, corresponding to 3$\sigma$ of the peak and integrated intensities, are given.

The most interesting result of our observations is the apparently different relative intensities of the HC$_3$N, SiC$_2$, and SiS lines in the two IRAS sources (see, e.g., the spectral ranges from 163–164, 217.5–218.5, 235.5–237.5, 272–273 GHz in Figures 1 and 2). IRAS 22272+5435 clearly exhibits a number of lines from HC$_3$N and SiC$_2$, while the two molecules are only marginally detected in IRAS 21318+5631. Although the line intensities in IRAS 22272+5435 are generally stronger than those in IRAS 21318+5631, it does not exhibit the SiS emission that is clearly detected in the later source.

### 3.2. Line Profiles

All the lines in IRAS 22272+5435 show a notably narrow single-peaked profile with an FWHM of about 10 km s$^{-1}$, much lower than the typical value of 20 km s$^{-1}$ we previously obtained for other CSEs. No high-velocity wing can be seen for any line. This is compatible with the CO observation of Hrivnak & Bieging (2005), implying that the carrier of the 21 $\mu$m feature could be destructured if there exist high-velocity shocks. The low expansion velocity, together with the fact that 21 $\mu$m sources have high mass-loss rates (Hrivnak & Kwok 1991), indicates a high density, which might favor the condensation of gas-phase molecules and the formation of the carrier of the 21 $\mu$m feature.
In contrast, the molecular lines in IRAS 21318+5631 consistently appear to be broader, with an FWHM ranging from 15–25 km s\(^{-1}\). C\(_4\)H and C\(_2\)H lines show a double-peaked profile. A narrow dip is clearly superimposed on the center of the CO and 13CO lines, which could be attributed to the presence of an outer cold cloud. There is apparently no asymmetrical profile revealed in both sources, suggesting that the gaseous envelopes may have an approximately symmetrical shape.

3.3. Rotation-diagram Analysis

A standard rotation-diagram analysis was performed to derive molecular excitation temperatures and column densities. Under the assumption that all the lines are optically thin and thermalized, and the level populations are in local thermodynamic equilibrium (LTE), the relation between the molecular column density \(N\) and the integrated line intensity of the source \(\int T_d dv\) can be given by

\[
\ln \frac{N_u}{g_u} = \ln \frac{3k}{8\pi^2Ss}\int T_d dv = \ln \frac{N}{Q(T_{\text{ex}})} - \frac{E_u}{kT_{\text{ex}}},
\]

where \(N_u, g_u,\) and \(E_u\) is the population, degeneracy, and excitation energy of the upper level, \(S\) is the line strength, \(\mu\) is the dipole moment, \(\nu\) is the line frequency, \(Q\) is the rotation partition function, and \(T_{\text{ex}}\) is the excitation temperature. Assuming that the source brightness distribution and the antenna beam have a Gaussian profile, the source brightness temperature was obtained by \(T_b = T_b(\theta_b^2 + \theta_i^2)/\theta_i^2\). The source diameter \(\theta_b\) is difficult to determine and may vary from species to species. In this study, according to the CO image of IRAS 22272+5435 by Nakashima et al. (2012), we simply assumed a constant value of \(\theta_b = 5''\) for both sources. Through observing more than one transition from the same molecule, we can deduce its \(T_{\text{ex}}\) and \(N\) using a straight-line fit to \(N_u/g_u\) versus \(E_u/kT_{\text{ex}}\).

The rotation diagrams for the molecules detected in the two CSEs are plotted in Figure 3. There is no significant difference between the obtained \(T_{\text{ex}}\) in the two sources. The resulting \(T_{\text{ex}}\) and \(N\) (or the upper limits) values are given in Table 2. The errors were estimated from the uncertainties of the measurements and fittings. We find \(T_{\text{ex}}(\text{SiC}_2) > T_{\text{ex}}(\text{SiS}) \sim T_{\text{ex}}(\text{HC}_3\text{N}) > T_{\text{ex}}(\text{C}_4\text{H}) > T_{\text{ex}}(\text{CS})\). For both sources, \(T_{\text{ex}}(\text{CS})\) is much lower than the other \(T_{\text{ex}}\) values, probably attributing to the large dipole moment of CS. Some molecules do not have enough transitions to construct the rotation diagrams. We calculated their column densities by assuming the \(T_{\text{ex}}\) values as given in Table 2. It should be noted that for optically thick lines the obtained \(N\) values only represent lower limits.

The molecular fractional abundance relative to \(H_2, f_X\), can be calculated by dividing the molecular column densities by that of \(H_2\). However, to our knowledge, there is no published report on the detection of \(H_2\) lines in the two sources. Davis et al. (2003) failed to detect \(H_2\) emission in IRAS 22272+5631. We thus simply assumed a typical value of \(f(H_2) = 10^{-4}\) for the abundance calculations. Although this assumption is somewhat arbitrary, the introduced uncertainties can be reduced when comparing the relative molecular abundances. Table 2 shows...
| Frequency (MHz) | Species | Transition (Upper–Lower) | TR (mK) | $T_A$ (K) | $\int T_A dV$ (K km s$^{-1}$) | $\Delta V_{P-V}$ (km s$^{-1}$) |
|---------------|---------|--------------------------|---------|---------|-----------------|-----------------|
the obtained \( f_X \) values and the abundance upper limits for nondetected molecules.

### 3.4. Isotopic Ratios

The isotopic ratios in CSEs can be altered by the products of nucleosynthesis in the stellar interior and drudge-up processes during the AGB phase. According to AGB nucleosynthesis theory, \(^{13}\text{C}\) in CSEs can be greatly enhanced (see, e.g., Milam et al. 2009), while the isotopic composition of sulfur is hardly affected. We detected the isotopologues \(^{13}\text{CO}, \text{C}\text{34S}, \text{and H}\text{13CN}, allowing us to estimate the isotopic ratios of carbon and sulfur, and to investigate the nucleosynthetic histories and mixing processes of the two sources. However, as the main lines, \( \text{CO}, \text{CS}, \text{and HCN}, \) are likely to be optically thick, we can only determine the lower limits of the \(^{12}\text{C}/^{13}\text{C}\) and \(^{32}\text{S}/^{34}\text{S}\) ratios, as given in Table 3. The much lower limits of \(^{12}\text{C}/^{13}\text{C}\) with respect to the solar value are unlikely to be fully attributed to the effect of optical depth, and thus indicate the enhancement of \(^{13}\text{C}\) due to nonstandard mixing processes. No difference between the \(^{32}\text{S}/^{34}\text{S}\) ratios in the two IRAS sources, IRC+10216, and the Sun was found, consistent with the prediction of AGB nucleosynthesis theory.

The standard AGB stellar model predicts that \(^{14}\text{N}\) in CSEs can be enhanced through the reactions \(^{13}\text{C}(p, \gamma)^{14}\text{N}\) and \(^{17}\text{O}(p, \alpha)^{14}\text{N}\). This is supported by the observation that the \(^{14}\text{N}/^{15}\text{N}\) ratio in IRC+10216 is much higher than the solar value. Although the \(^{13}\text{C}\) lines in our spectra are below the detection limit, we can roughly estimate the lower limit of the \(^{14}\text{N}/^{15}\text{N}\) ratios based on the \(^{13}\text{C}\text{15N}\)/\(^{13}\text{C}\text{14N}\) lower limit and the assumption that the \(^{12}\text{C}/^{13}\text{C}\) ratios are the same as that in IRC+10216. Our results show that the \(^{14}\text{N}/^{15}\text{N}\) ratios in the two sources appear to be higher than the solar value, supporting the enhancement hypothesis in AGB stars. The \(^{16}\text{O}/^{17}\text{O}\) ratio can also provide insight into the AGB nucleosynthesis history since \(^{17}\text{O}\) can be enhanced by the CNO cycle reactions and \(^{16}\text{O}\) can be consumed through hot bottom burning in AGB stars. Unfortunately, no \(^{17}\text{O}\) line lies within the observed frequency ranges. In summary, we did not find any anomalous isotopic ratio in the 21 and 30 \( \mu \text{m} \) sources.

### 4. Discussion

#### 4.1. Cyanopolyyne Chemistry

In the spectra of IRAS 22272+5435, CN manifests itself as six individual peaks at the 1.3 mm window (Figure 2), which can be divided into three fine-structure groups \( J = 3/2–3/2, \ldots \)
Table 2
Excitation Temperatures, Column Densities, and Abundances with Respect to H2

| Species  | IRAS 21318+5631 |                     | IRAS 22272+5435 |                     |
|----------|----------------|---------------------|-----------------|---------------------|
|          | T_e (K)        | N(cm^-2)            | f_N             | T_e (K)            | N(cm^-2)            | f_N             |
| SiO      | 29(3)          | <4 × 10^{13}        | <8 × 10^{-8}    | 29(3)              | <2 × 10^{13}        | <4 × 10^{-8}    |
| C2H      | 5(1.6)         | 5.1(0.6) × 10^{14}  | 9.4(1.1) × 10^{-7} | 5(1.6)            | 9.1(0.1) × 10^{14}  | 1.5(0.1) × 10^{-4} |
| C2H      | 56(14)         | 6.6(1.4) × 10^{15}  | 1.2(0.3) × 10^{-7} | 56(14)            | 3.6(2.6) × 10^{15}  | 5.9(4.3) × 10^{-6} |
| HC3N     | 7(1.7)         | 7.5(1.7) × 10^{13}  | 1.4(0.3) × 10^{-7} | 7(1.7)            | 2.0(0.3) × 10^{14}  | 3.3(0.5) × 10^{-7} |
| SiC2     | 8(0.3)         | 8.0(0.3) × 10^{13}  | 1.4(0.6) × 10^{-7} | 8(0.3)            | 2.0(0.5) × 10^{14}  | 3.3(0.8) × 10^{-7} |
| SiS      | 57(13)         | 2.1(0.7) × 10^{14}  | 3.9(1.3) × 10^{-7} | 57(13)            | <7 × 10^{13}        | <2 × 10^{-7}    |
| CS       | 15(3)          | 2.8(0.3) × 10^{14}  | 5.2(0.6) × 10^{-8} | 15(3)             | 3.4(0.1) × 10^{14}  | 5.6(0.2) × 10^{-7} |
| C3S      | 5(4)           | 3.4(0.7) × 10^{13}  | 6.3(1.3) × 10^{-8} | 5(4)              | 3.2(0.7) × 10^{13}  | 5.2(1.1) × 10^{-8} |
| CO       | 5(7)           | 5.7(0.1) × 10^{17}  | 1.1(0.1) × 10^{-3} | 5(7)              | 5.2(0.1) × 10^{17}  | 8.5(0.2) × 10^{-4} |
| 13CO     | 5(10)          | 5.4(0.2) × 10^{16}  | 1.0(0.1) × 10^{-3} | 5(10)             | 6.1(0.2) × 10^{16}  | 1.0(0.1) × 10^{-4} |
| CN       | 11(2)          | 1.1(0.2) × 10^{15}  | 2.0(0.4) × 10^{-6} | 11(2)             | 1.4(0.3) × 10^{15}  | 2.3(0.5) × 10^{-6} |
| CH3CN    | 6(2)           | <7 × 10^{13}        | <2 × 10^{-7}    | 6(2)              | 1.0 × 10^{14}       | 1.6 × 10^{-7}   |
| HCN      | 9(0.1)         | 1.9(0.1) × 10^{14}  | 3.5(0.2) × 10^{-7} | 9(0.1)            | 2.4(0.1) × 10^{14}  | 3.9(0.2) × 10^{-7} |
| H13CN    | 7(2)           | 7.2(0.3) × 10^{13}  | 1.3(0.1) × 10^{-7} | 7(2)              | 1.4(0.2) × 10^{14}  | 2.3(0.3) × 10^{-7} |
| HC15N    | 7(2)           | <7 × 10^{12}        | <2 × 10^{-8}    | 7(2)              | <5 × 10^{12}        | <1 × 10^{-8}    |
| HNC      | 7(2)           | 2.7(0.4) × 10^{13}  | 5.0(0.7) × 10^{-8} | 7(2)              | 5.1(0.2) × 10^{13}  | 8.4(0.3) × 10^{-8} |

Notes.
- Numbers in brackets represent error values; colons indicate uncertain values. For optically thick species, the given N and f_N values represent their lower limits.
- Assuming T_e = 57 K.
- Assuming T_e = 84 K.
- Assuming T_e = 54 K.
- The T_e values derived from CS are assumed.

Table 3
Isotopic Abundance Ratios

| Isotopic ratio | Species    | IRAS 21318+5631 | IRAS 22272+5435 | IRC+10216 | Solar |
|----------------|------------|-----------------|-----------------|-----------|-------|
| 12C/13C       | 12CO/13CO  | >12             | >9              | 45 ± 3    | 89    |
| H13CN/H12CN   | >3         | >2              | ...             | ...       | ...   |
| 33S/34S       | 33S/34S    | >8              | >11             | 21.8 ± 2.6| 22.5  |
| 14N/15N       | H15N/H14N  | >27             | >39             | >4400     | 272   |
|                | H13C14N/H12C13N | >292  | >1035       | ...       | ...   |

Notes.
- From the references in Kahane et al. (2000).
- From Lodders (2003).
- Assume that the 12C/13C ratio is the same as in IRC+10216.

J = 3/2−1/2, and J = 5/2−3/2 around 226.3, 226.6 and 226.8 GHz. We find that the intensity ratio between the 226.8 GHz and the 226.6 GHz groups is smaller than 1, significantly different from the intrinsic strength ratio of 1.8. The anomalous CN intensity ratios have been reported in C-rich and O-rich AGB stars (Bachiller et al. 1997b). If one attributed this to the effect of optical thickness, the required line opacity would be unreasonably large. Therefore, following Bachiller et al. (1997b), we interpret the observed anomalies as pumping by optical and/or near-infrared radiation.

HCN and its geometrical isomer HNC are important reactants for producing cyanopolyynes. Although both can be formed through a similar pathway, HCN has lower energy and thus is more stable than HNC. Under certain physical conditions, they can convert to each other. Therefore, the HNC/HCN abundance ratio can reflect the physical conditions that induce the production and isomerization of the two molecules. Johansson et al. (1984) found the HNC/HCN ratio in IRC+10216 to be 0.004, significantly lower than those found in dark cloud cores (>1). This could be attributed to the very limited region in the CSE over which HNC is formed (Nejad & Millar 1987). Our calculations show that the HNC/HCN ratios in IRAS 21318+5631 and 22272+5435 are lower than 0.14 and 0.22, respectively. Assuming that the H13CN/H12CN abundance ratio is equal to the 13C/12C ratio in IRC+10216, we obtain HNC/HCN ratios of 0.0085 and 0.0081 in IRAS 21318+5631 and 22272+5435, respectively. These values are similar to that of IRC+10216. Higher HNC/HCN ratios were observed in PNs (with an average of 0.5; Bachiller et al. 1997a), indicating ongoing chemistry during the AGB–PN–PN transition.

Under the same assumption as above, we obtain the CN/HCN abundance ratios of 0.34 and 0.22 in IRAS 21318+5631 and 22272+5435, respectively. As CN can be significantly produced from HCN through photodissociation in the PPN phases, the CN/HCN abundance ratio can be taken as an indicator of the degree of CSE evolution (Bachiller et al. 1997b). The CN/HCN abundance ratio in IRC+10216 is about 0.12 (Dayal & Bieging 1995), significantly lower than the average value of 9 in PNs (Bachiller et al. 1997a). This reflects the photodissociation from HCN into CN caused by the increasing temperature of the central sources. The CN/HCN
ratios of the two IRAS sources are close to that of IRC+10216, suggesting that the radiation fields of their central stars are not hard enough to substantially affect cyanopolyne chemistry. HC$_3$N is less abundant than CN and HCN in both sources. Because HC$_3$N in CSEs can be produced by CN and/or HCN via neutral–neutral reactions, the HC$_3$N/CN and HC$_3$N/HCN abundance ratios can serve as a tracer of circumstellar evolution. Our calculations show that the HC$_3$N/CN and HC$_3$N/HCN abundance ratios in IRAS 22272+5435 are higher than those in IRAS 21318+5631, indicating an enhancement of longer cyanopolyne molecules during the post-AGB evolution.

4.2. Comparison with Other CSEs

The molecules formed in CSEs depend not only on the parent molecules ejected from inner zones, but also the varying environments driven by various processes such as mass loss, dust condensation, shocks, UV radiation, and so on. Theoretically, a certain process can preferentially enhance or destroy certain molecules over others, and thus certain molecules can potentially serve as tools to investigate the circumstellar environments. However, all the processes are coupled together, making it extremely challenging to identify the key one influencing the abundance of a certain molecule from observations. For that, large number statistics of various molecules in CSEs are critically required. As part of a long-term project of studying circumstellar chemistry, our research group has carried out systematic millimeter-wavelength spectral line surveys of a CSE sample, including AGB stars, PPNs, and PNs (see the reference in Section 1). In order to ascertain whether the spectra of gas-phase molecules can be used to distinguish between the 21 and 30 μm sources and normal C-rich CSEs, we compare the line intensities of the two IRAS sources and other sources obtained in our previous observations. Since all the observations were performed utilizing the same instrumental settings, the systematic uncertainties are minimized when comparing these spectra. Our spectra cover a wide frequency range where lines arising from upper levels with different energies are detected, enabling us to investigate the coupled effects of excitation conditions, optical depths, and molecular abundances on line intensities.

Figure 4 shows the intensity ratios of the lines detected in IRAS 21318+5631 and 22272+5435. The latter clearly exhibits stronger SiC$_2$, C$_2$H, HC$_3$N, H$^{13}$CN, HNC, CN, and CH$_3$CN lines, and weaker SiS and C$_4$H lines. The generally stronger emission from carbon-bearing molecules indicates a more C-rich environment in IRAS 22272+5435. The different H$^{13}$CN/HCN ratios in the two sources can be in part attributed to the effects of optical depth.

In Figure 5 we compare the intensity ratios of the lines detected in the two IRAS sources and those in IRC+10216 and CRL 2688. The millimeter spectra of the latter two CSEs are taken from He et al. (2008) and Zhang et al. (2013). CRL 2688 is a bright PPN that may be completing a transition between the “21 μm phase” and the “normal phase” (Geballe et al. 1992), and thus is the immediate descendant of IRAS 22272+5435. We obtain the mean line-intensity ratios of IRAS 21318+5631 and 22272+5435 over IRC+10216 to be (1.6 ± 1.2) × 10$^{-2}$ and (2.6 ± 2.0) × 10$^{-2}$, respectively, and those over CRL 2688 to be (1.2 ± 0.9) × 10$^{-1}$ and (1.3 ± 0.7) × 10$^{-1}$, respectively. The line intensities in the two IRAS sources are typically 10–100 times fainter than those in IRC+10216 and CRL 2688, presumably due to their larger distances. Although the detected molecules in the two IRAS sources are much less than those in IRC+10216 and CRL 2688, we cannot draw the conclusion that they are less abundant in chemistry.

An inspection of Figure 5 clearly shows that compared to IRAS 21318+5631 and IRC+10216, IRAS 22272+5435 and CRL 2688 show a more similar pattern of the relative intensity ratios of molecular lines. This is compatible with the close evolutionary stages of IRAS 22272+5435 and CRL 2688. If
taking the average intensity ratios as the reference, the two PPNs both exhibit stronger HC$_3$N and CH$_3$CN emission, and weaker SiS emission with respect to IRAS 21318+562 and IRC+10216, suggesting that larger molecules are synthesized during the AGB–PPN transition. Nevertheless, there exist subtle differences between the intensity ratio patterns of IRAS 22272+5435 and CRL 2688, with the former showing enhancements of SiC$_2$ and C$_2$H. This might be a consequence of the extremely C-rich environment of this strong 21 μm source.

Compared to IRAS 22272+5435, the intensity ratio pattern of IRAS 21318+5631 is more similar to that of IRC+10216, which can be told from the standard deviations of the mean intensity ratios as shown by the dashed lines in Figure 5. Nevertheless, it exhibits relatively weaker emission from Si-bearing compounds, suggesting that this extreme carbon star has suffered from efficient dust condensation causing depletion of gas-phase Si-bearing molecules. The same properties have been found in CRL 3068, a prototypical extreme carbon star in our sample (Zhang et al. 2009b).

In order to obtain a useful indicator of the evolutionary stages of CSEs, we examine the abundance ratios of various molecules detected in our sample. We find that the CSEs in different evolutionary stages can be separated with the SiC$_2$/SiS and SiS/HC$_3$N abundance ratios, as shown in Figure 6. During the evolution from AGB stars to extreme carbon stars, circumstellar SiS and SiC$_2$ have a photospheric origin, and can be continually enhanced through stellar winds. When the extreme carbon stars reach the PPN phase, the envelopes greatly expand and are detached from the central stars. Increasing photochemical reactions cause the enhancement of SiC$_2$ and HC$_3$N. At the same time, Si-bearing molecules are deposited onto dust grains because of their refractory nature. These processes can take place on a timescale of $10^3$–$10^4$ years. Such a picture of chemical evolution is roughly sketched in Figure 6.
C-bearing compounds, and this 21 \( \mu m \) source does not show SiS and SiO lines that are usually observed in C-rich CSEs. Hrivnak & Kwok (1991) detected strong molecular bands of pure carbon molecules \( C_2 \) and \( C_3 \) in this source, which might be the major precursor of carbon dust. These observations demonstrate a remarkably C-rich environment of IRAS 22272+5435. The extreme C-rich nature can also be confirmed by the high \( H^{13}CN/^{13}CO \) abundance ratio. The HCN/CO line intensity has been found to be a good indicator of the C/O (Omont et al. 1993) in that HCN molecules are formed by the remaining carbon atoms that are not locked in CO. The abundance ratio of the less optically thick isotopologues, \( H^{13}CN/^{13}CO \), in IRAS 22272+5435 is about two times larger than that in IRAS 21318+5631, indicating a higher C/O ratio. It is therefore a natural speculation that the carrier of the 21 \( \mu m \) feature is very likely to be carbon-dominant materials, such as carbon nanotubes and fullerene derivatives.

In order to understand the environments favoring the formation and survival of the carrier of the 21 \( \mu m \) feature, we should investigate the molecules not restricted to C-bearing ones. Schöier et al. (2007) found that the abundance of SiS in CSEs increases with increasing C/O ratio, which can be explained in terms of photospheric LTE chemical models. In contrast to this scenario, IRAS 22272+5435 exhibits nondetection of SiS and a high C/O ratio. On the other hand, Schöier et al. (2007) showed a tendency of decreasing SiS abundance with increasing density of the wind, which reflects the freeze-out onto dust grains. The remarkably low expansion velocity (\( \sim 10 \text{ km s}^{-1} \); Nakashima et al. 2012) in IRAS 22272+5435 indicates a high density of the wind. As a result, we can conclude that SiS has been heavily adsorbed onto dust grains in this 21 \( \mu m \) source. Therefore, IRAS 22272+5435 is characterized by high dust condensation efficiency, so that surface reactions, such as hydrogenation of fullerene clusters, probably play an important role in the formation of the carrier of the 21 \( \mu m \) feature.

It is possible that the incorporation of Si into dust grains could produce solid state Si-bearing materials emitting a spectral signature at a position around 21 \( \mu m \), such as silicon disulfide in the form of independent grains, sulfurized SiC, and mantles on other grains (Goebel 1993), silicon carbide with N or C impurities (Speck & Hofmeister 2004), and oxidized SiC (Posch et al. 2004). However, it is hard to understand why These Si-bearing materials are formed exclusively in C-rich environments and can survive only on a very short PPN timescale. Probably, the Si-bearing materials and the carbon-dominant carrier of the 21 \( \mu m \) feature have a core-mantle structure or stick together in an aggregate structure.

Zhang et al. (2009c) and Li et al. (2013) examined several Ti-, S-, Si-, and Fe-based materials that have been proposed as the carrier candidates of the 21 \( \mu m \) feature, and found that the available abundances of these elements are too low to be responsible for the 21 \( \mu m \) feature. The hydrides of fullerenes (fulleranes) have been proposed as the carrier of the 21 \( \mu m \) feature (Webster 1995; Zhang 2020). However, the emission peaks of fullerenes shift from 19–20 \( \mu m \) depending on the degree of hydrogenation. This is inconsistent with the observations in which the peak wavelengths of this feature are nearly identical in different sources. Nevertheless, we cannot rule out the possibility that under special conditions, some fullerene derivatives or fulleranes, probably those that are most resistant to UV radiation, could be more favorably formed, and a “magic” combination of these materials can contribute to the observed peak. Zhang (2020) found that a tuned combination of fullerene isomers is able to match the 21 \( \mu m \) feature. Fullerenes could be readily dehydrogenated by UV irradiation or shocks, compatible with the short survival timescale of the 21 \( \mu m \) feature. Geballe et al. (1992) showed that the 21 \( \mu m \) feature sources also exhibit remarkably strong 3.4–3.5 \( \mu m \) emission. The features near 3.4–3.5 \( \mu m \) can be in part attributed to the C-H stretching modes of fulleranes (Zhang & Kwok 2013), seemingly supporting the idea that the 21 \( \mu m \) feature is to some extent relevant to fulleranes.

The remarkably narrow line widths and strong 21 \( \mu m \) feature in IRAS 22272+5435 are rare among CSEs. Is this behavior related to the 21 \( \mu m \) phenomenon? The slow expansion of the envelope can create a dense zone where the dust formation and solid surface reactions are efficient. Such an environment might favor the formation of the carrier of the 21 \( \mu m \) feature. On the other hand, we reasonably conjecture that the carrier is so fragile that it could be readily destroyed by accelerated stellar winds. Schöier et al. (2006) found that the abundance of SiO in C-rich CSEs is commonly higher than that predicted by equilibrium stellar atmosphere chemistry, and attributed this to a shock-induced nonequilibrium chemistry. As a result, the nondetection of SiO in IRAS 22272+5435 probably indicates the absence of shocks, which might be a necessary condition for the survival of the carrier of the 21 \( \mu m \) feature.

Regarding the carrier of the 30 \( \mu m \) feature, we could hardly draw valid conclusions from our observational results. It is conceivable that the carrier of the 30 \( \mu m \) feature should be negatively correlated with its gas-phase precursor in abundance. IRC+10216 is a stronger 30 \( \mu m \) source than...
IRAS 21318+5631 and IRAS 22272+5435 (Hony et al. 2002). Figure 4 shows that Si-containing molecules in the two IRAS sources are much more depleted than those in IRC+10216, seemingly suggesting that Si-containing molecules are unlikely to be the gas-phase precursor of the carrier of the 30 µm feature. Begemann et al. (1994) and Hony et al. (2002) presented plausible evidence supporting MgS as the carrier of the 30 µm feature. If this was the case, the strength of the 30 µm feature would be predominantly governed by the abundance of S because Mg is more abundant than S. According to the chemical equilibrium calculations of CSEs with a high C/O ratio (Agundez et al. 2020), carbon is first condensed in the most inner regions, followed by SiC and then a variety of Si-containing minerals, while the condensation of MgS occurs in very outer regions. The theoretical study of Zhukovska & Gail (2008) suggested that precipitation on SiC grains is the most promising mechanism of solid MgS formation, and if no SiC core is formed beforehand, the MgS condensation is inefficient until gas-phase SiS molecules are significantly converted into solid SiC. If the 30 µm feature arises from MgS, what is its possible gas-phase precursor? The abundance and direct condensation of gas-phase MgS are negligible in C-rich CSEs. Goebel & Moseley (1985) suggested that MgS can be efficiently synthesized through the surface reaction of Mg and H2S, although H2S is relatively under-abundant in C-stars. Through observational studies of CSE samples, Smolders et al. (2012) and Massalkhi et al. (2019), respectively, found that there are anti-correlations between the strength of the 30 µm feature and the abundances of SiS or CS, and thus concluded that condensed MgS is formed from gas-phase SiS or CS molecules. Further radio observations of more gas-phase molecules in larger samples could help to identify the gas-phase precursor of the carrier of the 30 µm feature.

Although the MgS hypothesis has undergone relatively little debate, Zhang et al. (2009d) argued that the available MgS mass is insufficient to be responsible for the 30 µm feature. Lombaert et al. (2012) reported that the “mass problem” can be solved if MgS is present on the outer layer of grains and has thermal contact with amorphous carbon and SiC. Nevertheless, the candidate carriers proposed by far do not provide an explanation for the observational results that all 21 µm emitters exhibit the 30 µm feature but there is no strict correlation between the strengths of the two features. Laboratory spectra suggested that the amorphous hydrocarbon with mixed sp²/sp³ bonds can emit a prominent feature around 30 µm (Grishko et al. 2001). On the other hand, Zhang & Kwok (2013) and Otsuka et al. (2014) found that fullerene-containing PNs and PPNs generally exhibit a strong 30 µm feature, suggesting that photochemical processing of amorphous hydrocarbons might lead to fullerene formation (García-Hernández et al. 2010; Micelotta et al. 2012). Experiments have revealed that fullerenes such as C₆₀H₃₆ can be rapidly synthesized through mixing fullerenes and hydrogen atoms (Iglesias-Groth et al. 2012), while moderately hydrogenated fullerenes can produce strong bands near 21 µm (Webster 1995; Zhang 2020). As such, we propose the highly speculative conjecture that the 21 µm and 30 µm features might be related to amorphous hydrocarbons. The 30 µm feature originates from the amorphous hydrocarbons (Grishko et al. 2001), or alternatively from the thermal contact of MgS and amorphous hydrocarbons (Lombaert et al. 2012). During the evolution of CSEs, once conditions are favorable, the amorphous hydrocarbons partially form the fullerene isomers emitting the 21 µm feature, which quickly vanish due to UV- or shock-induced dehydrogenation. This seems to offer a plausible explanation for the rarity of the 21 µm phenomenon and the observational correlation between the 21 and 30 µm sources.

5. Conclusions

We present 2 mm and 1.3 mm observations toward an extreme carbon star harboring the 30 µm feature, IRAS 21318+5631, and a PPN harboring the 21 and 30 µm features, IRAS 22272+5435. Our main goal is to investigate the relationship between the carriers of the 21 and 30 µm features and gas-phase chemistry, as well as to search for their gas-phase building blocks. Although the infrared spectra of the two IRAS sources show unusual emission features, their radio spectra are generally consistent with those of usual C-rich CSEs. Almost all the detected species are carbon-based. We did not detect any unexpected gas-phase molecules. There is no evidence that their isotopic ratios differ from other C-rich CSEs.

We compare the spectra of the two IRAS sources with those of other CSEs we previously obtained using the same instrument settings. The results show that the 30 µm sources do not exhibit unusual molecular spectra behavior, thus we cannot distinguish 30 µm sources from normal CSEs based upon radio spectra only. However, the 21 µm source exhibits relatively narrower line widths, stronger emission from long carbon-chain molecules, and nondetection of SiS and SiO. We infer that the formation of the carrier of the 21 µm feature requires an extreme C-rich and dusty environment, and tentatively assign it as fragile carbon-dominant compounds formed on surfaces of dust grains, such as fullerenes; while the carrier of the 30 µm feature might be related to amorphous hydrocarbons. Further observations of a larger sample of 21 and 30 µm sources are needed to reach firm conclusions.

It is shown that the millimeter spectra can serve as a useful indicator of the evolutionary stages of CSEs. The different molecule abundances in different CSEs may reflect the gas and dust processes, the alterations of chemical drivers, and/or different properties of their progenitor stars. Wide frequency-coverage observations of a large sample of CSEs with diverse properties allow us to assign a “circumstellar spectral classification” in the radio window. The current study based on very small number statistics is a small step toward achieving this ultimate goal.

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