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METHYLPOLYYNES AND SMALL HYDROCARBONS IN CRL 618

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ABSTRACT

We report on the detection with the *Infrared Space Observatory* of strong infrared absorption from NH_3 and C_2H_4 in CRL 618. The observed NH_3 and C_2H_4 bands arise from a region with kinetic temperatures ≈ 200 K, i.e., the dense gas in the photodissociation region associated to the dense torus surrounding the central star, as was the case for the polyynes and cyanopolyynes (see the companion Letter). Several absorption bands, probably arising from small gas-phase hydrocarbons, are observed between 5.5 and 11 μm . Two of these species have been identified with the 30 m IRAM telescope as the methylpolyynes $\text{CH}_3\text{C}_2\text{H}$ and $\text{CH}_3\text{C}_4\text{H}$. However, the absorption around 6.2 μm is particularly broad and could arise from the combination of these small hydrocarbons and from the aromatic $\text{C}=\text{C}$ stretching of polycyclic aromatic hydrocarbons of moderate size. These bands and those associated to the polyynes, cyanopolyynes, methylpolyynes, and benzene are not present in the infrared spectrum of the asymptotic giant branch star IRC +10216.

Subject headings: circumstellar matter — infrared: general — ISM: molecules — line: profiles — stars: individual (CRL 618, CRL 2688, NGC 7027)

1. INTRODUCTION

The large abundance of acetylenic chains, cyanopolyynes, methane, methylpolyynes, and the detection of benzene in CRL 618 (see our companion Letter, Cernicharo et al. 2001) indicate that during the evolution from the asymptotic giant branch (AGB) to the proto-planetary phase, C-rich stars will produce significant amounts of complex organic molecules. It is surprising that IRC +10216, being so particularly rich in radicals, has undetectable amounts of C_4H_2 , C_6H_2 , and benzene (see Fig. 3 of Cernicharo et al. 1999). Obviously, the physical conditions are very different. In CRL 618, Herpin & Cernicharo (2000) have detected water vapor and OH. They discuss the formation of these molecules as the result of CO photodissociation in the photodissociation region (PDR) that surrounds the H II region and of the destruction of molecules in the shocks associated with the high-velocity winds of CRL 618. It is probably in the same C-rich PDR that the formation of polyynes, benzene, cyanopolyynes, and other complex molecules has started from the photolysis of C_2H_2 and CH_4 . Similar physical processes also lead to the formation of radicals in the external regions of IRC +10216 through the action of the UV photons from the galaxy. In CRL 618, these processes occur in the inner region at much higher densities [$n(\text{H}_2) > 10^7 \text{ cm}^{-3}$] and with a much higher UV flux. Hence, all timescales are shortened compared to the external layers of IRC +10216. Therefore, we could expect the presence of other complex molecular species in CRL 618. In this Letter we report on the detection with

the *Infrared Space Observatory* (ISO)⁸ of strong absorption from NH_3 and C_2H_4 . Several absorption features in the mid-infrared spectrum of CRL 618 have also been detected, and we attribute them to the infrared bands of small hydrocarbons. We report on the identification at radio wavelengths of two of these species: methylacetylene ($\text{CH}_3\text{C}_2\text{H}$) and methylidyne ($\text{CH}_3\text{C}_4\text{H}$).

2. OBSERVATIONS

The ISO observations related to CRL 618 have been described in our companion Letter (Cernicharo et al. 2001). The data analyzed in this work are shown in Figures 1 and 2. The 30 m data were taken between 1999 and 2000 during the completion of a full spectral survey of CRL 618 at $\lambda = 3$, 2, and 1 mm. All the observations were performed using the wobbler switching mode. The secondary mirror was tilted every 2 s to produce a pointing change in the sky of $\pm 60''$. The resulting baseline in all the observations was extremely flat. The observations were calibrated using two absorbers at different temperatures. These data are being complemented by a systematic frequency sweep with the Caltech Submillimeter Observatory telescope at frequencies above 300 GHz. The 30 m data related to $\text{CH}_3\text{C}_2\text{H}$ and $\text{CH}_3\text{C}_4\text{H}$ are shown in Figure 3. The full frequency sweep will be presented elsewhere.

3. RESULTS AND DISCUSSION

In the companion Letter (Cernicharo et al. 2001), we report on the detection of several infrared bands around 15 μm corresponding to the bending modes of C_2H_2 , HCN, C_4H_2 , C_6H_2 , HC_3N , HC_5N , and benzene. The mid-infrared spectrum of CRL 618 between 7.2 and 9.7 μm is shown in Figure 1. Figure 1a shows that the region between 9 and 11 μm is full of absorption bands. The large number of strong and narrow features prompted us to search for molecules like NH_3 and C_2H_4 that have a large number of Q -subbranches. The modeling of this spectral region

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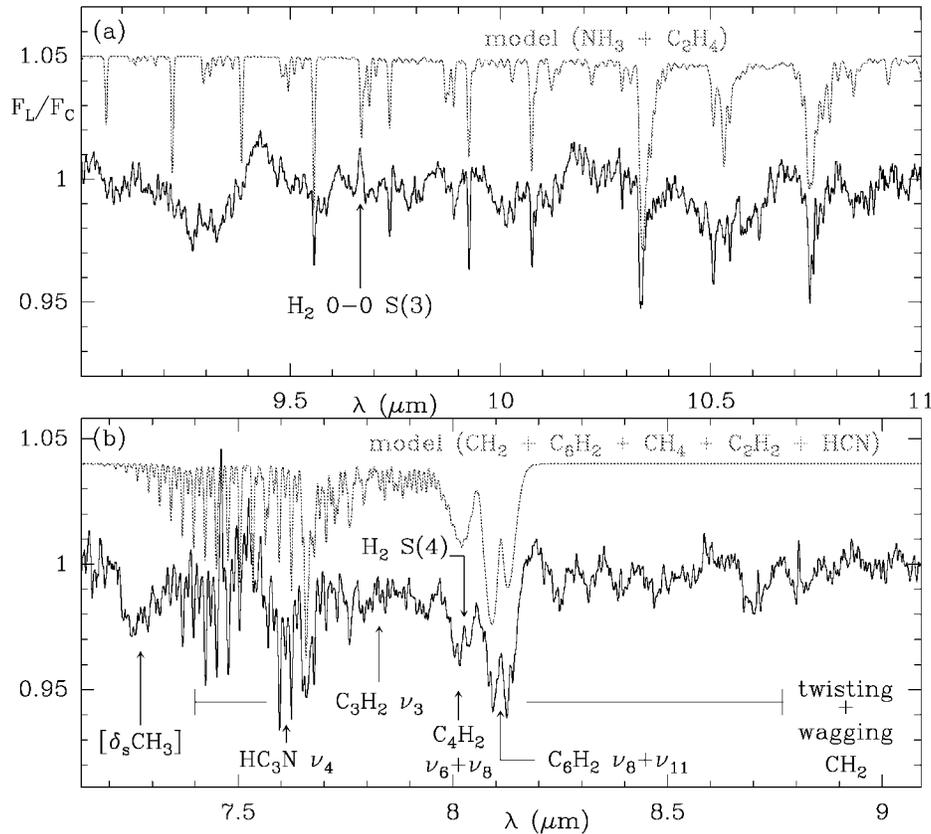


FIG. 1.—Mid-infrared spectrum of CRL 618 at selected wavelengths. The thin line in each panel corresponds to the model results discussed in the text. The feature at $7.27 \mu\text{m}$ corresponds to the symmetric bending of CH_3 . The broad range of absorption bands produced by wagging and twisting of CH_2 in small hydrocarbons is indicated by the horizontal line (Silverstein & Webster 1998).

in CRL 618 used the HITRAN database (Rothman et al. 1993) with $T_K = 200 \text{ K}$ and the same line width already considered for the other species. The column density we derive for ammonia and ethylene is 3×10^{16} and 5×10^{16} , respectively. Martín-Pintado et al. (1993) have derived from radio observations of ammonia $N(\text{NH}_3) \approx 4 \times 10^{16} \text{ cm}^{-2}$, which compares very well with our result. The agreement in position and intensity of the

NH_3 Q -subbranches is excellent but we see that many broad absorption features still remain to be identified, and the same happens in the region between 7 and $9 \mu\text{m}$. Here the combination bands $\nu_6 + \nu_8$ of C_4H_2 and $\nu_8 + \nu_{11}$ of C_6H_2 are clearly detected (see Fig. 1b and Cernicharo et al. 2001). Methane also presents strong absorption lines in this wavelength domain. The best model for CH_4 corresponds to a column density of $7 \times 10^{16} \text{ cm}^{-2}$. A cold component, $T_K = 70 \text{ K}$, was also included to fit the intensity of some of the narrow features around $7.5 \mu\text{m}$. This cold methane could arise from the external layers of the circumstellar envelope. The model shown in Figure 1b also includes the combination bands $\nu_4 + \nu_5$ of C_2H_2 and the $2\nu_2^0$ band of HCN. These features appear between the absorption produced by CH_4 and that of the polyacetylenes. The region above $8 \mu\text{m}$ (see Fig. 1b) presents some weak bands that certainly arise from heavy species and will be discussed below.

Figure 2 shows the $5.3\text{--}7.2 \mu\text{m}$ spectra of CRL 618, the bright planetary nebula NGC 7027, and the post-AGB object CRL 2688. The spectrum of CRL 618 shows a weak and broad absorption feature (10%) centered around $6.25 \mu\text{m}$ that appears in emission in the other two objects, in which it is generally attributed to the IR fluorescence of UV-pumped polycyclic aromatic hydrocarbon (PAH) molecules (see Tielens et al. 1999 for a recent review). Many abundant molecular species present in CRL 618, like CCH, C_3H_2 , H_2CO (Cernicharo et al. 1989), CH_3CN , NH_3 (Martín-Pintado et al. 1993; this Letter), etc., have vibrational transitions in this range, and we estimate that they will produce absorption depths of $\approx 1\%$. Even H_2O (Herpin & Cernicharo 2000) could produce $\approx 1\text{--}1.5\%$ narrow-line

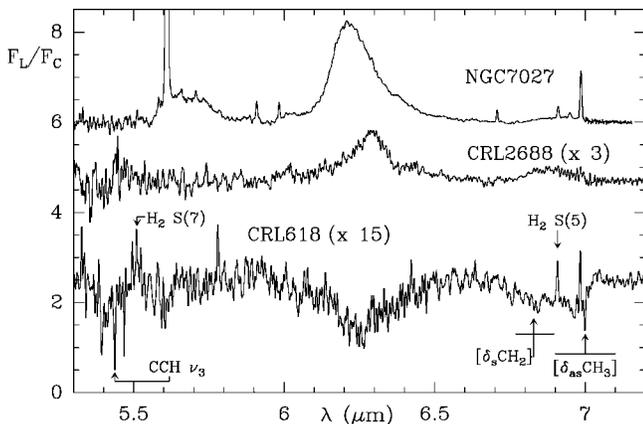


FIG. 2.—Mid-infrared spectra of NGC 7027, CRL 618, and CRL 2688 around $6.2 \mu\text{m}$. Pure rotational lines of H_2 in its $\nu = 0$ state are indicated. The typical wavelength range for the CH_3 asymmetrical bending and for scissoring methylene (CH_2) vibrations of alkanes are indicated (Silverstein & Webster 1998).

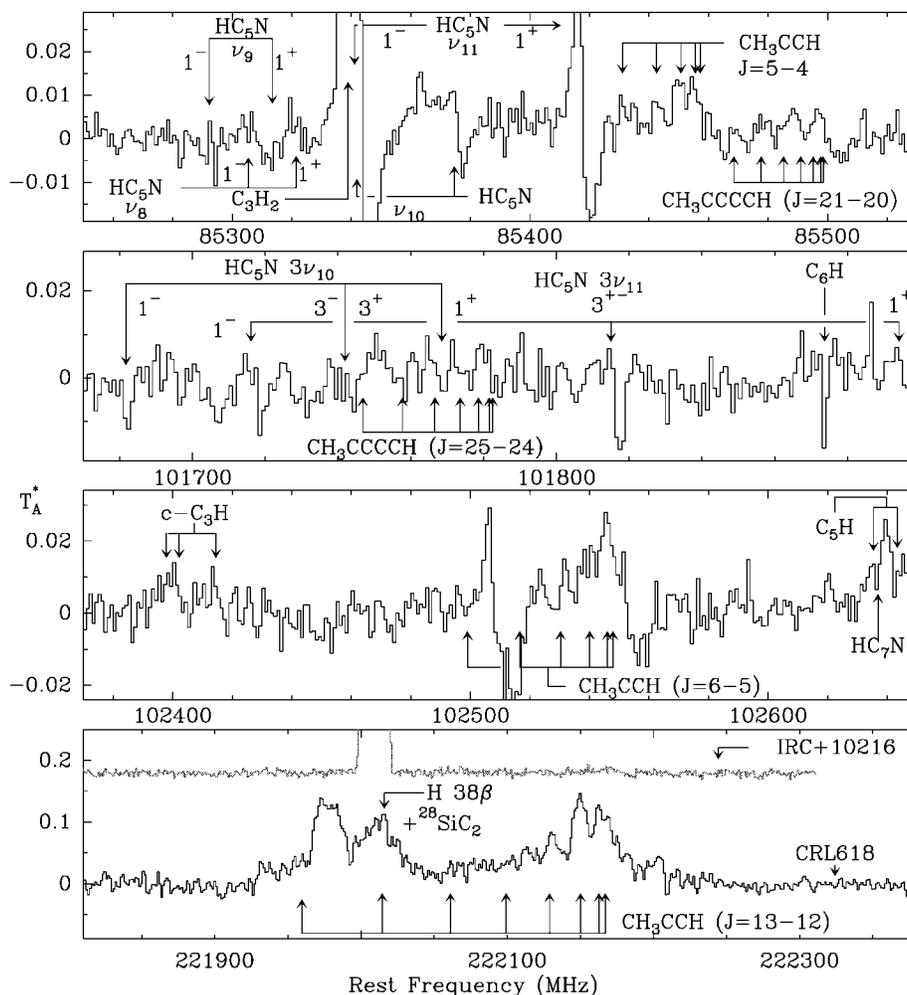


FIG. 3.—30 m IRAM telescope spectra of CRL 618 at selected frequencies. The bottom panel shows, for comparison purposes, the spectra of IRC +10216 and CRL 618 at the same frequency, with an arbitrary vertical-axis shift. The identified species are indicated by arrows. Note the P Cygni profiles of the pure rotational lines of HC_5N in the ν_{11} and $3\nu_{11}$ vibrational states.

absorptions in its $6\ \mu\text{m}$ bending mode. The observed absorption is, however, too large and intense to be explained by these molecules alone. Despite a general resemblance in the three objects, the absorption features in CRL 618 seem wider than the emission in NGC 7027 and CRL 2688. We could expect just the opposite as the emission process broadens the emission feature relative to the low-temperature absorption feature. Solid-state absorption bands, on the other hand, may well be broader than molecular PAHs due to the disorder inherent to amorphous materials. Aromatic molecules, such as PAHs, dust with an aromatic character, such as hydrogenated amorphous carbon, and small molecules with $\text{C}=\text{C}$ bonds show the $6.2\ \mu\text{m}$ band. Whether the carrier of this absorption feature in CRL 618 is a series of molecular-sized species or has dust grain dimensions is unclear. We note that while in NGC 7027 the emission appears at $6.2\ \mu\text{m}$ in CRL 2688, it is shifted to $6.3\ \mu\text{m}$. In CRL 618 the absorption maximum lies in between both wavelengths.

Among the three objects, only CRL 618 shows a forest of absorption bands above $5.5\ \mu\text{m}$ (see Figs. 1 and 2), which suggests that several gas-phase molecular species are producing absorption in the mid-infrared and contributing also to the broad $6.2\ \mu\text{m}$ absorption. Three of these bands can be easily identified as the symmetrical (δ_s) and asymmetrical (δ_{as}) bending of

methyl groups and as the scissoring δ_{sc} of methylene groups in small hydrocarbons. The wagging and twisting of the methylene group in many hydrocarbons produce a large number of weak bands in the range $1100\text{--}1350\ \text{cm}^{-1}$ ($7.4\text{--}9.1\ \mu\text{m}$; Silverstein & Webster 1998). It is thus tempting to look for molecules containing these groups. The best way to identify them, assuming they have a permanent dipole moment, is through the observation of their pure rotational lines.

The 30 m IRAM telescope observations of CRL 618 are characterized by a forest of lines showing P Cygni profiles at 3 and 2 mm and emission profiles at 1 mm. Most of these lines correspond to the pure rotational transitions of HC_3N , HC_5N , and its ^{13}C substituted species in highly excited vibrational states and will be analyzed in a forthcoming paper (J. Cernicharo et al. 2000, in preparation). The comparison of the radio data of IRC +10216 and CRL 618 is particularly interesting. The species detected in IRC +10216 are also detected in CRL 618 without any indication of P Cygni profiles or any enhancement of their abundance (they arise from the external layers of the circumstellar envelope of CRL 618). In CRL 618, however, many additional lines are present. In particular, several rotational transitions of CH_3CCH and $\text{CH}_3\text{C}_4\text{H}$ have been identified in our frequency sweep of this object. Figure 3 shows three rotational transitions of methylacetylene and two of meth-

ylodiacetylene, the latter being at a 6σ level. In the bottom panel of Figure 3 we can see that CH_3CCH is not detected in IRC +10216 at a very low noise level. Methylpolyynes are produced in CRL 618 in a much more efficient way than in IRC +10216, as was the case for polyynes and cyanopolyynes.

Using a large velocity gradient code, adopting the collisional cross sections of CH_3CN (Green 1986) for methylacetylene, and assuming a size of $1''5$ for the emitting region, we derive $T_k \approx 200$ K, $N(\text{CH}_3\text{CCH}) = 1.810^{16} \text{ cm}^{-2}$, and $N(\text{CH}_3\text{C}_4\text{H}) = 8 \times 10^{15} \text{ cm}^{-2}$. Hence, these species should contribute to the infrared absorption observed with *ISO*. In particular, the broad absorption found in the previous Letter around the bending mode of triacetylene could be partially due to CH_3CCH .

The infrared data can also be used to discard certain classes of molecules. Cumulated alkenes ($\text{H}_2\text{CC}_n\text{CH}_2$) will produce absorptions between 1900 and 2000 cm^{-1} associated with the asymmetrical $\text{C}=\text{C}$ stretching that is not present in the CRL 618 data. In addition, these species will have strong absorption around $600\text{--}800 \text{ cm}^{-1}$, which is missing after the identification of all narrow features around $15 \mu\text{m}$ (see Cernicharo et al. 2001). Only the first member of this family, ethylene (C_2H_4) seems to be abundant in CRL 618. Alkanes do not have strong absorption above $7.5 \mu\text{m}$. The lightest members (ethane, propane) produce an overlap of the δ_s and δ_{as} bending of CH_3 and of the δ_{sc} of CH_2 . These molecules, giving our spectral resolution, could show barely resolved narrow lines over a broad absorption background. Heavier alkanes will show absorption without detailed rotational structure at the frequencies of the δ_s and δ_{as} bending of CH_3 and between 3.25 and $3.4 \mu\text{m}$. When the length of the chain increases, the δ_s mode decreases in intensity being as low as one-third of the δ_{as} for $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ ($n > 7$). Monosubstituted alkanes [$\text{CH}_3\text{CHCH}_3(\text{CH}_2)_n\text{CH}_3$] produce a large number of absorption bands between 7.4 and $10 \mu\text{m}$. These species have similar intensities in their δ_s and δ_{as} CH_3 bending modes. Branched-chain alkenes, for example, $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$, will produce low absorption above $12 \mu\text{m}$ in their trans-configuration. Their cis-configuration, however, can be discarded, as they will show strong absorption above $12 \mu\text{m}$. We suggest that a series of relatively small alkanes, branched-chain alkanes and alkenes, unstrained cycloalkenes, unsaturated aromatic, and acetylenic species are responsible for the forest of bands shown in Figures 1 and 2. They certainly contribute to the absorption at $3.2\text{--}3.4 \mu\text{m}$ reported by Lequeux & Jourdain de Muizon (1990) and by Chiar et al. (1998), which is characteristic of saturated

aliphatic hydrocarbons. Branch-substituted alkenes and cycloalkenes will also produce absorption around $6.2\text{--}6.3 \mu\text{m}$. The problem in identifying these species is that, even at very high spectral resolution, they will show little rotational structure. These molecules have several low-energy vibrational levels producing hot bands, and often they also have strong combination bands appearing around the fundamental ones. Moreover, small hydrocarbons have many isomers with similar frequencies (within a few per centimeter) for their vibrational transitions. Finally, all these species will show a large line density. As the line width in CRL 618 is large, the rovibrational lines from these bands will overlap. As a consequence, the resulting spectrum from a few of these species will show little rotational structure. The $6.2 \mu\text{m}$ feature could have some contribution from these species and from large C-rich molecules like PAHs. Chiar et al. (1998) have observed a weak $3.3 \mu\text{m}$ emission feature off-peak in their spectrum of CRL 618, which provides some support for a contribution to the $6.2 \mu\text{m}$ band from PAH molecules.

The formation of long polyynes in the peculiar environment of CRL 618 can be understood from the photolysis of acetylene. The reactions $\text{C}_2\text{H}_2 + h\nu \rightarrow \text{C}_2\text{H} + \text{H}$ and $\text{C}_2\text{H} + \text{C}_{2n}\text{H}_2 \rightarrow \text{C}_{2n+2}\text{H}_2 + \text{H}$ are the path for the growth of acetylenic chains (Millar & Herbst 1994; Millar, Herbst, & Bettens 2000; Glassgold 1996). Polyynes longer than C_6H_2 could condensate or polymerize easily. The photolysis of methane $\text{CH}_4 + h\nu \rightarrow \text{CH}_2 + \text{H}_2$ could lead to the formation of methylpolyynes through the reactions $\text{CH}_2 + \text{C}_{2n}\text{H}_2 \rightarrow \text{H}_2\text{CC}_{2n-1}\text{CH}_2$ followed by $\text{H} + \text{H}_2\text{CC}_{2n-1}\text{CH}_2 \rightarrow \text{CH}_3\text{C}_{2n}\text{H} + \text{H}$. Other mechanisms involving shocks, grain desorption, or grain surface chemistry (Ruffle & Herbst 2000) could be important as well. Taking into account the high H_2 density in the inner layers of CRL 618 and the high UV flux, it is reasonable to expect a fast change of the chemical composition of its AGB envelope during its evolution toward the planetary nebula phase. Likely, this chemical processing will progress in short timescales to the formation of much larger C-rich molecular complexes and, hence, the infrared spectrum of CRL 618 will be dominated, at some moment of its evolution, by the emission of the unidentified infrared bands.

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