

Transitory O-rich chemistry in heavily obscured C-rich post-AGB stars

D. A. García-Hernández^{1,2}, P. García-Lario³, J. Cernicharo⁴, D. Engels⁵ and J. V. Perea-Calderón⁶

¹ Instituto de Astrofísica de Canarias, C/ Via Láctea s/n, E-38205 La Laguna, Spain

² Departamento de Astrofísica, Universidad de La Laguna (ULL), E-38206 La Laguna, Spain

³ Herschel Science Centre. European Space Astronomy Centre, Research and Scientific Support Department of ESA. Villafranca del Castillo, P.O. Box 50727. E-28080 Madrid. Spain

⁴ Group of Molecular Astrophysics, ICMM, CSIC, C/Sor Juana Inés de La Cruz N3, E-28049 Madrid, Spain

⁵ Hamburger Sternwarte, Gojenbergsweg 112, D-21029 Hamburg, Germany

⁶ European Space Astronomy Centre, INSA S.A. P.O. Box 78, E-28080 Madrid, Spain

E-mail: agarcia@iac.es

Abstract. *Spitzer/IRS* spectra of eleven heavily obscured C-rich sources rapidly evolving from asymptotic giant branch (AGB) stars to Planetary Nebulae are presented. IRAM 30m observations for three of these post-AGBs are also reported. A few (3) of these sources are known to exhibit strongly variable maser emission of O-bearing molecules such as OH and H₂O, suggesting a transitory O-rich chemistry because of the quickly changing physical and chemical conditions in this short evolutionary phase. Interestingly, the *Spitzer/IRS* spectra show a rich circumstellar carbon chemistry, as revealed by the detection of small hydrocarbon molecules such as C₂H₂, C₄H₂, C₆H₂, C₆H₆, and HCN. Benzene is detected towards two sources, bringing up to three the total number of Galactic post-AGBs where this molecule has been detected. In addition, we report evidence for the possible detection of other hydrocarbon molecules like HC₃N, CH₃C₂H, and CH₃ in several of these sources. The available IRAM 30m data confirm that the central stars are C-rich - in despite of the presence of O-rich masers - and the presence of high velocity molecular outflows together with extreme AGB mass-loss rates ($\sim 10^{-4}$ M_⊙/yr). Our observations confirm the polymerization model of Cernicharo [1] that predicts a rich photochemistry in the neutral regions of these objects on timescales shorter than the dynamical evolution of the central H II region, leading to the formation of small C-rich molecules and a transitory O-rich chemistry.

1. Introduction

Proto-planetary nebulae (PPNe) or post-AGB stars - especially those with the most massive progenitors - are usually heavily obscured by their thick circumstellar envelopes (CSE) as a consequence of the strong mass loss that they experience at the end of the asymptotic giant branch (AGB) phase (see e.g., [2]). Indeed, the departure from the AGB usually occurs when the star is completely invisible in the optical domain, being only detectable at IR wavelengths. Later, in the post-AGB phase, the central star reappears again in the optical and the UV photons ionize the CSE, forming a planetary nebula (PN). The UV radiation field is predicted to produce a rich photochemistry on very short timescales (from ~ 0.2 to a few yrs) leading to the formation of hydrocarbon molecules such as C_nH₂, HC_{2n+1}N, and C_n [1]. Present observations show that



carbon-chain polyynic radicals (C_nH) are the most abundant species in IRC +10216 [3]; a C-rich AGB star with no polycyclic aromatic hydrocarbon (PAH) emission bands in its mid-IR spectrum. However, polyynes (C_nH_2), cyanopolyynes, benzene (C_6H_6), and methyl-polyynes - the building blocks of PAHs - rather than carbon chain radicals, dominate the IR spectrum of more evolved objects such as CRL 618 [4,5].

CRL 618 - the prototype C-rich PPN CSE - is a unique object in the sense that it is a genuine factory of small aromatic molecules. Cernicharo et al. [5] reported the first detection, outside the Solar System, of the basic aromatic molecule benzene (C_6H_6) towards this source. The presence of a central compact H II region with a strong UV radiation field as well as the high-velocity ($\sim 200 \text{ km s}^{-1}$) outflows of molecular gas [6] indicate that the central star is rapidly evolving towards the PN stage; indeed the B0 central star has already reappeared in the optical range. O-bearing molecules such as OH and H_2O are also present in this C-rich PPN [7]. The presence of these O-bearing species in C-rich PPNe is naturally explained by the chemical models of Cernicharo [1] without invoking a change in the chemical composition (C/O) of the CSE. In addition, if the mass-loss rate is at least 10 times larger than that of CRL 618, then these models predict that C-rich PPNe could have masers from O-bearing species such as OH and H_2O . Here we report the detection of small hydrocarbon molecules such as polyynes (C_nH_2), benzene, etc. in a small sample (11) of Galactic C-rich post-AGB stars. The variable OH and H_2O maser emission seen in some of these strong mass-losing C-rich sources indicates a transitory O-rich chemistry, which confirms the chemical model predictions by Cernicharo [1].

2. The sample and the *Spitzer* and IRAM 30m observations

The sources in our sample were originally included in our *Spitzer*/*IRS* survey of hidden Galactic post-AGB candidates (GO program #30258; P.I.: P. García-Lario). This survey is intended to characterize the infrared properties of a large (88) and flux-limited sample of heavily obscured (no optical counterpart) post-AGB candidates selected from the ‘GLMP catalog of IRAS sources with infrared colors similar to those of known PNe’ [8]. Approximately half of this sample are non-variable OH/IR stars and the other half is composed by non-variable sources of unknown chemistry - sometimes with negative OH maser detections. The *Spitzer*/*IRS* spectra show that the CSE of most of these hidden post-AGB stars are O-rich - the evolutionary outcome of massive hot bottom burning (HBB) AGB stars [2,9] - although a few heavily obscured C-rich post-AGB stars are also found (see e.g., [10]). We concentrate here on the eleven hidden post-AGB stars, which turned out to be C-rich stars, as evidenced by our *Spitzer*/*IRS* spectra (see below). Eight sources in this sample do not show any optical counterpart, being even obscured at wavelengths shorter than $3 \mu\text{m}$ (e.g., not detected by 2MASS). Interestingly, three sources (IRAS 17552, IRAS 18529, and IRAS 19566) in our sample of heavily obscured C-rich stars are known to exhibit variable maser emission of O-bearing molecules such as OH and/or H_2O [11].

Figure 1 shows the reduced *Spitzer*/*IRS* spectra for all C-rich sources in our sample. The CSE of these post-AGBs are clearly C-rich as indicated by the detection of strong acetylene (C_2H_2) absorption at $13.7 \mu\text{m}$. Several sources show also strong absorption features attributed to polyynes (e.g., C_2H_2 , C_4H_2 , and C_6H_2 ; see [11]) and HCN. The dust spectral energy distributions indicate high mass-loss rates and show similar features than in CRL 618 [4]. Benzene (C_6H_6) is detected for the first time in IRAS 17552 and IRAS 19566 [11], bringing up to three the total number of benzene detections in Galactic post-AGB stars. Acetylene (C_2H_2) is usually detected in less evolved AGB stars such as IRAS 09024–5019 (the only AGB variable in our sample as indicated by the IRAS variability index) and its detection in all sources in our sample indicate that they are quickly evolving to the PN phase. In addition, the unidentified IR bands (e.g., those at 6.2 , 7.7 , 8.6 and $11.3 \mu\text{m}$, generally attributed to PAHs) are only present in IRAS 15038 (Figure 1); likely the most evolved source in our sample. Remarkably, some post-AGB stars like IRAS 19566 display strong absorption features at ~ 15.75 and $16.43 \mu\text{m}$ that could be attributed

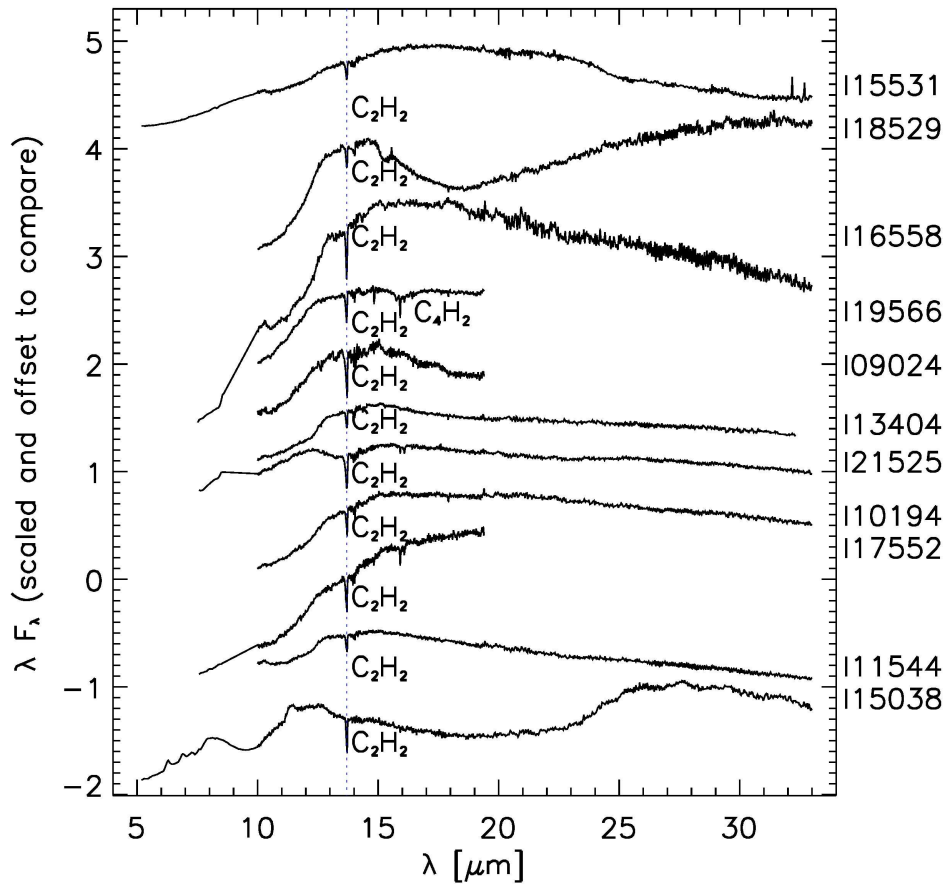


Figure 1. *Spitzer/IRS* spectra ($\sim 5\text{--}38\ \mu\text{m}$) of all heavily obscured C-rich post-AGB stars in our sample. The wavelength position of the acetylene (C_2H_2) absorption feature at $13.7\ \mu\text{m}$ is marked with a dotted vertical line.

to HC_3N and CH_3 , respectively. A few sources display also an unidentified absorption molecular feature at $17.92\ \mu\text{m}$, while one source (IRAS 17552) shows a strong absorption feature at $\sim 7.5\ \mu\text{m}$ that may be identified with CH_4 (see e.g., [12]).

We carried out complementary IRAM 30m observations of the few sources with variable maser emission. These observations confirm the C-rich nature of the central stars; as indicated by the detection of C-rich molecules such as CO and HCN together with the non detection of SiO. The IRAM 30m data reveal also the presence of high velocity ($\geq 100\ \text{km/s}$) molecular outflows with extreme mass loss rates ($\sim 10^{-4}\ \text{M}_\odot/\text{yr}$) in the previous AGB phase (see [11] for more details).

3. Formation of O-bearing molecules in C-rich PPNe

Our observations show that O-rich molecules may form in C-rich environments. As in the case of CRL 618, the prototypical C-rich PPN where O-bearing molecules are also detected, this can be explained by the chemical evolution models for the neutral layers of proto-PNe by Cernicharo [1], without the need to invoke a change in the chemistry (from O-rich to C-rich) of the central star. Our observations thus confirm the polymerization model of Cernicharo [1] that predicts a rich photochemistry in the neutral regions of these objects on timescales shorter than the dynamical evolution of the central H II region, leading to the formation of small C-rich molecules (small hydrocarbons and carbon clusters) and a transitory O-rich chemistry (formation of OH, H_2CO ,

and H₂O). This happens in zone II (see Figure 1 in [1]), where the CO is being photodissociated.

4. Conclusions

The analysis of heavily obscured transition sources with *Spitzer/IRS* confirms that most of these sources are non-variable OH/IR stars (O-rich), the result of the evolution of massive HBB AGB stars, but also a significant number of C-rich sources are found. We have detected small hydrocarbons, the building blocks of PAHs, in a small sample (11) of Galactic C-rich post-AGB stars [11]. In addition, benzene (C₆H₆) is clearly detected in two stars, bringing up to three the total number of Galactic post-AGB stars where this molecule has been detected [11]. The simultaneous detection of variable OH and H₂O maser emission seen in strong mass-losing C-rich sources confirms the chemical model predictions by Cernicharo [1]. As observed [11], these models predict the formation of small C-rich molecules and clusters, and a transitory O-rich chemistry as a result of time dependent chemistry and CO photodissociation.

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