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Spectral Line Surveys of Evolved Stars

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Abstract. The observation of evolved stars in selected evolutionary stages allow us to track the evolution of the physical properties and chemical composition of the matter that is being returned to the interstellar medium during these last stages of the life of stars. While the dust component can be characterized through the observation of the spectral energy distribution in the infrared part of the spectrum, spectral line surveys carried out in a wide spectral band provide the best probe of the physical properties and chemical composition of the gas phase. In this lecture we review the different line surveys carried out toward these objects and their impact in our understanding of the chemical complexity evolution in the circumstellar envelopes around evolved stars.

Keywords. astrochemistry, line: identification, surveys, stars: AGB and post-AGB

1. Introduction and history

Stars evolving out of the main sequence experience some of the most drastic changes of all its life, from the huge expansion that convert them into giant or supergiant stars and the mass loss process that creates a circumstellar envelope around them, to the transformation into a white dwarf or supernova at the very end of its life which injects huge amounts of energy into the circumstellar and nearby interstellar medium.

Among the various types of objects embraced by the generic term "evolved stars", a particularly interesting one are Asymptotic Giant Branch (AGB) stars, which are red giant stars resulting from low mass progenitors ($\lesssim 8$ $M_\odot$) that undergo mass loss processes producing extended circumstellar envelopes composed of gas phase molecules and tiny dust grains. Dredge-up processes during the AGB phase selectively bring carbon from the interior of the star to the stellar surface so that the amount of carbon can eventually exceed that of oxygen. Thus, AGB stars can be M stars ([C]/[O] < 1) or C stars ([C]/[O] > 1) depending on the carbon-to-oxygen abundance ratio in the stellar surface. The physical conditions in the atmosphere of AGB stars (with temperatures of 2000-3000 K and densities higher than 10^{13} cm^{-3}) make the material to be mainly molecular with the composition being determined by thermochemical equilibrium. In this region stable molecules dominate, with CO reaching a large abundance and the [C]/[O] ratio determining which other abundant molecules will be present: stable oxygen bearing molecules in M stars and carbon-bearing molecules in C stars. These stable molecules incorporate into the stellar wind and in the outer layers exposed to the interstellar ultraviolet (UV) field start to be photodissociated releasing radicals which then react forming new species. The evolution of the star from a cool red giant to a hot white dwarf controls the transition from the AGB to the planetary nebula phase, in which the star now emits a large flux of

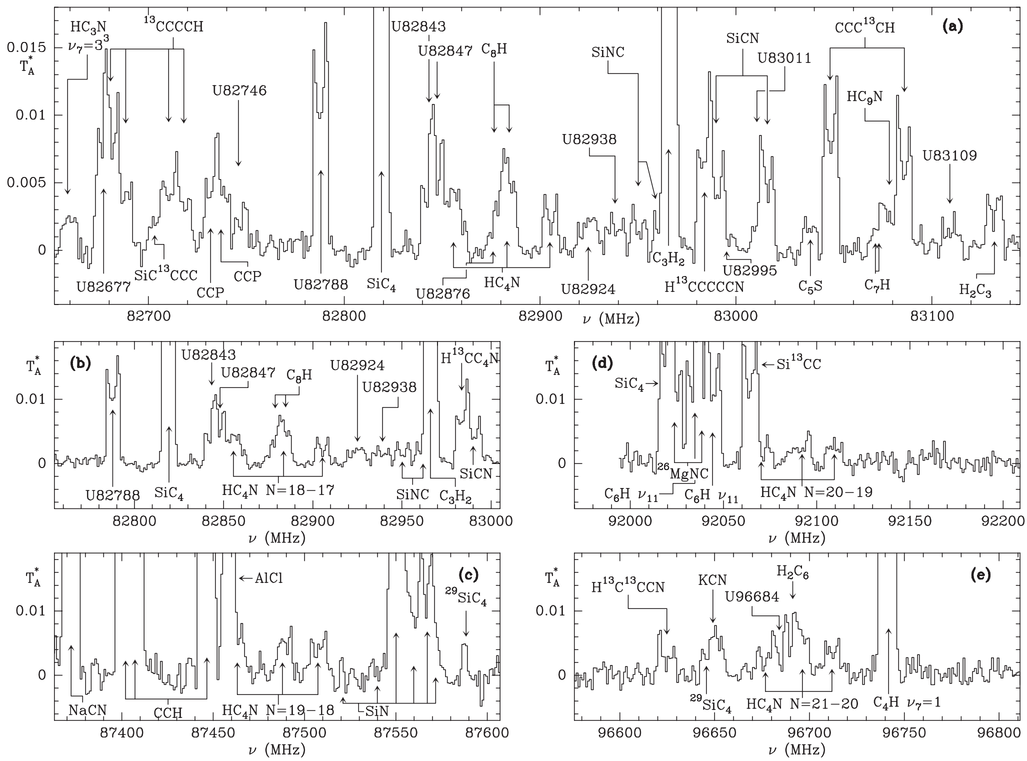

Figure 1. Spectra of IRC +10216 observed with the IRAM 30-m telescope as a part of the 3mm line survey. This zoom in frequency to the line survey shows a forest of lines coming from several species, their isotopes, and even their vibrationally excited states. Figure updated from the detection of HCCCCN by Cernicharo *et al.* (2004).

UV photons that irradiate the expanding circumstellar gas inducing important changes in the chemical composition.

Circumstellar envelopes (CSEs) of evolved stars foster a remarkably complex chemistry (see Fig. 1,2). The mechanisms behind the chemical synthesis, how it varies from the inner to the outer layers of the expanding envelope, its relationship to dust grain formation, and its evolution from the asymptotic giant branch (AGB) to the post AGB-phases, are all important issues that have yet to be understood (Cernicharo *et al.* 2004, Herpin & Cernicharo 2001, Herpin *et al.* 2002). With this purpose, observations at different wavelength ranges are clearly required. The atmosphere and the inner dust condensation regions are best probed by infrared (IR) ro-vibrational lines or by high-J lines in the ground and vibrationally excited states of abundant species such as CO, HCN and SiS (Fonfría *et al.* 2008, Cernicharo *et al.* 1996a, Decin *et al.* 2010). The outer and colder layers of the CSE are best probed by molecular rotational lines at millimeter wavelengths (Cernicharo *et al.* 2000, Kemper *et al.* 2003, Agúndez & Cernicharo 2006, He *et al.* 2008). Based on a large set of high spectral resolution data, the physical conditions of the different regions of the CSE can be well constrained providing a complete picture of the object (see, e.g., Agúndez 2009, Cernicharo *et al.* 2000, Pardo *et al.* 2004, Pardo *et al.* 2005, Pardo *et al.* 2007a,b).

The observation of evolved stars in selected evolutionary stages allow us to track the evolution of the physical properties and chemical composition of the matter that is being returned to the interstellar medium during these last stages of the life of stars. While

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the dust component can be characterized through the observation of the spectral energy distribution in the infrared part of the spectrum, spectral line surveys carried out in a wide spectral band provide the best probe of the physical properties and chemical composition of the gas phase.

Carbon-rich evolved stars.

The by far most studied C star is IRC +10216, which has been the target of different spectral line surveys. In the early 80's Johansson *et al.* (1984) carried out the first such survey with the 20-m Onsala telescope at $\lambda \sim 3.8$ mm, covering the frequency range 72.2-91.1 GHz. Some years after IRC +10216 was surveyed in the $\lambda \sim 0.9$ mm band with the JCMT (339.6-364.6 GHz; Avery *et al.* 1992) and the CSO (330.2-358.1 GHz; Groesbeck *et al.* 1994) telescopes, in the $\lambda \sim 8$ mm band (28-50 GHz) with the 45-m Nobeyama telescope (Kawaguchi *et al.* 1995), and in the $\lambda \sim 2$ mm spectral region (130-160 GHz) with the IRAM 30-m telescope (Cernicharo *et al.* 2000). These line surveys showed us that the spectrum of IRC +10216 at millimeter wavelengths is plenty of emission lines corresponding to rotational transitions of different types of molecules present in the circumstellar envelope. An important outcome of these line surveys (see Fig. 1,2) has been the identification of new molecules in space, such as the metal halides NaCl, AlCl, KCl, and AlF (Cernicharo & Guélin 1987b), the metal-bearing molecules MgNC, MgCN, AlNC, AlCN, SiCN, and NaCN (Guélin *et al.* 1986; Kawaguchi *et al.* 1993; Ziurys *et al.* 1993,2002; Guélin *et al.* 2000,2004; Turner *et al.* 1994). Due to the carbon-rich nature of the circumstellar gas, most of the lines arise from carbon-bearing molecules such as the carbon chain radicals C_2H, C_4H, C_5H, C_6H, C_7H, and C_8H (see Cernicharo & Guélin 1996b, and references therein), the carbenes H_2C_3 and H_2C_4 (Cernicharo *et al.* 1991a,b), the cyclic hydrocarbons c-C_3H_2 and c-C_3H, HCN and the cyanopolyynes HC_3N, HC_5N, HC_7N, and HC_9N (Cernicharo *et al.* 2000), the related radicals CN, C_3N and C_5N, the sulfur carbon chains CS, C_2S, C_3S (Cernicharo *et al.* 1987a), and C_5S (Bell *et al.* 1993; Cernicharo *et al.*, in preparation), and the silicon carbon-bearing molecules SiC (Cernicharo *et al.* 1989), SiC_2 (Thaddeus *et al.* 1984), c-SiC_3 (Apponi *et al.* 1999), and SiC_4 (Ohishi *et al.* 1989), and many diatomic and triatomic molecules among others (Cernicharo *et al.* 2000). These molecules are either concentrated around the central star or distributed in a hollow shell of radius ~ 15" (Guélin *et al.* 1993, Guélin *et al.* 1997), and have rotational temperatures in the range 15-90 K (Agúndez 2009). Depending on the spectral region covered, each line survey sample different types of molecules and excitation conditions. For example, at centimeter wavelengths observed lines either belong to heavy species or are low excitation transitions of molecules of medium weight, whereas at wavelengths shorter than 1 mm most of the lines either arise from relatively light molecules or correspond to high excitation transitions of medium weight molecules.

The new generation of low-noise and wide-band heterodyne receivers installed on radiotelescopes in recent years has made possible to carry out sensitive line surveys of IRC +10216 such as those performed by He *et al.* (2008) at $\lambda \sim 2$ mm (130-160 GHz) with the 12-m ARO telescope and at $\lambda \sim 1.3$ mm (219.5-267.5 GHz) with the 10-m SMT telescope, that carried out with IRAM 30-m telescope at $\lambda \sim 3$ mm in the frequency range 80-115.8 GHz (Cernicharo *et al.* in preparation), the one made by Tenenbaum *et al.* (2010) with the 10-m SMT telescope at $\lambda \sim 1.3$ mm (214.5-285.5 GHz), and the recent line survey carried out with the SMA interferometer by Patel *et al.* (2011) in the frequency range 293.9-354.8 GHz. These sensitive line surveys have detected many weak lines arising from rare isotopologues and vibrationally excited states of abundant molecules (see Fig. 1,2), even reaching the confusion limit in some regions of the spectrum. They have also permitted the detection of new molecules with relatively low abundances, such as the radicals

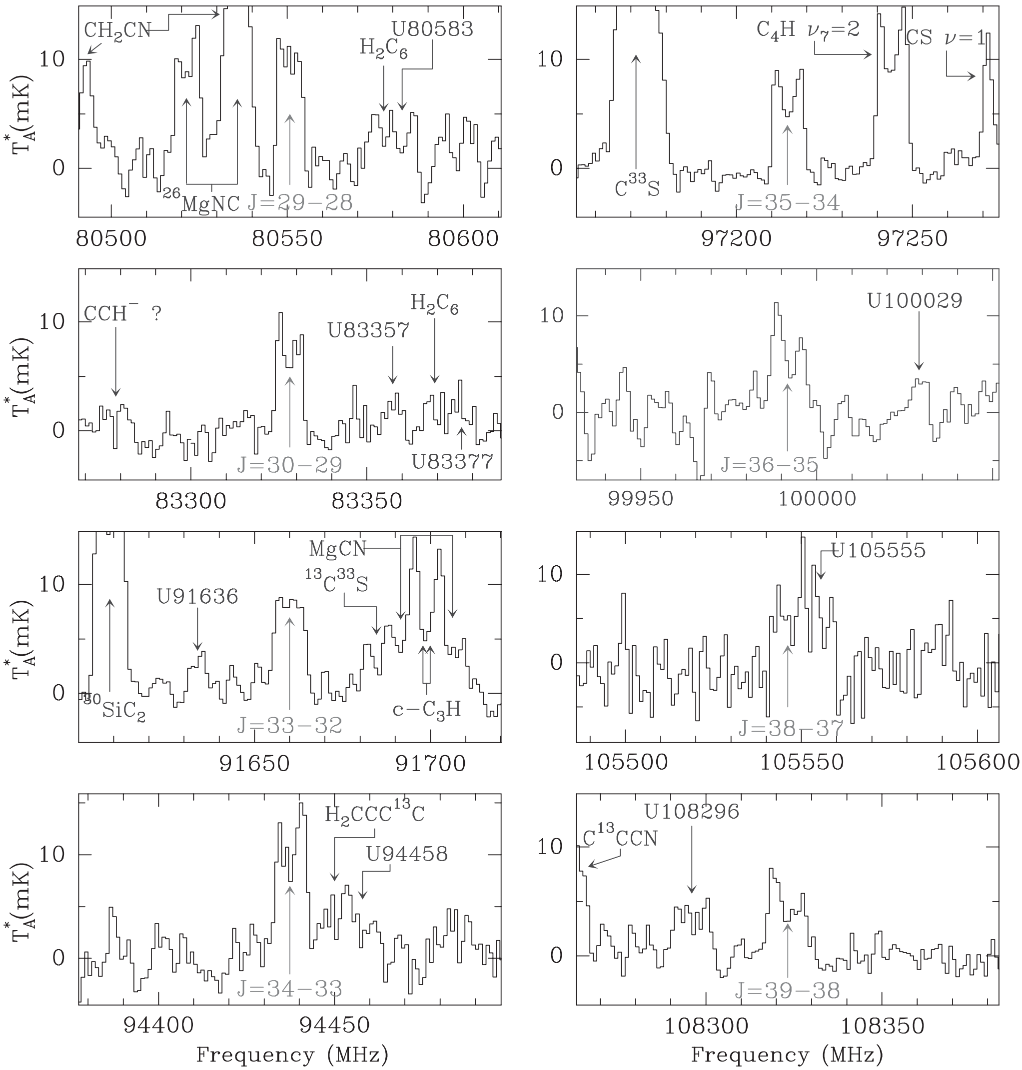

Figure 2. Spectra of IRC +10216 observed with the IRAM 30-m telescope, showing a series of lines from C_5N^-. The marginal weak line U83278 is worth noting, because it is within 0.1 MHz of the J=1-0 line of CCH^- (see Cernicharo *et al.* 2008).

SiNC (Guélin *et al.* 2004) and HC_4N (Cernicharo *et al.* 2004), the cyanides KCN and FeCN (Pulliam *et al.* 2010; Zack *et al.* 2011), as well as the recently discovered negatively charged molecules C_6H^-, C_4H^-, C_8H^-, C_3N^-, C_5N^- (see Fig. 2), and CN^- (McCarthy *et al.* 2006; Cernicharo *et al.* 2007; Remijan *et al.* 2007; Thaddeus *et al.* 2008; Cernicharo *et al.* 2008; Agúndez *et al.* 2010a).

Of great interest is also the extension of spectral line surveys from the radio region to the infrared part of the spectrum, as it allows to probe warm regions of the envelope closer to the star. Low spectral resolution spectra in the far-infrared region, λ = 45-197 μm, have been obtained with the Long Wavelength Spectrometer (LWS) on board the Infrared Space Observatory (ISO) toward several carbon-rich objects such as IRC +10216, CRL 618, and NGC 7027 (Cernicharo *et al.* 1996a; Herpin *et al.* 2002). These spectra show emission lines corresponding to highly excited rotational transitions

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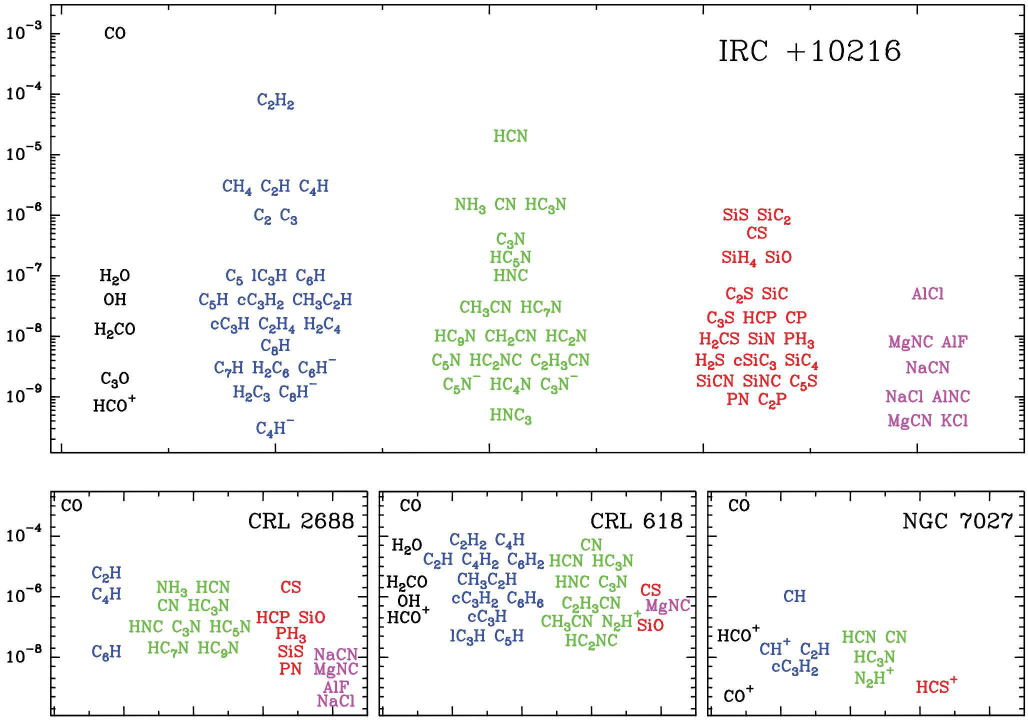

Figure 3. Molecular abundances relative to H_2 in the carbon-rich evolved stars IRC +10216, CRL 2688, CRL 618, and NGC 7027 (from Agúndez 2009).

of molecules which are abundant in the warm circumstellar regions, such as CO and HCN. Another nice example is the line survey of IRC +10216 carried out by Fonfría *et al.* (2008) with the IRTF telescope in the wavelength range 11-14 μm, where a forest of lines corresponding to rovibrational transitions of C_2H_2 and HCN is observed and used to derive their abundances in the 1-100 R_* zone, as well as the physical conditions in the inner circumstellar envelope, where the high-J lines of these species are formed.

The proximity of IRC +10216 to us ($\sim$ 130 pc) and the relatively large mass loss rate ($\sim 2 \times 10^{-5}$ $M_\odot$ yr^{-1}) makes it to be the prototype of AGB star and justifies the extensive observational studies carried out on it. Spectral line surveys have however been performed on other C stars such as CIT 6, observed with the 12-m ARO and SMT telescopes by Zhang *et al.* (2009a) in the frequency ranges 131-160 GHz, 219-244 GHz, and 252-268 GHz, and CRL 3068, which has been surveyed with the same telescopes by Zhang *et al.* (2009b) in the frequency ranges 130-162 GHz and 219.5-267.5 GHz. These two objects, CIT 6 is located at $\sim$ 400 pc and has a mass loss rate of $\sim 3 \times 10^{-6}$ $M_\odot$ yr^{-1} while CRL 3068 is at $\sim$ 1200 pc and has a mass loss rate of $\sim 1.2 \times 10^{-4}$ $M_\odot$ yr^{-1}, have less intense lines than IRC +10216, so that only the lines of the most abundant molecules can be detected. At this level of sensitivity both sources show a chemical composition very similar to that of IRC +10216.

More evolved carbon-rich stars have also been studied through line surveys. The pre-planetary nebula CRL 2688, which is in a slightly more evolved stage than IRC +10216, has been surveyed at $\lambda = 3$ mm (85-116 GHz) by Park *et al.* (2008), who have found a molecular composition quite similar to that of IRC +10216. Another pre-planetary nebula in a more evolved stage is CRL 618, which has been observed with the IRAM

30-m telescope in the frequency range 80-276 GHz (Pardo *et al.* 2004; Pardo *et al.* 2005; Pardo *et al.* 2007a,b), allowing for an accurate description of the molecular envelope. In this object the central star emits an important UV flux which alter the chemistry of the molecular envelope ejected during the previous AGB phase (Cernicharo 2004b). A more extreme object is the planetary nebula NGC 7027, whose extremely hot central star ($T_* \sim 220{,}000$ K) irradiates with a strongly ionizing radiation field the circumstellar gas. Zhang *et al.* (2008) have carried out a line survey of this object at millimeter wavelengths (71-111 GHz, 157-161 GHz, and 218-267 GHz) with some of the detected lines arising from rotational transitions of molecules and a large fraction of them from recombination transitions of H^+ and He^+. The evolution of the molecular abundances with the evolutionary phase along the sequence of carbon-rich objects IRC +10216 → CRL 2688 → CRL 618 → NGC 7027 is shown schematically in Fig. 3. We see that the pre-planetary nebula CRL 2688, which is in a more evolved stage than IRC +10216, has a chemical composition that is still quite similar to that of the latter object, with high abundances of organic molecules with a large unsaturated character, such as C_2H, C_4H, CN, HCN, or HC_3N. CRL 2688 is about ten times further than IRC +10216, although its mass loss rate is about ten times larger, so that it is still possible to detect species with moderately low abundances such as HCP, PH_3, as well as several metal-containing molecules. The pre-planetary nebula CRL 618 is clearly in a more evolved stage than CRL 2688, so that it starts to show important differences in the chemical composition, as is the relatively large abundance of oxygen-bearing molecules such as H_2O and H_2CO. It is also worth to note that the abundance ratios [HNC]/[HCN] or [HC_3N]/HCN are noticeably enhanced and the appearance of aromatic hydrocarbons such as benzene. Most of these difference are due to the strong enhancement of the UV radiation field which emanates from the central white dwarf, which makes the circumstellar material to be severely photoprocessed. Finally, the planetary nebula NGC 7027 shows a chemical composition which is clearly different from the previous less evolved objects. The presence of positive ions is much more important, with species such as CO^+, CH^+, and HCS^+, and in general terms the chemical complexity of the molecules decreases as a consequence of the huge UV field emitted by the very hot central star (see e.g. Bachiller *et al.* 1997; Herpin *et al.* 2002).

Oxygen-rich evolved stars.

The chemical composition of the circumstellar gas around oxygen-rich evolved stars is generally thought to be noticeably less rich than that around carbon-rich objects. Therefore less efforts have been undertaken to carry out line surveys on oxygen-rich objects than on carbon-rich ones. Only recently, the new generation of low-noise and wide-band receivers has stimulated astronomers to perform sensitive line surveys of oxygen-rich evolved stars at millimeter wavelengths. The first such survey was carried out towards the supergiant VY Canis Majoris (Tenenbaum *et al.* 2010) with the 10-m SMT telescope at $\lambda \sim 1.3$ mm (214.5-285.5 GHz). Observations at millimeter wavelengths of this object have revealed a chemical complexity with unexpected molecules such as NaCl, PN, HNC, and HCO^+ being present in the different circumstellar outflows around the central star (Ziurys *et al.* 2007).

Sensitive line surveys of the oxygen-rich evolved stars OH 231.8+4.2 and IK Tau are also being carried out with the IRAM 30-m telescope covering all accessible spectral windows, from $\lambda = 3$ mm to $\lambda = 0.9$ mm, and preliminary results indicate the existence of a prominent chemical diversity with molecules such as SiO, NS, HNCO, CH_3OH among others (Sánchez Contreras *et al.* 2011). IK Tau has also been recently surveyed by Kim *et al.* (2010) at selected wavelengths in the submillimeter domain using the APEX telescope.

Observations of oxygen-rich evolved stars such as VY Canis Majoris, IK Tau, TX Cam, RX Boo, IRC +10011, and R Cas have also been carried out by Polehampton *et al.* (2010) in the far-infrared region of the spectrum using the LWS instrument on board ISO.

2. Results from the Herschel Space Observatory

IRC +10216 (CW Leo) is one of the brightest infrared sources in the sky, thus an ideal target to be observed with the *Herschel Space Observatory* (Pilbratt *et al.* 2010). The HIFI instrument (de Graauw *et al.* 2010) provides both a high resolution and a wide spectral coverage. The first is necessary for resolving the complex kinematics characteristic of IRC +10216, allowing us to distinguish between the contribution from the inner acceleration zone (Fonfría *et al.* 2008, Cernicharo *et al.* 2011) and from the expanding envelope where the gas reaches the terminal velocity (Cernicharo *et al.* 2000, Agúndez 2009). The wide spectral coverage is mandatory to obtain a complete inventory of lines to study in detail the chemical content and molecular excitation. A complete line survey of this source has been carried out with HIFI. Preliminary results are shown by Cernicharo *et al.* (2010a,b) (see Fig. 4). In addition to HCN masers and lasers from all vibrationally excited states of this molecule below 7000 K (see also Cernicharo *et al.* 2011; Cernicharo *et al.* 1996), the HIFI line survey of IRC +10216 shows a forest of lines of SiC_2 arising from levels with energies up to 1000 K and the presence of some hydrides such as HCl (Cernicharo *et al.* 2010b) and HF (Agúndez *et al.* 2011). Complete line surveys of the O-rich evolved stars VY CMa and OH231.8 will be performed in the next months with HIFI.

In addition to these sources a large number of evolved stars have been observed with low spectral resolution using SPIRE and PACS (Griffin *et al.* 2010; Poglitsch *et al.* 2010) within the Key Program (KP) MESS (Groenewegen *et al.*). The main results from this KP have been shown in the special issue of Astronomy and Astrophysics devoted to these instruments on board Herschel (vol. 518). Among them it is worth to the the detection of warm water in IRC +10216 (Decin *et al.* 2010) and its interpretation in terms of a photochemistry in the inner region due to the clumpy structure of the envelope (see also Agúndez *et al.* 2010b). While HCN dominates the far-IR spectrum of C-rich objects, H_2O is the main contributor to the SPIRE and PACS spectra of O-rich evolved stars.

Finally, the HIFISTARS KP is devoted to the observation with HIFI of selected lines of CO, H_2O, HCN, SiO, SiS, NH_3 and many other species in a large sample of evolved stars (see e.g., Bujarrabal *et al.* 2010; see also the different papers from this KP in the special issue of A&A devoted to HIFI -vol 521).

3. Chemistry in evolved stars

The basic chemical processes taking place in the envelopes around AGB stars were already summarized by Lafont *et al.* (1982), focusing on IRC +10216, although they are extensible to any other AGB star. They identified four different formation mechanisms of molecules: thermochemistry in the regions near the stellar photosphere and freeze out of the abundances in the immediately outer layers, gas phase chemical reactions dominated by kinetics, grain processes, and photochemistry.

It is now well established since the pioneering work of Tsuji (1973) that the [C]/[O] abundance ratio in the stellar photosphere is the most important parameter which determines the type of molecules found in circumstellar envelopes. The high stability of CO causes this molecule to have a large abundance, locking most of the limiting reactant and allowing for the reactant in excess to form either carbon-bearing molecules when [C]/[O]

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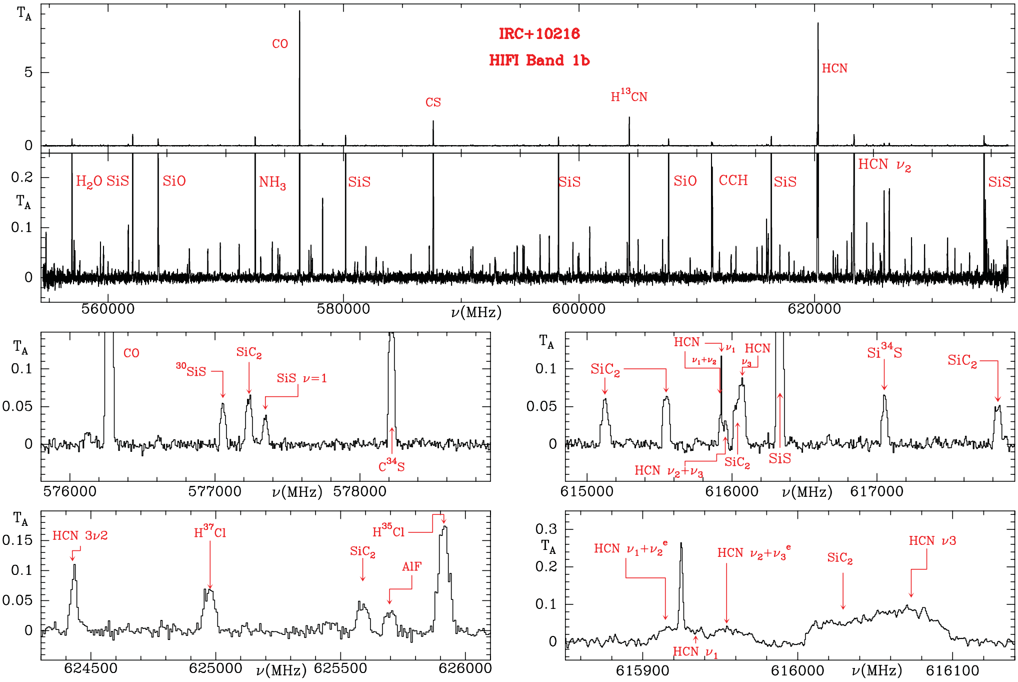

Figure 4. Spectra of IRC +10216 observed with HIFI band 1b. The two upper panels present the complete spectrum at two different intensity scales. The panels below show different 3 GHz wide ranges of the survey. All data have been smoothed to a spectral resolution of 2.8 km s^{-1} except for the right bottom panel which shows the spectrum around several vibrational lines of HCN with the nominal WBS resolution (1.1 MHz, $\simeq$0.5 km s^{-1}). Note the narrow feature of HCN shown by the $\nu_1 + \nu_2^{1e}/\nu_1$ J=6-5 line at $\sim$615.92 GHz (see Cernicharo *et al.* 2010a).

$>$ 1, and oxygen-bearing molecules when [C]/[O] $<$ 1. This simple fact provides a good explanation of the overall chemical composition in the inner envelopes of AGB stars, although there are notable exceptions that thermochemical equilibrium calculations cannot explain, such as the presence, with moderately high abundances, of HCN, CS, and NH_3 in oxygen-rich objects and that of water vapor and ammonia in carbon-rich objects. This points towards the existence of non-equilibrium chemical processes being at work in the inner regions of circumstellar envelopes, that could be either induced by shocks (Cherchneff 2006) or perhaps by UV photons penetrating from the interstellar medium to the inner regions through a clumpy envelope (Agúndez *et al.* 2010b).

In the intermediate layers of circumstellar envelopes, when the temperature has decreased below $\sim$ 1000 K, refractory elements start to condense and form solid dust grains. An important effect is that some molecules containing refractory elements such as Si decrease their abundances in the gas phase as they incorporate into dust grains. Another effect, yet to be studied in detail, is that some molecules may form mantles on the surface of dust grains and may participate in dust surface reactions forming new molecules that can return to the gas phase by several desorption mechanisms, such as thermal desorption or desorption induced by interstellar UV photons or cosmic rays.

As the gas expands density decreases and the column density of material located towards the interstellar medium do so. Thus, in the outer circumstellar layers molecules start to be exposed to the ambient interstellar UV field and are then photoprocessed,

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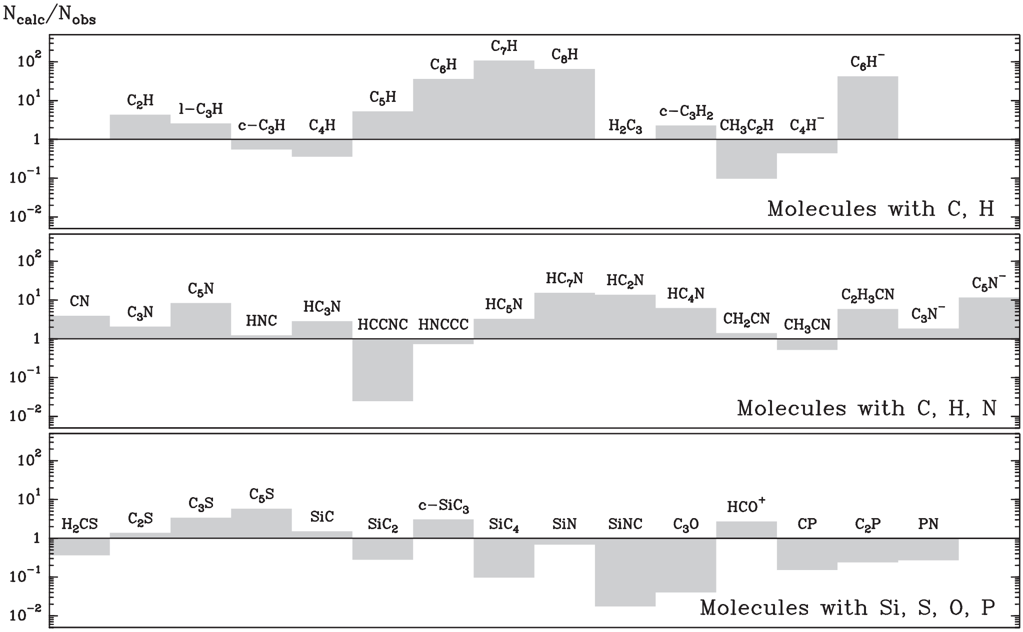

Figure 5. Comparison between column densities calculated (N_{calc}) with a chemical model and values derived from observations (N_{obs}) of IRC +10216 (from Agúndez 2009).

they are mostly dissociated but also ionized, producing radicals and ions which can participate in rapid gas phase reactions to form new molecules. This photochemistry has been extensively studied through chemical models, most of which have focused on the carbon star IRC +10216 as this object harbors the largest variety of molecules among all known evolved stars (Cherchneff *et al.* 1993; Millar & Herbst 1994; Cordiner & Millar 2009). Such models have successfully explained the formation of a large fraction of the molecules observed in the outer layers of IRC +10216 and of other carbon-rich AGB stars. To illustrate this we show in Fig. 5 a comparison between the column densities calculated by a chemical model of IRC +10216 and the values derived from observations carried out at millimeter wavelengths with the IRAM 30-m (see Agúndez 2009). We see that for most of the molecules the differences between calculated and observed column densities are within a order of magnitude, which we may consider as a reasonably good agreement taking into account the uncertainties of both the abundances derived from observations and calculated with the chemical model. There are however important discrepancies for some molecules, such as the long carbon-chain radicals C_6H, C_7H, and C_8H whose abundances are overestimated by the chemical model, probably due to an underestimation of the photodestruction rates, or species such as HCCNC, SiNC, or C_3O which are underestimated due to the lack of efficient formation routes in the chemical model.

The chemistry of oxygen-rich AGB stars has been less well studied through chemical models. A few ones have been carried out in the past (e.g. Willacy & Millar 1997), although the recent discovery of an enhanced chemical complexity in some oxygen-rich evolved stars will certainly need of a revisit of chemical models aiming to explain the formation of the newly detected molecules.

4. The future

ALMA will provide an angular resolution permiting to resolve the molecular emission in the dust formation zone of AGB stars. Toward these objects in will be possible to reach the maximum angular resolution provided by ALMA as the brightness temperature of the CO, HCN, SiO, SiS lines will be above 1000 K. The available data in the submillimeter domain with the SMA towards IRC+10216 (Patel *et al.* 2011) shows the presence of a large number of unknown narrow lines certainly formed in the innermost zone of the envelope. These future high angular resolution and extremely sensitive observations will reveal new families of complex molecular species that participate in the formation and growth of dust grains. The physical conditions of the dust formation zone have been traced so far only through the most abundant molecules (CO, HCN, SiS, SiO). The chemistry of the most complex molecules in the innermost zone remains still a mystery that ALMA will help to solve.

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Discussion

Paola Caselli: Why did you not expect to see so many SiC_2 lines and which fraction of Si is locked in SiC_2?

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José Cernicharo: From millimeter data alone the SiC_2 emission seems to arise from the external shell where the kinetic temperature is low. The fact that with Herschel/HIFI we have detected lines involving levels with energies as high as 1000 K means that SiC_2 is produced in the inner envelope with an abundance of 1-2 10^{-7}. This abundance is perhaps enhanced by a factor of 2 when the gas reaches the external envelope (Cernicharo *et al.* 2010a).

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