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Carbon Chemistry of Circumstellar Envelopes

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ABSTRACT

The chemical composition of envelopes surrounding cool evolved stars, as determined from microwave spectroscopic observations, is reviewed. Emphasis is placed on recent observations with the new large mm-wavelength telescopes and interferometer arrays, and on new theoretical work, especially concerning ion-molecule chemistry of carbon-bearing species in these envelopes. Thermal (as opposed to maser) emission lines are discussed. Much progress has been made in the past few years in the theoretical understanding of these objects. It is already clear, however, that observations with the new generation of mm-telescopes will require substantial improvements in the theoretical models to achieve a thorough understanding of the data now becoming available.

INTRODUCTION

This paper reviews our understanding of the circumstellar molecular envelopes of evolved, late-type stars in terms of their envelope chemical composition. There have been several good reviews of this general topic in the last few years (refs. 1-7) so in this paper I will emphasize the results of recent observations and theoretical work on the subject, especially with the new instruments for millimeter wavelengths which provide significant improvements in sensitivity and angular resolution compared with past work. I will deal largely with the microwave "thermal" line emission in the envelopes with emphasis on molecules containing carbon, and will largely neglect masers, which are worth a separate review (see refs. 8 and 9).

The chemistry of circumstellar envelopes (CSE's) of evolved stars are of interest for several reasons.

First, they offer us the possibility of constraining theoretical models for the rapid phase of stellar evolution which must occur in the interiors of stars in the mass range ~1-10 $M_\odot$, as these stars evolve into white dwarfs. The elemental and isotopic composition of the CSE must reflect the surface composition of the star at the time that the matter was ejected from the photosphere. The surface composition must in turn be determined by the nuclear processing in the interior coupled with the convective dredge-up of processed material to the surface (ref. 10). Consequently one might hope to use the envelope composition to help understand the rapid post-AGB evolution to the white dwarf stage. Indeed, since observed envelopes generally have relatively constant outflow velocities, spatially-resolved information on isotope and element abundances could, in principle, be read as a chronology of the stellar photospheric composition.

CSE's are also a major source of element enrichment and of dust grains in the interstellar medium (ISM). Current estimates of the rate of mass returned from stars in the initial mass range 1-10 $M_\odot$ are of the order one solar mass per year averaged over the whole galaxy. This rate, with the element enrichment as a result of nuclear burning, is large enough to imply that mass loss from AGB stars must play a major role in galactic chemical evolution. In particular, carbon in the ISM is probably produced and returned mainly by the red giants. The $^{12}C/^{13}C$ isotope ratio in the ISM must also be affected by the nucleosynthesis processes in these stars, in which ^{13}C may become strongly enriched compared to the solar abundance. It is therefore important to quantify as accurately as possible the rate of return to the ISM of matter and of nucleosynthesis products.

Microwave spectroscopic imaging of CSE's is now increasing our understanding of these issues by providing detailed information on the elemental, isotopic, and chemical composition; the temperature and density structure; and the composition and abundance of the dust component. The gas composition and structure are obtainable more or less directly from the observations while dust properties can to some extent be inferred from observations of the gas.

ENVELOPE CHEMICAL COMPOSITION DEDUCED FROM MICROWAVE SPECTROSCOPY

Thermodynamic Equilibrium Models

The simplest picture of a CSE is that of a spherical uniformly-expanding wind of material ejected from the star by a process not yet well understood. Provided that the rate at which material leaves the star is constant over time (clearly an untenable assumption over long timescales), the CSE then has a density varying as $1/r^2$ with distance from the star. In the simplest picture, the composition of the envelope is assumed to be determined by chemical reactions at or just above the photosphere. The reactions occurring in this region have been modelled on the assumption of chemical equilibrium (refs. 11-16). It has been argued that, once material has been ejected from the star, the rapid decrease in gas density with increasing radius will cause the "freezing out" of molecular abundances once the dynamical timescale (the time in which the density changes by a significant amount) is less than the chemical reaction timescale (i.e., the inverse of the important reaction rates). Freeze-out is generally expected to occur close to the star, compared with the observed extent of CSE's (up to ~0.1 pc), so that the chemical composition is predicted to be determined chiefly by the equilibrium chemical composition near the photosphere.

The most important predictions of the chemical equilibrium models are:

1. Hydrogen is almost entirely converted to molecular form by three-body reactions as long as the gas density exceeds 10^{11} cm^{-3} and the photospheric temperature is less than 2500 K (ref. 16). These conditions are expected to hold for most late-type giants, and in fact H I is generally undetected in CSE's (ref. 2), except for the recent observation of H I in α Ori (ref. 17), a star whose photospheric temperature is well above 2500 K.

2. Abundances of molecules other than H_2 depend critically on the C/O ratio. If there are more carbon than oxygen atoms (C/O > 1) essentially all the available O is tied up in CO, with the remaining C divided between HCN and C_2H_2. If C/O < 1, all C goes into CO and the remaining O is in the form of H_2O. Nitrogen is predominantly in the form of N_2 in either case.

3. Second-row elements like Si and S are predicted to form molecules with relatively large abundances, e.g., SiO and SiS (see ref. 15). In fact, grain formation is thought to alter dramatically the gas phase abundance of elements such as Si and Al. Grain formation is poorly understood, however, and is generally not included in chemical equilibrium models. (For example, the models of Tsuji (ref. 13) were computed for gas temperatures down to 500 K, low enough that grain formation is likely to be important, but this process is not included in the model calculations.) The form in which Si is incorporated into grains may depend on the C/O ratio. If C/O > 1, silicon carbide may be formed, while if C/O < 1, the dominant form may be silicates.

Of the most abundant predicted species, H_2, N_2, and C_2H_2 have no microwave transitions, while H_2O is detected as a maser, making column density determinations very uncertain. (C_2H_2 is detected by its mid-IR ro-vibrational transitions--see the review by Wannier in reference 18). CO and HCN are detected by their mm-wavelength emission lines in many CSE's, and the line intensities confirm in a rough way that both molecules are abundant. However, the spectra often indicate large optical depths in the lines, especially for CO, so that accurate CO column densities are not always reliably determined. In fact, the CO profiles have been used to derive total mass loss rates by <u>assuming</u> a CO/H_2 abundance ratio, guided by expectations from chemical equilibrium models (see refs. 19-21).

For HCN, large abundances are also implied by the line intensities. In one case, the C-rich envelope of IRC+10216, HCN excitation has been modelled to derive the space density of HCN as a function of radius (ref. 22). However, since the molecule is radiatively excited, one cannot infer a total gas density from the observations, so as for CO, the absolute HCN abundance is not well-known. HCN has been detected in more than 20 C-rich CSE's, but in only a few O-rich cases (ref. 4). H_2O is found as maser emission (in the 22.3 GHz line) in ~150 O-rich envelopes, but in none of the C-rich objects. These figures are largely in accord with the predictions of the chemical equilibrium models, although the presence of HCN in O-rich CSE's is difficult to explain in that context.

Equilibrium chemistry may be a reasonable approximation for the few most abundant species, which are closed-shell, stable molecules. However, the equilibrium models are clearly inadequate to explain the observations of the less-abundant species. Some of the most obvious failures of the chemical equilibrium picture are:

1. OH must be present in the envelopes of the O-rich stars with maser emission (the OH/IR stars), but OH is not predicted in any significant amount.

2. SiS and SiO are detected in their thermal (non-maser) emission lines in many CSE's, but the observed abundances derived from observations are 100-1000 times less than predicted by equilibrium chemistry.

3. Complex organic species are not predicted but are observed. The most

notable case is IRC+10216, in which many such molecular species have been detected. These include

a. Long carbon chain molecules (HC_xN, with odd x up to 11; C_xH species, with integer x up to 6).

b. Organic rings like C_3H_2 and SiC_2.

4. Ammonia (NH_3) is detected with an abundance much larger than predicted by equilibrium chemistry.

The shortcomings of the equilibrium models have led to the consideration of other mechanisms for producing the observed abundances of the rarer species. These mechanisms include photon and cosmic ray initiated chemical reactions; and grain processes.

Photochemical Processes

Two kinds of processes are of interest:

1. Direct photodissociation or ionization by the interstellar UV field, which can penetrate the CSE by an amount depending on the dust optical depth and molecular column densities as seen from the outside. This mechanism was first proposed by Goldreich and Scoville (ref. 23) to explain the presence of OH in O-rich envelopes. Further calculations have been made by Huggins and Glassgold (ref. 24). The reaction of interest is simply $H_2O + h\nu \rightarrow OH + H$, yielding the OH needed for maser emission. The predicted UV penetration depth seems to be in agreement with the observed sizes of OH masers (refs. 25-27).

A similar mechanism has been proposed to explain the large abundance and extent of CN emission toward IRC+10216 (ref. 28). In this case, the abundant species HCN is photodissociated to H + CN. In fact, essentially all molecular species are expected to be dissociated at sufficiently large radii, though the quantitative effect depends on the details of the dissociation mechanism. In particular, CO is believed to be dissociated from UV lines, rather than the continuum (cf. refs. 29, 30). This effect, coupled with the large abundance of CO, implies that CO is self-shielding to much larger radii than most other species (ref. 51), a conclusion which is consistent with the much larger extent of CO emission (~6') than of HCN (~45") in IRC+10216.

Glassgold (ref. 31) and Glassgold and Huggins (ref. 32) have also considered the effects of UV photons produced in a stellar chromosphere. They find that for α Orionis, chromospheric radiation can play a significant role in determining the ionization structure of the CSE.

2. A second process is reaction between neutrals and ionic molecules. The molecular ions may be produced by interstellar UV ionization of the abundant species (CO, H_2O, N_2, C_2H_2) yielding HCO^+, H_3O^+, or N_2H^+. These ions may then react with other molecules to produce a variety of products. Another source of ionization is cosmic rays which penetrate throughout the envelope to ionize H_2, leading to the formation of H_3^+, which in turn can produce the molecular ions mentioned above (see ref. 30).

Chromospheric UV may also be capable of generating molecular ions in the inner CSE, if the star possesses a chromosphere. In some cases, a nearby hot star (a binary companion or a nearby O-star) may produce UV sufficient to influence the envelope chemistry (ref. 24).

Theoretical models for ion-neutral chemistry in molecular CSE's have been calculated by various authors. For the O-rich (C/O < 1) case, early work by Goldreich and Scoville (ref. 23) dealt mainly with reactions of H_2 and H_2O. Related calculations were made by Huggins and Glassgold and by Scalo and Slavsky (refs. 24 and 33), who extended the models to include S and Si chemistry. More recently, Slavsky and Scalo (ref. 34) and Mamon, Glassgold, and Omont (ref. 30) have presented more refined and extensive calculations which attempt to incorporate all important physical effects. Slavsky and Scalo (ref. 34) employ some 135 reactions among 45 species and 8 elements.

For the carbon-rich CSE's, detailed photochemically-initiated ion-neutral reaction networks have been calculated by Nejad, Millar, and Freeman (ref. 35), Glassgold, Lucas, and Omont (ref. 36), Nejad and Millar (ref. 37), and Glassgold et al. (ref. 38). Nejad and Millar (ref. 37) include 270 reactions with 85 species and although these authors note that nearly all the important reaction rates are laboratory measurements, about 50% of all the rates used are only estimates. Moreover, Glassgold et al. (ref. 38) have pointed out that the temperature dependence of ion-molecule reactions may differ from assumptions commonly made in extrapolating laboratory values to the lower temperatures found in CSE's. Thus, despite the increase in model sophistication, there is evidently some room for improvement in precision.

Comparison of Chemical Models with Observations

Carbon-rich CSE's

The archetypical example of a carbon-rich CSE is the carbon star IRC+10216. It has a large mass loss rate and hence a dense envelope, and it is relatively nearby (~200 pc), so that trace molecules are more easily detected than in more distant CSE's. Its proximity to us also makes possible spatially-resolved studies of the envelope structure with a fair amount of detail at a resolution of a few arcseconds, now attainable at mm-wavelengths. Moreover, the envelope of IRC+10216 appears to be basically spherical, so that spherically-symmetric models (which are universally assumed) should bear some resemblance to reality.

Evidence for photochemical reactions in IRC+10216 was found by Wootten et al. (ref. 28) in the large abundance (and apparent angular size) of CN, which they interpreted as a result of photodissociation of HCN. Further evidence was given by Bieging, Chapman, and Welch (ref. 22), based on interferometric mapping of HCN, which shows a cutoff in the HCN emission at a radius of $\sim 10^{17}$ cm. The photochemical models of Glassgold et al. (refs. 36, 38) predict that the HCN abundance falls to 10% of its initial value at $R = 7 \times 10^{16}$ cm, while CN reaches a maximum abundance at 6×10^{16} cm. Similar results were obtained by Truong-Bach et al. (ref. 39) in their analysis of data from the 20-m Onsala telescope. Thus, photodissociation models seem to account for the observed size of the HCN emission as well as the product CN molecule.

A second molecule detected in IRC+10216 is C_2H, which is almost certainly a photodissociation product of acetylene (C_2H_2) (see ref. 40). Truong-Bach et al. (ref. 39) have mapped C_2H with the Onsala telescope and modelled the C_2H_2 photodissociation. Their model predicts that C_2H is distributed in a shell with a peak abundance of 5 x 10^{16} cm radius. However, they could not resolve the shell structure with the 45" telescope beamwidth. More recently, Bieging and Rieu (ref. 41) have mapped the C_2H emission at 87 GHz toward IRC+10216, using the U.C. Berkeley mm-interferometer. With a synthesized beam of ~8", they clearly resolve the C_2H emission into a ring-like structure as expected for a spherical shell distribution. The observed size of C_2H emission is in good agreement with the predictions of Nejad and Millar (ref. 37) and of Glassgold et al. (ref. 36) in that the observed radial extent is as predicted; however, the absolute abundances are discrepant by factors of 2 to 5. Considering the model uncertainties, this should be considered rather good agreement.

Other molecular species for which both theoretical predictions and high-resolution observations have recently been made include HNC and HC_3N. Both are predicted to form in sequences of photon-initiated ion-molecule reactions (refs. 36-38, 43). Mapping of HNC and HC_3N (J=10-9) by Bieging and Rieu (ref. 41) with the Berkeley interferometer and of HC_3N (J=12-11) by Likkel et al. (ref. 42) with the Caltech instrument, all show the predicted shell structure with approximately the expected dimensions.

Although detailed excitation calculations have not yet been completed for these species, the observed lines are optically thin. Therefore, since the molecules are linear rotors, the emission intensity can be used to derive total column densities directly, so long as the level populations approximately follow a Boltzmann distribution at some reasonable temperature. Assuming a "standard" mass loss rate for IRC+10216, one can derive molecular abundances for comparison with the published theoretical values. For HNC, the calculations of Glassgold and Mamon (ref. 43) are in excellent agreement with the observations, while Nejad and Millar (ref. 37) predict a size ~2 times larger than observed.

For HC_3N, the results of Bieging and Rieu (ref. 41) show a ring-like distribution with a filled center--i.e., at the position of the star the line brightness temperature at line center is not zero, but is reduced to ~40% of the value at the peak of the ring. Likkel et al. (ref. 42) do not detect emission in the J=12-11 line at the stellar position at line center. This result may be a consequence of more limited sampling of spatial frequencies in their data. The overall size and morphology of the HC_3N ring are otherwise in good agreement for the two transitions, which suggests that real abundance effects, not excitation, are responsible for the ring-like brightness distribution. By way of comparison with theoretical models, the work of Glassgold and Mamon (ref. 43) is in good agreement in radial distribution, but their predicted HC_3N abundance is ~5 times too low. Nejad and Millar (ref. 37) predict too-extended a distribution and an abundance ~15 times too low. Glassgold and Mamon, by including the effects of cosmic ray ionization in the interior envelope, can reproduce the "filled center" seen by Bieging and Rieu (ref. 41) with rather good agreement in molecular abundances. This agreement suggests that the reaction

$$H_2CN^+ + C_2H_2 \rightarrow H_2C_3N^+ + H_2$$

followed by dissociative recombination to yield HC_3N may be an important pathway to producing HC_3N in the inner envelope, where H_2CN^+ is produced from reactions initiated by cosmic rays. Since HC_3N is the simplest of the cyanopolyynes (HC_xN), whose remarkably large abundances have been a puzzle (see ref. 4), these results suggest that cosmic ray-initiated chemistry may be important in forming the longer carbon chains as well.

Although the rather good agreement between recent observations and photochemical models implies that molecular ions play an important role in CSE chemistry, detection of the ions has proved elusive. For IRC+10216, Lucas et al. (ref. 44) have set a low upper limit on the emission of HCO^+. The model of Glassgold et al. (ref. 38) is just consistent with this limit, although subject to assumed model parameters such as the rates of mass loss and cosmic ray ionization. HCO^+ has recently been detected in several other CSE's (ref. 45 and Omont, private communication), but these objects all have evidence for shocked winds or internal sources of ionization, so that the photochemical models may not be directly applicable in predicting the HCO^+ abundance.

Oxygen-rich CSE's

Comparison of observations with chemical model predictions for the O-rich envelopes is hampered by a lack of quantitative observational data. Emission lines of OH, H_2O, and SiO have been detected from a large number of stars, but virtually all of these are masers. Since the maser excitation and amplification processes are poorly understood, it is not possible to get reliable column densities or abundances of these molecules for comparison with theoretical chemical models. Relatively few other, non-maser, lines have been detected toward O-rich CSE's, although that situation is now improving with the operation of the new large mm-wavelength telescopes of IRAM and Nobeyama. One species of interest is HCO^+, which Mamon et al. (ref. 30) have argued should be fairly abundant in O-rich CSE's. However, the excitation conditions and other envelope properties of known CSE's make the predicted emission from HCO^+ very weak. As noted above, the objects in which HCO^+ has so far been detected have anomalous properties which may make photochemical models inappropriate for comparison.

Neutral species whose thermal line emission has been observed include SO and SiO. Sahai and Howe (ref. 46) have detected SO in several O-rich CSE's. They derived abundances of $\sim 10^{-5}$, much higher than equilibrium chemical models predict ($\sim 10^{-8}$). They argue that the high SO abundance supports the non-equilibrium chemical models of Scalo and Slavsky (refs. 33, 34), in which SO is a product of reactions with OH produced by photodissociation of H_2O. Thermal SiO emission has been detected now in more than 20 O-rich CSE's, and shows abundances which are inconsistent with equilibrium chemical models. However, the SiO gas phase abundance is probably strongly affected by grain processes, which we consider briefly in the next section.

Grain Processes

Circumstellar envelopes are important sources of dust grains for the interstellar medium. Most of our information about the grain component in CSE's is obtained from infrared observations, since the thermal dust emission at microwave frequencies is very weak (though detectable--e.g. ref. 47). However, it has been possible to draw certain conclusions about the grains and gas-grain processes from microwave spectroscopic observations.

In the case of oxygen-rich CSE's, the presence of strong SiO maser emission from vibrationally excited states implies a large abundance of gas-phase SiO close to the star. Morris and Alcock (ref. 48) pointed out that emission from ground state SiO is also detected, with intensities which imply abundances of SiO 100 to 1000 times less than predicted by chemical equilibrium models. This discrepancy suggests that SiO is quickly depleted onto grains from the gas relatively close to the star ($R < 10^{15}$ cm), possibly just outside the zone of SiO maser action. The form which the Si takes is not entirely certain, but the presence of the 9.7 μm feature (usually in absorption) in spectra of many OH/IR stars (ref. 49) suggests that the Si is predominantly in silicates.

For the C-rich envelopes, SiO maser emission is not observed, so there is no comparable constraint on the gas phase abundance of Si close to the star. Even so, observations of SiS toward IRC+10216 (ref. 50) implied an abundance of SiS some two orders of magnitude less than predicted by chemical equilibrium models. Sahai et al. argued that since sulfur appears to be relatively undepleted, it is the silicon which has been removed from the gas phase, probably in the form of SiC, and incorporated into grains.

Recent interferometer maps of the SiS and SiO distributions toward IRC+10216 (refs. 41, 42) show that these species are spatially extended, but with intensities corresponding to molecular abundances about 100 times lower than predicted from chemical equilibrium. Bieging and Rieu (ref. 41) find that the SiS abundance as a function of radius is roughly constant, though possibly showing some (factor of 5) enhancement at $R = 3 \times 10^{16}$ cm, and with a cutoff for $R > 6 \times 10^{16}$ cm. This abundance variation is consistent with a large initial depletion of Si onto grains for $R < 10^{15}$ cm, and some chemical production of SiS in the outer envelope, followed by UV photodissociation at large R. This picture is consistent with some of the chemical models of Scalo and Slavsky (refs. 33 and 34).

CONCLUDING REMARKS

In this review, I have tried to summarize the ways in which microwave spectroscopic observations of circumstellar envelopes can give us essential information on the processes of stellar evolution at the end of the asymptotic giant branch and on the enrichment of the interstellar medium in elements and in grains. There has been much progress recently in both the observations and their theoretical interpretation. Photochemical models for CSE's can now account at least in a rough way, and sometimes with remarkable accuracy, for both the distribution and abundances of a number of molecular species which have been observed with high angular resolution. Much of the theoretical effort has focussed on the C-rich envelope of IRC+10216, and a desirable goal would be a comprehensive, fully self-consistent model that can explain all observations at once. The extension of such modelling to other CSE's will also be important as the quality of the observational data continues to improve. As we have seen, this improvement in the data is especially striking for the O-rich CSE's. An increasing number of such objects are now detected in a growing list of molecules--some of which (for example, C-bearing species like HCN) are not expected on theoretical grounds. The presence of these species is a challenge to the chemical model-builders. A point perhaps worth noting again is the need for better chemical rate coefficients. Most important reactions are probably adequately understood over a limited range of temperatures, but in extrapolating to the wide range of conditions possible in CSE's, there is some room for improvement.

Finally, the increases in resolution and sensitivity which are now becoming possible with the new large single-dish telescopes and with interferometer arrays will require improvements in analysis. To do justice to the observational data, one may be forced to abandon the usual assumptions of spherical symmetry, uniform outflow velocity, and constant mass loss rate, at least in specific cases. As a consequence, the calculations of radiative transfer and of molecular excitation may be significantly complicated, raising the need for improved computer codes to handle more realistic cases than have been treated in the past. It seems clear, though, that the improvements in observational data already appearing in print will warrant such a computational effort. Further progress in understanding CSE's and the physical processes associated with them will depend on both new observations and their careful analysis.

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