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We will discuss molecular envelopes around post main sequence stars. Topics that will be covered include chemical composition, physical properties, mass loss and evolution. In view of the following papers by Drs. Snyder and Goldreich we will have little to say about circumstellar masers here.

Hydrogen is the most abundant element in most stars. We are interested in whether it is in atomic or molecular form in the circumstellar envelopes. The Arecibo radio telescope was used at 21-cm wavelength to search for atomic hydrogen in various evolved stars (Zuckerman et al. 1980). The 21-cm line was not detected in any star: the best limits were obtained for the very cold, infrared sources IRC+10216, CIT6, IRC+10011, and NML Tau. The first two are carbon-stars ( $[C]/[O] > 1$ ) and the latter two are oxygen-rich ( $[O]/[C] > 1$ ). In all cases no more than 10% by mass of the circumstellar hydrogen is in atomic form. The best limit for IRC+10216 is  $\lesssim 1\%$  H by mass if the model of Kwan and Hill (1977) is adopted or  $\lesssim 0.2\%$  H by mass if, instead, more recent  $J = 2 \rightarrow 1$  CO data (Knapp 1979) are utilized.

That the preponderance of the hydrogen is molecular is not surprising if chemical equilibrium abundances are achieved in the photosphere and then these same abundances are maintained in the circumstellar shell. However, Balmer emission in Miras indicates that at least some of the hydrogen is atomic at least some of the time (possibly due to shocks in the atmosphere). Also, the ambient interstellar radiation field will photodissociate molecular hydrogen far from the star. Thus, the 21-cm limits place constraints on the importance of these and other mechanisms of dissociation. For  $\alpha$  Ori the much higher photospheric temperature suggests that much (most) of the hydrogen will be atomic but, unfortunately, strong 21-cm emission from background hydrogen rendered the Arecibo measurement nearly useless in spite of considerable effort to subtract out this background.

For other elements the  $[C]/[O]$  ratio is probably the most important in determining the over-all chemical composition in the envelope. From

photospheric spectra one can easily deduce if C/O is greater or less than unity. But quantitative determinations of C/O in M giants are still lacking.

For carbon-stars IRC+10216 is the prototype and 17 molecules have been identified in its envelope either in the radio (CO, CN, CS, HCN, HNC, C<sub>2</sub>H, SiS, SiO, HC<sub>3</sub>N, HC<sub>5</sub>N, HC<sub>7</sub>N, C<sub>4</sub>H, C<sub>3</sub>N, CH<sub>3</sub>CN) or in the infrared (C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>) or in both. Since Dr. McCabe has discussed this star in detail we will add only a few remarks here. Except for a small amount of SiO no oxygen-containing molecules (other than CO of course) have been detected. Indeed, the [SiS]/[SiO] ratio is greater than unity as expected only in a carbon-rich environment (Tsuji 1973). The chemistry is clearly different from the chemistry in the interstellar medium since HCO<sup>+</sup> and N<sub>2</sub>H<sup>+</sup> are not seen in IRC+10216. Also [HNC]/[HCN] is  $\lesssim$  1/100 as expected for chemical equilibrium at  $T \sim 1000$  K (McCabe et al. 1979) but very different from the interstellar ratio ( $\sim 1$ ). It is perhaps significant that of 12 polyatomic molecules, 9 are linear.

Wannier and Linke (1978) have measured isotopic ratios for IRC+10216 and find a large [<sup>14</sup>N]/[<sup>15</sup>N] ratio indicative of cold CNO processing. Since [C]/[O] > 1 in conjunction with [C]/[H]  $\gtrsim$  solar implies carbon production in the 3 $\alpha$  process, we have evidence in IRC+10216 for the products of two different nuclear burning processes.

The molecular inventory in envelopes around oxygen-rich stars is sparser: OH, H<sub>2</sub>O and SiO masers, thermal mm- $\lambda$  emission from SiO and CO, and evidence for NH<sub>3</sub> and CO in the infrared. SiS emission is not seen (Palmer and Zuckerman 1978), so [SiS]/[SiO] is less than unity as expected in an oxygen-rich environment. TiO and other simple molecules have yet to be detected at infrared and optical wavelengths.

Calculations of Tsuji (1973) and Vardya (1966) suggest that SiO is the dominant gas phase carrier of silicon in these stars. Results of Morris et al. (1979) and Lambert and Vanden Bout (1978) imply that  $\sim 99\%$  of the silicon is in the grains in the outer parts of the circumstellar shell but this is unlikely to be the case in the inner shell where the SiO maser is produced. Thus the bulk of the silicon is apparently incorporated into grains between 10<sup>14</sup> and 10<sup>16</sup> cm from the central star in agreement with the inner dust boundary determined from 11 $\mu$ m interferometry for a limited sample of stars (Sutton 1979, discussed below).

There seems to be some, although by no means universal, agreement that the grains in oxygen-rich stars are mainly "silicates", (e.g. Mg<sub>2</sub>SiO<sub>4</sub>), and in carbon-stars mainly graphite and SiC. How large are the grains? Theoretical estimates (e.g. Salpeter 1974) are inconclusive and so are the observations. For example, the presumed graphite and SiC grains in IRC+10216 are estimated to have radii  $a \sim 1\mu$ m from a fit to the far-infrared spectrum (Campbell et al. 1976). But impure grains with enhanced far-IR emissivities could be a lot smaller. In the carbon-rich Egg Nebula (CRL 2688) the very large percentage polarization in the scattered light implies  $a < 0.1\mu$ m (Schmidt et al. 1978) whereas if the

grains in planetary nebulae (PN's) are graphite then the absence of a  $\lambda 2200 \text{ \AA}$  feature in their spectra implies  $\alpha > 0.04 \mu\text{m}$  (Mathis 1978). It might be argued that the grains in PN's form in the ionized gas and therefore may be different from grains that form in the neutral clouds around IRC+10216 and CRL 2688. However, since molecular clumps exist inside PN's (Beckwith et al. 1978) the bulk of the dust emission may be associated with this neutral gas rather than the ionized gas.

How do circumstellar clouds fare as a source of interstellar grains? Silicate grains are probably produced in proto-stellar nebulae, oxygen-rich red giants and, possibly, planetary nebulae. Graphite is probably produced in carbon-stars and planetary nebulae. We acknowledge the existence of other, more exotic, suggestions for the composition of the grains (e.g. carbyne, organic polymers, and tholins) but do not evaluate them here.

Total mass loss rates, summed over the entire galaxy, are probably comparable for evolved stars (red giants plus PN's) and for proto-stellar nebulae. Estimates are  $\sim \text{few} \times M_{\odot}/\text{yr}$ . Therefore, at present, it is difficult to choose between a pre and post main sequence origin for the interstellar dust. It is even conceivable that much of the dust in interstellar molecular clouds forms in situ if radiative association rates are very fast for very large molecules (Smith and Adams 1978).

Where does the dust form in the circumstellar shell? Since oxygen-rich giants and supergiants typically have photospheric temperatures between 2000 and 3500 K and silicates condense at  $T \lesssim 1200 \text{ K}$ , it is to be expected that most of the dust will form at least a few stellar radii from the center of these stars. For cool carbon-stars the situation is not, a priori, so obvious, since  $T_{\text{photosphere}} \sim 2000 \text{ K}$  and SiC and graphite can condense at  $T \sim 1700 \text{ K}$ . Some recent observations bear on this question.

For uniform outflow the gas density drops as  $r^{-2}$ . The shape of most radio emission profiles are consistent with  $\rho_{\text{gas}} \propto r^{-2}$ , although in IRC+10216 Wannier et al. (1979) find evidence for an outflow rate decreasing with time. The dust density distribution around evolved stars was measured first by means of lunar occultations but recently infrared interferometry (e.g. Sutton 1979) has emerged as a powerful technique. Sutton's  $11 \mu\text{m}$  visibility curves for a limited sample of stars suggest that if  $\rho_{\text{dust}} \propto r^{-2}$  then most of the dust condensation begins near the radius at which  $T \sim T_{\text{condensation}}/2$  (i.e. beyond  $10 R_{*}$ ). Also  $\rho_{\text{dust}} \propto r^{-2}$  appears to fit the data for IRC+10216 much better than the two shell model suggested by the older lunar occultation data. Alternatively, the visibility curves can be fitted with dust condensation beginning near the radius at which  $T \sim T_{\text{condensation}}$ , provided that  $\rho_{\text{dust}} \propto r^{-1.5}$ .

What might cause an  $r^{-1.5}$  dependence in  $\rho_{\text{dust}}$ ?  $\dot{M}$  could be declining as a function of time but this seems unlikely to be true in all cases. The gas could be decelerating but this seems unlikely at large  $r$ . Perhaps the most likely explanation for an  $r^{-1.5}$  dependence is dust forma-

tion between  $10^{14}$  and  $10^{16}$  cm from the center of the star. That the dust forms at  $r \sim 10^{15}$  cm is consistent with the infrared energy distribution and  $10\mu$  silicate depth in the spectra of OH/IR stars (Werner et al. 1979). At larger distances from the star we have the scattered light profiles of McMillan and Tapia (1978) who find  $\rho_{\text{dust}}$  somewhere in the range  $r^{-1.5}$ – $r^{-3.0}$  (with  $r^{-2}$  preferred) around  $\alpha$  Ori. These results apply to  $r$  between  $4 \times 10^{16}$  and  $2 \times 10^{17}$  cm.

Information is available on the azimuthal shapes of some circumstellar clouds. Non spherical shapes may be due to rotation, magnetic fields and non-radial pulsation. Capriotti (1978) has even suggested that the asymmetries in the shapes of PN's may be related to the galaxy since there is a tendency for the long axis to lie parallel to the plane of the Milky Way. Some less evolved objects (e.g. IRC+10216, VY Cma, the Egg Nebula, OH 0739-14, CRL 618 and M1-92) show very large percentage polarization ( $\sim 30\%$ ) in scattered light with  $\lambda \lesssim 1\mu\text{m}$  indicative of asymmetrical dust distributions (the latter four objects are classified as bi-polar nebulae). The grain masses in the scattering nebulae in the Egg Nebula and M1-92 are  $\sim 10^{-4} M_{\odot}$ , comparable to those deduced from far IR emission in some PN's (Schmidt et al. 1978). However, polarization is yet to be detected from PN's even though many look similar, superficially at least, to bi-polars.

A  $\lambda 6000 \text{ \AA}$  photograph of IRC+10216 shows an elongated  $2'' \times 4''$  image (Becklin et al. 1969) but no asymmetry is apparent at  $11\mu\text{m}$  on a smaller scale ( $\lesssim 1''$ , Sutton 1979) or at  $1.3 \text{ mm}$  on a larger scale ( $\sim 60''$ , Wannier et al. 1979). (There is a report [McCarthy 1979] of asymmetry at  $5\mu\text{m}$  with, however, a position angle that bears no apparent relation to the  $6000 \text{ \AA}$  image.) The envelope around  $\alpha$  Ori appears to be roughly symmetric (Bernat and Lambert 1976; McMillan and Tapia 1978).

A long standing question in the evolution of red-giant stars is what accelerates the gas and causes mass loss. Although radiation pressure on the dust probably is responsible for acceleration of the gas to  $v_{\infty}$ , some other mechanism probably initiates the mass loss. As we have seen above, the observational evidence suggests that the bulk of the dust forms outside of  $10^{14}$  cm from the central star. At this distance there is already some evidence (although not completely compelling) for outflow at velocities  $\lesssim v_{\infty}/2$ . For early M stars, for example, there are H $\alpha$  asymmetries (Boesgaard and Hagen 1979); for late M stars there are H $_2$ O and SiO maser velocities. In each case, however, there still remain ambiguities (e.g. the maser velocity spread may be due to turbulence rather than outflow [Moran et al. 1979]) and, indeed, at this symposium Don Hall has suggested a substantially different picture than the one outlined below. Nonetheless, we feel that, at this time, the published literature suggests the following picture. For K and M stars mass loss is initiated by processes other than radiation pressure on dust which only forms at  $r \gtrsim 10^{14}$  cm. Between  $10^{14}$  and  $10^{16}$  cm the formation process continues and the gas is accelerated to  $v_{\infty}$  by radiation pressure on the dust. At  $r \gtrsim 10^{16}$  cm  $1612 \text{ MHz}$  OH maser and SiO and CO thermal emission are produced. At much greater distances the molecules are photo-

dissociated by the ambient interstellar radiation field and the circumstellar gas is decelerated in the interstellar medium.

For K and early M stars (which are not pulsating) Mullan (1978) has suggested that large M results from a hydrodynamic expansion of the chromosphere-corona when the sonic point is located in the (high-density) chromosphere. For pulsating late M stars (Miras and SR's) shocks levitate the atmosphere raising the density at the sonic point substantially (Wood 1979). Whether the pulsation is in the fundamental mode or the 1st harmonic is still controversial (Wood 1978; Hill and Willson 1979) and relates to models for the evolution of these stars (Wood and Cahn 1977).

Finally we consider the evolutionary state of stars with circumstellar envelopes. As stars evolve up the red giant branch for the second time it is generally agreed that their core masses, luminosities and mass loss rates steadily increase. For Miras  $\sim 10^{-7} M_{\odot}/\text{yr}$  is added to the core but, typically,  $\sim 10^{-6} M_{\odot}/\text{yr}$  is lost via expansion of the circumstellar envelope. So the subsequent state of the red giant star, i.e. planetary nebula or supernova, is determined by its initial mass and the mass loss. Wood (1978) has suggested that V Hya, a carbon-star with CO emission (Zuckerman et al. 1977), may be a pre-supernova. Knapp (1979) suggests that IRC+10216 may be a massive star undergoing extreme ( $\sim 10^{-4} M_{\odot}/\text{yr}$ ) mass loss. On the other hand, R Cr B stars, proposed as precursors of supernovae of type I by Wheeler (1978), do not seem to have molecular envelopes detectable to radio astronomy.

Although we may be looking at a few pre-supernova, most of the red giants with circumstellar envelopes will, no doubt, eventually evolve into planetary nebulae. Which of the many objects now under study by astronomers are actually pre-planetary nebulae (PPN's) is rather controversial. One school of thought is that the PPN's are to be found among the very red giant stars with CO radio emission, most of which are probably carbon-rich (Zuckerman et al. 1978, Zuckerman 1978). Another group prefers peculiar emission line objects such as V 1016 Cyg and HM Sge (Purton 1979). Our view is that if the latter objects are PPN's then they will evolve into only low mass PN's but not the bright  $\sim 0.2 M_{\odot}$  PN's whose pictures appear in elementary astronomy texts. For example, V 1016 Cyg contains only a small amount of ionized gas (Kwok et al. 1978) and apparently little neutral gas since neither CO nor  $2\mu\text{m}$  H<sub>2</sub> emission has been detected.

The matter can be largely resolved if [C]/[O] ratios can be determined for PN's. For the gas the best tool seems to be the UV lines of CIII and CIV. For IC 418 and NGC 7662, C/O  $\sim 1$  is indicated although observational problems still remain (Harrington et al. 1979; Torres-Peimbert et al. 1979). Even if the observational problems are resolved the meaning of C/O ratios near unity may remain ambiguous. If during the PPN phase all of the less abundant of the two elements goes into CO which is later photodissociated by the central star of the PN, and the

bulk of the left-over C or O is incorporated into the dust, then the gas may always show  $C/O \sim 1$  largely independent of its origin in C-rich or O-rich material (Harrington 1979). If so, it will be necessary to determine the composition of the dust as well as the gas. To date, the handful of PN's ( $\sim 8$ ) with apparent  $10\mu\text{m}$  silicate or  $11\mu\text{m}$  SiC features are roughly divided between the two.

This research was partially supported by National Science Foundation Grants AST 76-17600 and AST 77-28475 to the Universities of Maryland and Texas, respectively.

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#### DISCUSSION FOLLOWING ZUCKERMAN

*Snyder*: Professor Zuckerman, do you really believe in circumstellar tholins?

*Winnewisser*: We do not believe in tholins - let us please have the next question!

*Zuckerman*: I like Bishun Khare and Carl Sagan.

*Elitzur*: You have shown numbers for  $M_{\text{H}}/M_{\text{total}}$ . How did you derive  $M_{\text{total}}$ ?

*Zuckerman*: For IRC+10011 I used the mass loss rate ( $\dot{M}$ ) suggested by Goldreich and Scoville. For IRC+10216 I took  $\dot{M}$  from Kwan and Hill. For CIT6 and NML Tau I assumed  $\dot{M} = 10^{-5} M_{\odot}/\text{yr}$ .

*Greenberg*: I could not understand how  $\alpha$  Orionis can be spherical. This assertion is inconsistent with some linear polarization measurements of Tinbergen (unpublished) which have been analyzed by him, de Jager and myself, and which seem to provide firm evidence for dust grains distributed non-spherically and even seem to provide a size estimate of  $a \approx 0.05 \mu\text{m}$ .

*Zuckerman*: My remark that  $\alpha$  Orionis appears "reasonably" symmetric is based on observations of light scattered by dust (Tapia and McMillan) and on K-line scattering (Bernat and Lambert).

*Kwok*: Whether dust is the cause or effect of mass loss has been long debated. Clean silicates suffer from an inverse greenhouse effect

in the sense that they are relatively transparent in the near IR, but emit more strongly at  $10\mu$ . For a 2000 K star, silicate grains can condense at only 0.07 stellar radii above the star (Gilman, unpublished manuscript). The infrared interferometry results are dependent on grain size distribution, grain temperature distribution, etc., and are not obviously incompatible with the above picture.

*Zuckerman:* I believe that the weight of the observational evidence, combined with the calculations of Jones and Merrill, suggests that the picture I painted is probably correct. However other possibilities may still be viable.

*Hall:* Why do you believe the dust in the envelope of IRC+10216 is graphite?

*Zuckerman:* This is the cononical view of the major constituent of carbon-star dust. SiC, for example, appears to be much less abundant. But perhaps the dust is primarily something else that no one has thought of.

*Kwok:* There are two well observed grain-formation processes: one is condensation in red-giant envelopes and the other is condensation in ionized ejecta from stars, for example, WC stars, novae, and the nuclei of planetary nebulae. The dust usually associated with planetary nebulae is probably formed under a different process than the dust seen in objects like IRC+10216.

*Zuckerman:* It could be. I acknowledged the possibility in my paper.

*Hall:* Why do you believe the dust size is  $\sim 1\mu$  in IRC+10216?

*Zuckerman:* This conclusion is based on a fit to the far-infrared spectrum obtained by Campbell et al.  $1\mu$  is appropriate for pure graphite or SiC, but smaller sizes would be possible if the grains have impurities with enhanced far-IR emission.

*Hall:* McCarthy & Low report substantial departures from spherical symmetry in 10216 at 5 and  $10\mu$ . Is this inconsistent with your conclusions?

*Zuckerman:* My remark that IRC+10216 appears symmetric at  $11\mu$  was based on the work of Sutton et al. If McCarthy and Low did indeed measure an asymmetry, it bears no obvious relationship to that seen in the 6000 Å photograph obtained by the Cal Tech IR group. Therefore, it appears important to confirm McCarthy's measurement.

*Clark:* Why do you think that the ground vibrational state ("thermal") SiO is situated as far out as the OH?

*Zuckerman:* I read it in the literature.

*Morris:* There is no direct observational evidence. The distribution is inferred from the widths, shapes, and intensities of the  $v=0$  SiO lines, all of which are accounted for by models of extended envelopes (Morris & Alcock, Ap. J. 1977).

*Silk:* Can you set a lower limit on the mean rate of mass ejection of grains into the interstellar medium via mass loss from evolved stars?

*Zuckerman:* It could probably be done, but I have not yet done it.