

## THE ROLE OF DUST IN CIRCUMSTELLAR CHEMISTRY

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### ABSTRACT.

The outer envelopes of the outflows from late-type stars where the dust and molecules have already been formed and the matter has been accelerated to its terminal velocity are the focus of this review. One major role for grains in the circumstellar chemistry is the protection of molecules against photodissociation by ambient interstellar ultraviolet photons. Also, in more distant regions where the grains become sufficiently cool as they flow away from the central star, the dust may serve as a condensation sink for molecules which can be bound into mantles.

### 1. INTRODUCTION

Some red giants are losing as much as  $10^{-4} M_{\odot} \text{ yr}^{-1}$  (see, for example, Zuckerman 1980, Morris and Zuckerman 1985, Olofsson 1986). These very high rates of mass loss can dramatically change the total mass of a star and therefore profoundly affect its ultimate fate. Furthermore, such high mass loss rates are important for replenishing the interstellar medium from which new stars form.

While there is still considerable uncertainty about the physical mechanism that causes the mass loss, it seems that a reasonable and self-consistent interpretation of the currently available data is that the mass loss is a two step process (Jones, Ney and Stein 1981, Willson and Bowen 1986, Jura 1986b). Pulsations or some related mechanical process first levitate the matter above the photosphere. The gas which is initially cool in the photosphere (roughly at  $T \sim 3000 \text{ K}$ ) falls, though perhaps not monotonically, to a lower temperature as it radiates and expands. At some point, solid grains form; after which, radiation pressure on the dust is sufficiently large that the matter is then expelled to infinity.

Red giants that are losing large amounts of mass are enshrouded by their own circumstellar shells so that they are efficient factories for the manufacture of molecules and dust, and therefore they are strong sources of infrared and radio emission. Because of advances in the relevant technology during the past 15 years, it has been possible to

study in considerable detail the mass outflows from many of these stars.

The grains in circumstellar outflows play both direct and indirect roles in the circumstellar chemistry. First, grains perform many of the same functions that they do in the interstellar medium such as shielding molecules from dissociating radiation by ambient ultraviolet photons. Also, indirectly, the grains help control the density and temperature of the outflowing gas which ultimately affects the rate of chemical reactions and the formation of different species.

In the picture described by Lafont, Lucas and Omont (1982), there are several zones in a circumstellar outflow. The effects of grains on the chemistry are best understood in the outer envelopes where the material has reached its terminal velocity and is coasting to infinity. The inner regions where the molecules and grains are largely synthesized and the matter is accelerated is not nearly so well understood. For example, while the picture of the "freeze-out" of different molecules at thermodynamic equilibrium as they flow out of the star is attractive (McCabe, Smith and Clegg 1979), it does not include nonequilibrium effects from shocks that accelerate the outflows.

## DIRECT EFFECTS OF GRAINS ON CIRCUMSTELLAR CHEMISTRY

### 2.1. Photochemistry

Circumstellar grains are sufficiently small that the extinction rises through the optical and ultraviolet regions of the spectrum. Consequently, as in the interstellar medium, dust extinction protects molecules from photodissociation by ambient interstellar ultraviolet photons.

Photodissociation becomes important when its rate becomes comparable to the dynamic outflow time,  $r/v$  where  $r$  is the distance from the star and  $v$  is the outflow velocity of the material. In a spherically symmetric shell, the photodissociation rate,  $I(r)$ , at radius  $r$ , is approximately given by (Jura and Morris 1981, Huggins and Glassgold 1982):

$$I = I_0 \exp(-1.4\tau[r]) \quad (1)$$

In this equation,  $I_0$  is the rate for photodissociation in the interstellar medium and  $\tau$  is the radial optical depth at the wavelength of the dissociating photons. If  $\dot{M}$  is the mass loss rate and  $\chi$  is the dust opacity ( $\text{cm}^2 \text{gm}^{-1}$ ), then:

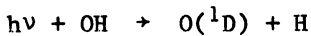
$$\tau(r) = \chi \dot{M} / (4\pi r v) \quad (2)$$

Equations (1) and (2) have been generalized by Jura (1983b) for non-spherically symmetric outflows.

With the conspicuous exception of  $\alpha$  Ori, in most red giants there appears to be an anti-correlation between the strength of the chromospheric emission and the amount of circumstellar matter (Jennings and Dyck 1972, Jura 1986b). Therefore, we can assume that in most cases the dissociating ultraviolet arrives from the interstellar medium rather than being produced by the mass-losing star itself.

Consider now the photochemistry for oxygen rich stars. After  $H_2$ , the most abundant molecules in the outflows are thought to be CO and  $H_2O$ . The  $H_2O$  is photodissociated to produce OH (Goldreich and Scoville 1976), and therefore the OH is expected to have a much greater spatial extent than the  $H_2O$ . Both of these molecules display maser emission which can be mapped with radio interferometers to measure their distributions in the sky. OH masers are typically formed  $10^{16}$  to  $10^{17}$  cm from the central star (Bowers, Johnston and Spencer 1983) which is considerably further than the  $10^{14}$  cm where the  $H_2O$  masers originate (Spencer *et al.* 1979). Also, as can be seen from equation (2), it is expected that the spatial extent of OH should increase with  $\dot{M}$ , and Huggins and Glassgold (1982) have shown that the available data display this predicted result. Quantitatively, it appears that the dust to gas ratio in circumstellar outflows is comparable to the standard value in the interstellar medium of  $1000 \text{ cm}^2 \text{ gm}^{-1}$  in the ultraviolet (see Spitzer 1978). Other estimates by independent means are in agreement with this typical value for the dust to gas ratio for both oxygen-rich and carbon-rich stars (Sopka *et al.* 1985, Knapp 1985, Jura 1986a).

Van Dishoeck and Dalgarno (1984) have shown that photodissociation of OH can lead to a significant production of  $O(^1D)$  atoms:



This process could lead to a detectable amount of emission at 6300 Å.

In carbon rich envelopes, photodissociation is also important. For example, in the well studied star IRC +10216, we expect from equations (1) and (2) and the mass loss rate of  $4 \times 10^{-5} M_{\odot} \text{ yr}^{-1}$  (Kwan and Hill 1977) that if  $\chi = 1000 \text{ cm}^2 \text{ gm}^{-1}$ , photodissociation should be important at about  $10^{17}$  cm from the star (Jura 1983a). This appears to be the case for HCN as is displayed by its interferometric map (Bieging, Chapman and Welch 1984) and of a predicted product of the photodissociation of HCN, CN, which is mapped to have a wide spatial extent (Wooten *et al.* 1982). Single beam maps of  $HC_7N$  (Nguyen-Q-Rieu, Graham and Bujarrabal 1984) also seem to show a marked decrease of the fractional abundance at about  $10^{17}$  cm from the star as would be expected from photodissociation. However, the rapid decrease in the fractional abundance of SiS which is indirectly inferred to occur at  $3 \times 10^{15}$  cm from the star (Nguyen-Q-Rieu *et al.* 1984) is not the result of photodissociation because it occurs too close. An alternative explanation, such as condensation onto grains (see below) may be appropriate.

Finally, as in the interstellar medium, some molecules are so abundant that they are "self-shielding". That is, the amount of outflowing gas is so large that the opacity is mainly produced by the molecules themselves, rather than the dust. Both  $H_2$  and CO are probably self shielding (Morris and Jura 1983, Glassgold and Huggins 1983). If the transitions that lead to destruction are sufficiently separated in frequency, then self-shielding can be smaller for minor isotopes so that  $^{12}CO$  and  $^{13}CO$  may have different spatial extents, and one should not directly use the ratios of  $^{12}CO$  to  $^{13}CO$  to measure the  $^{12}C/^{13}C$  ratio of the outflowing material (see Knapp 1985).

After a molecule is photodissociated, radicals may be produced and there may be subsequent gas-phase chemical reactions (Nejad, Millar and Freeman 1984, Glassgold, Lucas and Omont 1985) and radiative association (Herbst 1982). The recent discovery of HCN around oxygen rich stars (Deguchi and Goldsmith 1985) might be explained by a sequence of reactions following the photodissociation of CO (Deguchi, Claussen and Goldsmith 1986). If this picture is correct, we can imagine that since  $^{13}\text{CO}$  may be photodissociated closer to the star than is CO, there may be a particularly large abundance of  $\text{H}^{13}\text{CN}$  around oxygen-rich stars.

## 2.2 Condensation Onto Grains

As matter flows out from a mass-losing star, gas and grains collide and interact in a complex fashion. The physics of these processes are not understood in full generality, and it is useful to consider relatively simple cases such as the outer envelopes where the grains have already formed and the matter has achieved its terminal velocity.

In general, the grains are streaming supersonically through the gas because of the radiation pressure exerted by the central star, but at a sufficiently low speed (usually  $\ll 10 \text{ km s}^{-1}$ , Kwan and Hill 1977, Sopka et al. 1985) that sputtering is probably quite negligible (see Draine and Salpeter 1979). Instead, the collision speeds are such that we might expect most molecules that collide with a grain to stick at least for some short time (see Leger 1983).

The desorption time of a molecule that adheres to a grain depends upon the dust temperature. The temperature of the grains is controlled by radiative heating from the central star in balance with infrared emission by the dust. As the grains flow away from the star, they become cooler. Eventually, the grains may cool sufficiently that at some radial distance  $r_0$ , the time that a molecule dwells on the grains is long compared to the dynamical outflow time,  $r_0/v$ . In this case, we may assume that the molecule has been incorporated into the grain mantle. The critical quantity for determining whether an individual molecule sticks is its binding energy compared to the internal thermal energy of the grain material, while whether a large fraction of a particular species sticks is determined by the column density of grains measured radially from  $r_0$  to infinity.

Quantitatively, let  $f_X(\infty)$  denote the fraction of molecule X remaining in the gas phase at very large distance from the star. Jura and Morris (1985) have shown that:

$$f_X(\infty) = \exp(-\alpha\tau_{UV}(r_0[X])Q_{IR}^{1/2}\beta^{-1/2}Q_{UV}^{-1}) \quad (3)$$

In equation (3),  $\alpha$  is the probability that a molecule that collides with a grain sticks (Leger 1983, Burke and Hollenbach 1983),  $Q_{IR}$  and  $Q_{UV}$  are the geometric efficiencies for grain absorption in the infrared and ultraviolet, respectively, and  $\tau_{UV}$  is the radial optical depth in the ultraviolet, and thus measures the total column of grains that a molecule encounters on its outward flow. The quantity  $\beta$  is a measure of the momentum in the mass outflow,  $\dot{M}v$ , compared to the momentum available in the radiation from the central star,  $L/c$ , such that:

$$\beta = (\dot{M}v)/(L/c) \quad (4)$$

For almost all known mass-losing red giants,  $\beta < 1$  (Jura 1986b). This quantity  $\beta$  enters into estimating the amount of adsorption onto grains because radiation pressure on the dust drives the material supersonically through the gas and therefore controls the rate of gas-grain collisions.

The binding energies of such common molecules as  $H_2$ , CO and  $NH_3$  are sufficiently low, that we expect from equation (3) that most of these species remain in the gas phase. This is consistent with observations. Another way to check equation (3) is to observe the  $3.1 \mu m$  ice absorption feature since this results from  $H_2O$  adhering to grains. While there are still considerable uncertainties in the precise parameters, there is good agreement between theory and observations (Soifer et al. 1981) for the well studied star OH 231.8 +4.2.

Condensation onto grains may also occur for rather refractory molecules such as SiO where there is good evidence that the gas-phase abundance in the outer envelope is relatively low (Morris et al. 1979). It will be most interesting to perform detailed interferometric maps of this molecule.

### 2.3 Small Grains or Large Molecules?

The size distribution of circumstellar grains is not very well known. If grains are assumed to be spheres of radius  $a$ , it seems that in the interstellar medium,  $n(a)$  varies as  $a^{-3.5}$  (Mathis, Rumpl and Nordsieck 1977). This power law predicts a large number of small grains, and Leger and Puget (1984) have recently shown that very small grains may, for many purposes, be considered to be large molecules such as polycyclic aromatic hydrocarbons (PAH's). Unfortunately, at the moment, there is almost no direct information about the synthesis of these species. PAH's are thought to be present in carbon-rich planetary nebulae (see Leger and Puget 1984), but we do not yet know whether they are formed in the outflows from the pre-planetary red giant or whether they are synthesized in the shocks that are created by the ionized gas as it sweeps into the neutral envelope of the progenitor star (see Kwok 1982). It will be most interesting to determine if PAH's are present in the circumstellar envelopes around carbon rich red giants.

I thank Mark Morris and Ben Zuckerman for many conversations. This work has been partly supported by NASA and the NSF.

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## DISCUSSION

OMONT: Have you checked the influence of the reaction  $^{13}\text{C}^+ + ^{12}\text{CO} \rightarrow ^{12}\text{C}^+ + ^{13}\text{CO}$ , on the enhancement of  $^{12}\text{CO}/^{13}\text{CO}$  in the external envelope due to self-shielding?

JURA: It is clearly important! Very detailed calculations are appropriate.

GUELIN: We have indeed observed at Pico Veleta at least one carbon star where  $\text{H}^{13}\text{CN}$  emission is much stronger than  $^{13}\text{CO}$ .

SAHAI: Your conclusion that period of pulsation  $P$  increases as dustiness ( $F(12\ \mu\text{m})/F(2\ \mu\text{m})$ ), increases seems to contradict the earlier conclusion that more dusty objects are pulsators and less dusty objects are non-pulsating since the longer the period of an object, when it is longer than 1000 days, the smaller the chance of that object being found to be a pulsator.

JURA: There is no reason to think that most M stars earlier than M5 are really very long period variables.

LEGER: What is your interpretation of this increase in rate of mass loss with period?

JURA: Actually L.A. Wilson has done detailed hydrodynamic calculations but not much of a chemistry and she does find, even though these calculations are primitive, that rate of mass loss increases with period.

GREENBERG: In your plot of  $12\ \mu\text{m}/2\ \mu\text{m}$  fluxes vs. period, one could perhaps infer a very sharp boundary at some critical period with a take-off in dust formation for periods longer than the critical one.

JURA: The  $2\ \mu\text{m}$  points were taken from the two micron sky survey while the  $12\ \mu\text{m}$  points were taken from the IRAS survey. Since they were acquired at such different epochs, only very crude conclusions can be reached.

VARDYA: Is it not true that the stars in the  $\log S_{12\ \mu\text{m}}/S_{2\ \mu\text{m}}$  vs  $P$  plot which lie at short periods are mostly SRa or SRb variables whereas those of larger periods are mostly Mira variables?

JURA: The role of pulsation in driving the mass loss is not fully understood. At the moment it seems that there is a better correlation of mass loss with period rather than whether the star is a mira or a semi-regular.

D'HENDECOURT: Regarding your suggestion about carbon stars producing the PAHs, is it not worthwhile to try to find the  $3.3\ \mu\text{m}$  and  $11.3\ \mu\text{m}$  lines in absorption towards these cool stars?

JURA: Yes.