

# PAHs in circumstellar envelopes

## I. Processes affecting PAH formation and growth

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**Abstract.** Analytical expressions are presented to estimate the interactions of gas particles with polycyclic aromatic hydrocarbons (PAHs) described as large flat plates. This modelization enables us to determine the collision rate of gas particles with PAHs, the drag force of gas particles on PAHs and the energy exchanged between PAHs and gas particles.

These results are applied to the case of the circumstellar envelopes of C-stars where PAHs are considered to form and grow. As a result of these calculations, the drift velocities of PAHs are estimated and found to be negligible in comparison with the gas thermal velocity. The determination of PAH temperatures in the envelope is also carried out. Finally, the results are discussed in the context of the role of PAHs in the formation of dust particles.

**Key words:** ISM: molecules – molecular processes – stars: circumstellar matter – stars: carbon rich

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### 1. Introduction

Since Léger & Puget (1984) and Allamandola et al. (1985) first proposed polycyclic aromatic hydrocarbons (PAHs) as carriers of the so-called ‘unidentified infrared (UIR) bands’, it has been claimed that these molecules may be the most abundant molecules in the interstellar medium (ISM) after H<sub>2</sub> and CO (Léger et al. 1989a). However, the question of their existence is still open and it is therefore of great interest to study the processes contributing to their formation and growth in astrophysical media.

It is known since 1983 that one of the more promising places for the formation of PAHs are the circumstellar envelopes (CSEs) of carbon rich late type red giants, also known as C-stars, where the densities ( $n_{\text{H}} \simeq 10^{13} \text{cm}^{-3}$  and  $n_{\text{C}_2\text{H}_2} \simeq 10^9 \text{cm}^{-3}$ ) and temperature range ( $500 \text{K} \leq T \leq 1000 \text{K}$ ) are favourable for chemical reactions of formation of PAHs from acetylene

(Keller & Sedlmayr 1983). It has been suggested that PAH formation constitutes the first step in the chemical pathway to dust in C-star shells (Keller 1987, Gail & Sedlmayr 1987a, Allamandola et al. 1989). The physical properties of dust have been and are still extensively studied in CSEs. On the other hand, there are few studies concerning the physical properties of PAHs in stellar shells (Omont 1986, Cherchneff et al. 1991, 1992).

One of the aims of this paper is to propose a description of the effects of gas particles on PAHs under the physical conditions relevant to the interstellar medium, and especially to circumstellar environments. The calculations are achieved with the simple assumption that PAHs can be considered as large and flat plates. Using this modelization, analytical expressions are derived in Sect. 2 for the collision rate, drag force and energy input of gas particles to PAHs. Applying these analytical relations to PAHs in CSEs enables us to determine PAH drift velocities and temperatures, as shown by calculations presented in Sects. 3 and 4, respectively. These results are used in Sect. 5 to examine the formation and growth processes of PAHs and the role of PAHs in the formation of dust particles in the CSEs of C-stars.

### 2. Particle, momentum and energy flux onto PAHs

#### 2.1. Collision rate

Assuming that PAHs are the carriers of the interstellar UIR bands, Léger et al. (1989a) have concluded, by comparison of the IR spectra of compact PAHs and PAHs with protuberant rings, that interstellar PAHs should be rather compact molecules. Moreover, using the relative intensities of the spectra of the UIR bands and models for the excitation of PAHs, Allamandola et al. (1987, 1989) have estimated that the molecular size of interstellar PAHs should be of about 50 carbon atoms. Such compact PAHs containing 50 carbon atoms have a typical diameter of about 1.2 nm. Since hydrogen atoms and molecules and helium atoms, which are the most abundant species in the circumstellar winds of C-stars, have characteristic dimensions

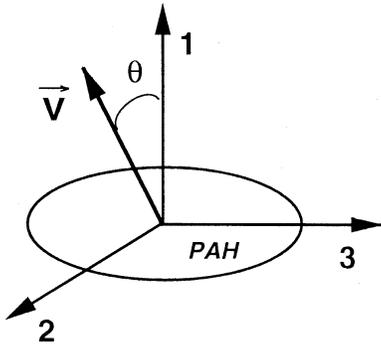


Fig. 1. Coordinate system for PAHs.

smaller than 0.2 nm, interstellar PAHs can be regarded in a first approximation as large and flat molecules.

However, this description may prove incorrect in the case of circumstellar environments where it is expected that the chemical pathway for the formation of PAHs from acetylene favors the formation of PAHs containing rings with five carbon atoms (Keller 1987, Cherchneff et al. 1992, Goeres 1993). Such molecules should be non planar by the combination of five and six carbon atom rings. An extreme case corresponds to the predicted formation of fullerene-like molecules, as in the case of R Coronae Borealis stars (Goeres & Sedlmayr 1992). In the case of C-giants which we consider here, molecules like corannulene, which is constituted by a five carbon atom ring surrounded by five fused 6-membered aromatic rings, are expected to form. However, the exact nature of circumstellar PAHs is still under investigation (Goeres 1993). Due to these uncertainties we describe PAHs as large flat molecules in the following. Moreover, we consider only pericondensed PAHs which are the most stable PAHs under the conditions of pressure and temperature encountered in CSEs (Keller 1987).

In all the calculations presented here we therefore assimilate PAHs to flat plates with surface  $A$ . Furthermore, we suppose that PAHs are moving with a drift velocity  $V$  relative to the gas, which is mainly composed of atomic and molecular hydrogen and of helium atoms as is the case in all astrophysically relevant media. The gas is assumed to be in Maxwellian equilibrium, with density  $n$ , temperature  $T$  and thermal velocity  $v_{th}$ :

$$v_{th} = \sqrt{\frac{2k_B T}{\mu}}, \quad (1)$$

where  $\mu$  is the mean particle mass and  $k_B$  the Boltzmann constant.

The number flux  $N_\theta$  incident on a PAH at angle of attack  $\theta$  is given by:

$$N_\theta = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_1 A f dv_1 dv_2 dv_3 \quad (2)$$

with the geometric parameters defined in Fig. 1 and the distribution function  $f$  given by:

$$f = \frac{n}{(\sqrt{\pi} v_{th})^3} \times$$

$$\exp \left[ -\frac{(v_1 - V \cos \theta)^2 + (v_2 - V \sin \theta)^2 + v_3^2}{v_{th}^2} \right]. \quad (3)$$

To account for all possible orientations, we calculate the flux averaged over the angles:

$$\begin{aligned} N_{PAH} &= \int \int N_\theta \frac{d\Omega}{4\pi} \\ &= n A v_{th} \left[ \frac{2S^2 + 1}{4S} \operatorname{erf}(S) + \frac{\exp(-S^2)}{2\sqrt{\pi}} \right], \end{aligned} \quad (4)$$

where we have defined:

$$S = \frac{V}{v_{th}} \quad (5)$$

and used the notation  $\operatorname{erf}$  for the error function.

The result of Eq. (4) can be compared to that obtained from a similar calculation applied to a sphere (see Dominik et al. 1989):

$$\frac{N_{PAH}}{2A} = \frac{N_{sphere}}{4\pi r^2} \quad (6)$$

where  $N_{sphere}$  is the number flux of gas particles incident onto a sphere with radius  $r$ . An excellent approximation of Eq. (4) is provided by:

$$N_{PAH} = n A v_{th} \frac{1}{\sqrt{\pi}} \sqrt{1 + \frac{\pi}{4} S^2}, \quad (7)$$

which is exact in the limits  $S \gg 1$  and  $S \ll 1$  and is accurate to within 2.5% in all cases.

The limiting case for small velocities  $V$  provides good results in C-star envelopes where the drift velocity of PAHs is negligible (see Sect. 3). On the other hand, in the case of C-type shocks propagating in molecular clouds the magnetic field leads to a drift velocity of molecules relative to ions of some  $\text{km.s}^{-1}$  (Flower et al. 1990). This may enhance the collisional rate of PAHs with gas particles and thereby modify some reaction rates.

Eq. (4) can be also used when one considers the contribution of only one type of particle ( $i$ ) impinging onto the PAH. One has then to substitute  $n_i$  and  $v_{th i}$ , the density and thermal velocity of the considered particles, for  $n$  and  $v_{th}$  in Eq. (4).

Both atomic hydrogen and acetylene molecules are involved in the chemical process of PAH growth (Keller 1987; Gail & Sedlmayr 1987a; Frenklach & Feigelson 1989, Cherchneff et al. 1992) and it is therefore of interest to study their interaction with PAHs. Considering first the case of hydrogen atoms impinging onto PAHs, we deduce from Eq. (4) a collision rate with a PAH containing  $N_C$  carbon atoms:

$$k_H^{col} = 3.510^{-10} \left( \frac{N_C}{6} \right) \left( \frac{T}{1000K} \right)^{1/2} \text{ cm}^3 \text{ s}^{-1} \quad (8)$$

where we have supposed that  $S \ll 1$  and used the relation of Omont (1986) for the radius of a typical interstellar PAH:

$$R_{PAH} = 0.9 N_C^{1/2} \text{ \AA}. \quad (9)$$

Applying Eq. (4) to the case of molecules of acetylene incident on a PAH we obtain a collision rate of acetylene with a PAH containing  $N_C$  carbon atoms equal to:

$$k_{C_2H_2}^{col} = 6.9 \cdot 10^{-11} \left( \frac{N_C}{6} \right) \left( \frac{T}{1000 \text{ K}} \right)^{1/2} \text{ cm}^3 \text{ s}^{-1}. \quad (10)$$

The collision rates obtained in Eqs. (8) and (10) provide upper limits for the chemical reaction rates of acetylene and atomic hydrogen with PAHs, which are more precisely discussed in Sect. 5.1.

## 2.2. Momentum transfer to PAHs

The flux of momentum  $\mathbf{F}_{\theta_i}$  incident on a PAH at an angle of attack  $\theta$  is given by:

$$\mathbf{F}_{\theta_i} = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mu \mathbf{v} v_1 A f dv_1 dv_2 dv_3. \quad (11)$$

The net flux also includes the momentum of the re-emitted particles.

The most abundant particles are, on the one hand, hydrogen molecules and helium atoms, which do not attach or react with PAHs and are therefore likely to be reemitted, and on the other hand, hydrogen atoms which may on the contrary attach and react. At low temperatures ( $T < 100\text{K}$ ) the trapping fraction of atomic hydrogen interacting with PAHs is indeed likely to be near unity (see for instance the study of Burke & Hollenbach (1983) about the interactions of hydrogen atoms with amorphous carbon). However, the trapping fraction of atomic hydrogen on PAHs probably rapidly decreases with temperature and is probably very low in the regions of interest surrounding stars. Moreover, we shall show in Sect. 5.1 that less than 1% of the impinging hydrogen atoms actually react with PAHs in the CSEs of C-stars. We consequently neglect the effect of possible interactions between PAHs and atomic hydrogen in the present calculation. The other molecules interacting with PAHs all have abundances lower than  $10^{-4}$  relative to hydrogen and can be therefore neglected here. In the calculation presented here we therefore consider that gas particles are all re-emitted. In order to simplify the calculation we furthermore assume that PAHs act as a specularly reflecting surface. A more exact treatment of the problem taking precisely into account all PAH-gas interactions (sticking, accommodation) would probably not lead to extremely different results, as has been assumed in the case of dust particles (Dominik et al. 1989).

The flux of momentum from re-emitted particles  $\mathbf{F}_{\theta_r}$  has the same form as  $\mathbf{F}_{\theta_i}$  with a velocity  $\mathbf{v}'$  for the re-emitted particles equal to:

$$\mathbf{v}' = v - \frac{2\mu m_{\text{PAH}}}{\mu + m_{\text{PAH}}} [\mathbf{n}_1 \cdot (\mathbf{V} - \mathbf{v})] \mathbf{n}_1, \quad (12)$$

where  $m_{\text{PAH}}$  is the mass of the PAH. Adding the contributions of  $\mathbf{F}_{\theta_i}$  and  $\mathbf{F}_{\theta_r}$  and averaging over the angles leads to the following

expression of the drag force of gas  $\mathbf{F}_g$ :

$$\mathbf{F}_g = -Anv_{\text{th}}^2 \frac{\mu m_{\text{PAH}}}{\mu + m_{\text{PAH}}} \frac{\mathbf{V}}{V} \times \left[ \frac{\text{erf}(S)}{4S^2} (4S^4 + 8S^2 - 3) + \frac{\exp(-S^2)}{2\sqrt{\pi}S} (2S^2 + 3) \right]. \quad (13)$$

In the limiting cases of small and large velocity  $V$ , Eq. (13) reduces to:

$$\mathbf{F}_g = \begin{cases} -\frac{4}{\sqrt{\pi}} An v_{\text{th}} \frac{\mu m_{\text{PAH}}}{\mu + m_{\text{PAH}}} \frac{\mathbf{V}}{V} & S \ll 1 \\ -An v_{\text{th}} \frac{\mu m_{\text{PAH}}}{\mu + m_{\text{PAH}}} \frac{\mathbf{V}}{V} & S \gg 1 \end{cases} \quad (14)$$

The following expression gives an approximation of Eq. (13) to better than 1% in all cases:

$$\mathbf{F}_g = -Anv_{\text{th}}^2 \frac{\mu m_{\text{PAH}}}{\mu + m_{\text{PAH}}} \frac{\mathbf{V}}{V} S \frac{4}{\sqrt{\pi}} \sqrt{1 + \frac{\pi}{16} S^2}. \quad (15)$$

In the envelopes of C-giants the drag force acts against the radiation pressure which is responsible for the acceleration of PAHs (Cherchneff et al. 1991). A drift velocity of PAHs relative to the gas occurs as a result of this competition. This point is discussed in detail in Sect. 3.

## 2.3. Energy transfer to PAHs

The flux of energy (kinetic and internal)  $E_{\theta_i}$  transferred from the gas to a PAH at an angle of attack  $\theta$  is given by:

$$E_{\theta_i} = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left[ u + \frac{1}{2} \mu v^2 \right] v_1 A f dv_1 dv_2 dv_3. \quad (16)$$

where  $u$  is the internal energy of the gas particles, which we assume equal to  $j/2k_B T$  for a gas with  $j$  internal degrees of freedom.<sup>1</sup> After averaging over the angles, one obtains the following expression:

$$E_i = N_{\text{PAH}} u + An k_B T v_{\text{th}} \times \left[ \frac{\text{erf}(S)}{8S} (4S^4 + 12S^2 + 3) + \frac{\exp(-S^2)}{4\sqrt{\pi}} (2S^2 + 5) \right] \quad (17)$$

which may be approximated to:

$$E_i = \frac{j}{2} k_B T N_{\text{PAH}} + \begin{cases} \frac{2}{\sqrt{\pi}} An k_B T v_{\text{th}} & S \ll 1 \\ \left( \frac{1}{2} \mu V^2 \right) \frac{1}{2} An V & S \gg 1 \end{cases} \quad (18)$$

in the respective limits  $S \gg 1$  and  $S \ll 1$ .

To estimate the energy flux due to the re-emitted particles  $E_r$  an energy accommodation coefficient  $\alpha$  is usually introduced as follows:

$$E_r = (1 - \alpha) E_i + \alpha E_{\text{eq}}, \quad (19)$$

<sup>1</sup> In the regions surrounding C-stars considered in the following sections, only the rotational degree of freedom of molecular hydrogen has to be taken into account.

where  $E_{\text{eq}}$  is the flux of energy that would correspond to re-emitted particles in complete equilibrium with the PAH at temperature  $T_{\text{PAH}}$ ,  $E_{\text{eq}} = (\frac{j}{2} + 2)k_{\text{B}}T_{\text{PAH}}N_{\text{PAH}}$ . The net energy flux  $E_{\text{g}}$  from the gas to the PAH is equal to  $E_i - E_r$ . In the case of low drift velocities the energy flux reduces to:

$$E_{\text{g}} = \alpha N_{\text{PAH}} \left[ \left( \frac{j}{2} + 2 \right) k_{\text{B}}T - \left( \frac{j}{2} + 2 \right) k_{\text{B}}T_{\text{PAH}} \right], \quad (20)$$

which is analogous to the expression adopted by Burke & Hollenbach (1983) in their study of gas-grain interactions in the ISM.

Hollenbach & McKee (1979) have proposed the following type of expression for the energy accommodation coefficient  $\alpha$  in a case with no drift velocity:

$$\alpha = (1 - \alpha^0) \exp \left[ -\frac{2k_{\text{B}}(T_{\text{PAH}} + T)}{D} \right] + \alpha^0, \quad (21)$$

where  $\alpha^0$  is the high-temperature hard-sphere limit defined as:

$$\alpha^0 = \frac{2m_{\text{X}}m_{\text{C}}}{(m_{\text{X}} + m_{\text{C}})^2}. \quad (22)$$

In the expression for  $\alpha^0$ ,  $m_{\text{X}}$  is the mass of the impinging particle while  $m_{\text{C}}$  is the mass of a carbon atom. In Eq. (21)  $D$  represents the surface absorption energy for the particles colliding with the PAH. Burke & Hollenbach (1983) have successfully applied the model to graphite and we anticipate that we will not commit large errors by applying the results of this model to PAHs.

For the calculations carried out in Sect. 4 the species we consider are helium atoms, atomic and molecular hydrogen. For the adsorption energy of hydrogen atoms on a PAH, whose value has been much discussed so far (see Omont 1986), we adopt the most recently published value equal to 0.3 eV (Klose 1992). For helium atoms and hydrogen molecules we use the adsorption energies of Burke & Hollenbach (1983).

### 3. Drift of PAHs in circumstellar envelopes

#### 3.1. Equilibrium drift velocities of PAHs

In the envelopes of C-giants PAHs are accelerated by radiation pressure (Cherchneff et al. 1991). To limit the acceleration, a drag force due to gas particles appears which introduces a drift velocity between PAHs and the gas particles. An upper estimate of this drift velocity can be reached by calculating the equilibrium drift velocity  $V_0$  where both radiation and gas pressure are equal.

The radiation force on a PAH at distance  $R$  from the star may be written:

$$F_{\text{rad}}(R) = A \int_0^{\infty} Q_{\text{pr}} \frac{F_{\nu}(R)}{c} d\nu, \quad (23)$$

where  $F_{\nu}$ ,  $c$  and  $Q_{\text{pr}}$  represent the radiation flux from the star, the velocity of light and the radiation pressure efficiency of the considered PAH, respectively.

Following the method of Lucy (1971, 1976) for the treatment of radiative transfer in an extended stellar atmosphere, we write the radiation flux:

$$F_{\nu}(R) = F_{\nu}(R_{\star}) \left( \frac{R_{\star}}{R} \right)^2, \quad (24)$$

where  $F_{\nu}(R_{\star})$  is the flux at the photosphere of the star, which we assume equal to  $\pi B_{\nu}(T_{\star})$ , the flux of a sphere of uniform brightness emitting as a blackbody at the effective temperature  $T_{\star}$  of the star.  $B_{\nu}(T_{\star})$  represents the well-known Planck function  $B_{\nu}(T_{\star}) = 2h\nu^3/c^2 [\exp(h\nu/k_{\text{B}}T_{\star}) - 1]$ . A more exact treatment of the radiative transfer using the code of Winters (1994) for the radiative flux in circumstellar envelopes has not been used here because it would not provide much different results and, furthermore, would prevent the use of meaningful analytic expressions.

In order to estimate  $F_{\text{rad}}$ , we use the expressions of the Planck mean of the radiation pressure cross-section of PAHs from Cherchneff et al. (1991):

$$\begin{aligned} \overline{K}(T_{\star}) &= \frac{1}{\sigma T_{\star}^4} \int_0^{\infty} A Q_{\text{pr}} \pi B_{\nu}(T_{\star}) d\nu \\ &= \text{Max}(\overline{K}^-(T_{\star}), \overline{K}^+(T_{\star})), \end{aligned} \quad (25)$$

where  $\sigma$  is the Stefan constant. The quantities  $\overline{K}^-(T)$  and  $\overline{K}^+(T)$  represent the contributions to  $\overline{K}(T)$  at low and high radiative temperatures, respectively, and are defined as functions of temperature and of  $N_{\text{C}}$ , the number of carbon atoms of the PAH, according to Cherchneff et al. (1991):

$$\begin{aligned} \log \overline{K}^-(T) &= -13.24 - 2.7 N_{\text{C}}^{-0.113} \log T \\ &\quad - \exp(-2.7(\log T - 2.33)), \\ \log \overline{K}^+(T) &= -8.59 \left[ \frac{\log T - 3.28 N_{\text{C}}^{-0.096}}{17.47} \right]^{-0.282}. \end{aligned} \quad (26)$$

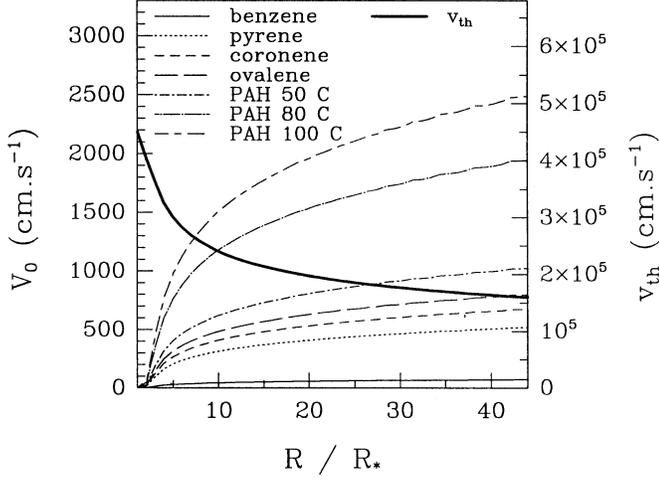
Combining Eqs. (23) to (25), we obtain the following expression for the radiative force on a PAH:

$$F_{\text{rad}}(R) = \frac{\sigma T_{\star}^4}{c} \left( \frac{R_{\star}}{R} \right)^2 \overline{K}(T_{\star}). \quad (27)$$

Equating the radiative force  $F_{\text{rad}}$  to the drag force  $F_{\text{g}}$  at a given position in the envelope allows the calculation of the equilibrium drift velocity of PAHs. We have carried out this calculation for the stationary models of C-star envelopes of Winters et al. (1994) (henceforth WDS).

We have used a model characterized by the stellar parameters  $M_{\star} = 0.7 M_{\odot}$ ,  $L_{\star} = 2.4 \cdot 10^4 L_{\odot}$ ,  $\dot{M}_{\star} = 8.10^{-5} M_{\odot} \text{yr}^{-1}$ , where  $M_{\star}$ ,  $L_{\star}$  and  $\dot{M}_{\star}$  are the stellar mass, luminosity and mass loss, respectively. The model moreover assumes a carbon to oxygen ratio of  $\epsilon_{\text{C}}/\epsilon_{\text{O}} = 1.40$  and yields a reliable description for the carbon star IRC+10216.

The drift velocity of some PAHs are plotted as a function of distance from the star in Fig. 2 for this circumstellar shell. The values of some thousand cm/s obtained for the equilibrium



**Fig. 2.** Equilibrium drift velocity of some PAHs in the envelope of a typical C-giant [WDS model for IRG+10216] as a function of distance from the star.

drift velocities are always 2 orders of magnitude lower than the value of the gas thermal velocity  $v_{th}$ . Applying the limiting case of  $S \ll 1$  for the expression of the drag force  $F_g$  we obtain from the equality of  $F_{rad}$  and  $F_g$  the following estimate of the equilibrium drift velocity of PAHs in circumstellar envelopes:

$$V_0 \simeq 3.10^{-2} v_{th} \left( \frac{R}{3R_*} \right)^{-2} \left( \frac{T_*}{2500K} \right)^4 \left( \frac{N_C}{50} \right)^{-1} \times \left( \frac{\overline{K(T_*)}}{10^{-19} \text{cm}^2} \right) \left( \frac{n}{10^7 \text{cm}^{-3}} \right)^{-1} \left( \frac{T}{1000K} \right)^{-1} \quad (28)$$

From Fig. 2 and Eq. (28) it is clear that drift of PAHs can be neglected to a very good approximation in C-star CSEs.

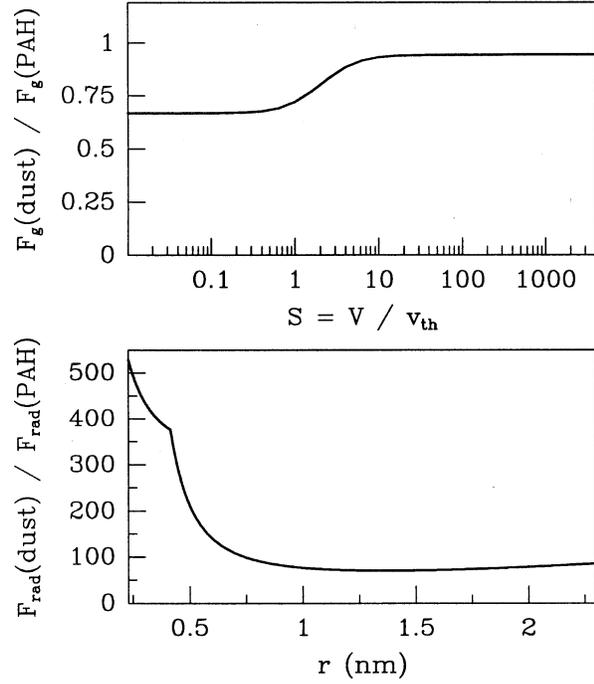
### 3.2. Comparison between PAHs and dust particles

In contrast to the low PAH drift velocities, Dominik et al. (1989) have obtained drift velocities of a few  $\text{km s}^{-1}$  for spherical dust particles with a radius of 1 nm in the envelope of C-giants stars. Such a radius is comparable to that of a pericondensed PAH with about 100 carbon atoms (see Eq. (9)). It is therefore worth looking at the reason explaining the differences of drift velocities between PAHs and dust particles. For this purpose, let us compare the radiative and drag forces undergone by a PAH and by a dust particle with same radius  $r$ .

The drag force on a dust particle can be obtained from a calculation similar to that performed in Sect. 2.2 for a PAH and leads to:

$$\mathbf{F}_g = -\pi r^2 n v_{th}^2 \frac{\mu m_{dust}}{\mu + m_{dust}} \frac{\mathbf{V}}{V} \times \left[ \frac{\text{erf}(S)}{4S^2} (4S^4 + 4S^2 - 1) + \frac{\exp(-S^2)}{2\sqrt{\pi}S} (2S^2 + 1) \right] \quad (29)$$

where  $m_{dust}$  is the mass of the dust particle and  $r$  its radius (Dominik et al. 1989).



**Fig. 3.** Upper diagram: Dust particle to PAH ratio of the gas drag force as a function of parameter  $S$  for a PAH and a dust particle of same radius in the envelope of a typical C-giant. Lower diagram: Dust particle to PAH ratio of the radiative force as a function of radius for a PAH and a dust particle of same radius in the envelope of a typical C-giant.

Fig. 3 (upper diagram) shows the ratio  $F_g(\text{dust})/F_g(\text{PAH})$  as a function of parameter  $S$ . This ratio does not depend on the position in the envelope and on the radius chosen for the comparison. It can be seen in Fig. 3 that the drag force on a dust particle and on a PAH of the same radius are always comparable. This result therefore provides no explanation for the difference of several orders of magnitude between the drift velocities of dust particles and PAHs in C-star CSEs.

The radiative force on a dust particle at a distance  $R$  from the star has been estimated by Dominik et al. (1989) as:

$$F_{rad}(R) = \frac{1}{2} \left( \frac{R_*}{R} \right)^2 \frac{\sigma T_*^4}{c} \pi r^2 \text{Min} \left( 1, \frac{2\pi r}{1\mu} \right). \quad (30)$$

The ratio  $F_{rad}(\text{dust})/F_{rad}(\text{PAH})$  is represented in Fig. 3 (lower diagram) as a function of radius  $r$  in the envelope of a typical C-giant star. This ratio does not depend on the position in the envelope. We observe that the ratio decreases with increasing radius but is always of the order of  $10^2$ . This proves that PAHs are not accelerated by stellar radiation as efficiently as dust particles of comparable size. A similar result has already been derived by Cherchneff et al. (1991) to demonstrate that PAHs have a negligible role in the acceleration process of stellar winds.

Since PAHs are less accelerated than dust particles but undergo similar gas drag force for comparable size, PAHs have drift velocities much smaller than dust particles.

#### 4. Temperature of PAHs in circumstellar envelopes

In order to use Eq. (20) for determining net energy flux, one has to know the temperature of the PAHs. Alternatively, PAH temperatures may be determined by using Eq. (20) and balancing the energy gains to the energy loss of PAHs.

Heating of PAHs proceeds via collisions with gas particles (see above) and absorption of radiation from the neighbouring star (Cherchneff et al. 1991) and/or the interstellar radiation field. In the case of C-star envelopes, the ultraviolet photons from the ISM are absorbed by dust grains before reaching the region near the star, so that only collisions and absorption of stellar emission contribute to the heating of PAHs. Moreover, since C-stars are thought to have a very weak chromospheric activity (Johnson & Luttermoser 1987) we restrain the stellar emission to the contribution of the photosphere.

Cooling of PAHs occurs via emission from their rotationally and vibrationally excited states (Cherchneff et al. 1991) and possibly by ionization (Verstraete et al. 1990) and ejection of hydrogen. As far as concerns photoionization and hydrogen photoejection, they are negligible because of the weak UV stellar radiation. The value of about 8 eV for the PAH ionization potential probably much hinders PAH thermoionization. On the other hand, the loss of hydrogen from PAHs has an activation energy of some eV and could occur at the temperatures prevailing near the star. However, since we have not taken into account the effects of chemical reactions on the heating of PAHs via collisions, and in particular the energy gained by recombination of PAHs radicals with hydrogen and of PAHs ions with electrons, we also neglect hydrogen ejection and ionization as a cooling process for PAHs.

The heating rate of PAHs via absorption of stellar radiation may be written:

$$H_{\text{PAH}} = \int_0^{\infty} \sigma_{\nu}^{\text{abs}} J_{\nu}(R) d\nu, \quad (31)$$

where  $J_{\nu}$  is the mean specific intensity. To perform the calculations we have used the results of the radiative transfer code of Winters (1994) who kindly provided us with the values of  $J_{\nu}$  as a function of frequency  $\nu$  for various distances  $R$  from the star centre. The values of  $J_{\nu}(R)$  were then fitted by a modified Planck distribution  $W(R)B_{\nu}[T_{\text{rad}}(R)]$ , where  $W$  and  $T_{\text{rad}}$  represent a dilution factor and a radiative temperature, respectively. We note that the dilution factor we have obtained for the best fit is different from the quantity  $(R/R_{\star})^2$  or  $1/2(1 - \sqrt{1 - (R/R_{\star})^2})$  usually introduced for the calculation of the temperature or molecular species in CSEs (MacCabe 1982, Cherchneff et al. 1991). Similarly  $T_{\text{rad}}$  is not equal to  $T_{\star}$  as assumed by MacCabe (1982) and Cherchneff et al. (1991). Fig. 4 shows the results obtained for  $J_{\nu}$  from the radiative transfer code and from the fit formula as function of frequency  $\nu$  at various positions in the envelope. From Fig. 4 it can be seen that both the maximum and the corresponding value of  $\nu$  are well reproduced by the fit formula. The fitting procedure therefore provides a good estimate of  $J_{\nu}$  in the frequency range of the maximum intensity, which

is also the frequency range in the infrared where PAHs most absorb ( $3 \mu\text{m} < \lambda < 30 \mu\text{m}$ ).

In Eq. (31),  $\sigma_{\nu}^{\text{abs}}$  is the PAH absorption cross-section. As in the study of Cherchneff et al. (1991) we use the Eqs. (25) for the Planck mean of the absorption cross-sections, so that the heating rate for one PAH can be finally written:

$$H_{\text{PAH}}(R) = \overline{K(T_{\text{rad}})} W(R) \sigma T_{\text{rad}}(R)^4. \quad (32)$$

The cooling rate of PAHs via emission is equal to:

$$C = 4\pi \int_0^{\infty} j_{\nu} d\nu, \quad (33)$$

where  $j_{\nu}$  represents the emission coefficient of PAHs in units of  $\text{erg cm}^{-3} \text{s}^{-1} \text{ster}^{-1} \text{Hz}^{-1}$ . Applying Kirchhoff's law for thermal emission of PAHs, we obtain  $j_{\nu} = n_{\text{PAH}} \sigma_{\nu}^{\text{abs}} B_{\nu}(T_{\text{PAH}})$  where  $n_{\text{PAH}}$  is the PAH density. Rewriting Eq. (33) for one PAH and using Eq. (25) we deduce:

$$C_{\text{PAH}} = 4\overline{K(T_{\text{PAH}})} \sigma T_{\text{PAH}}^4. \quad (34)$$

The temperature of a PAH can finally be obtained from the equality:

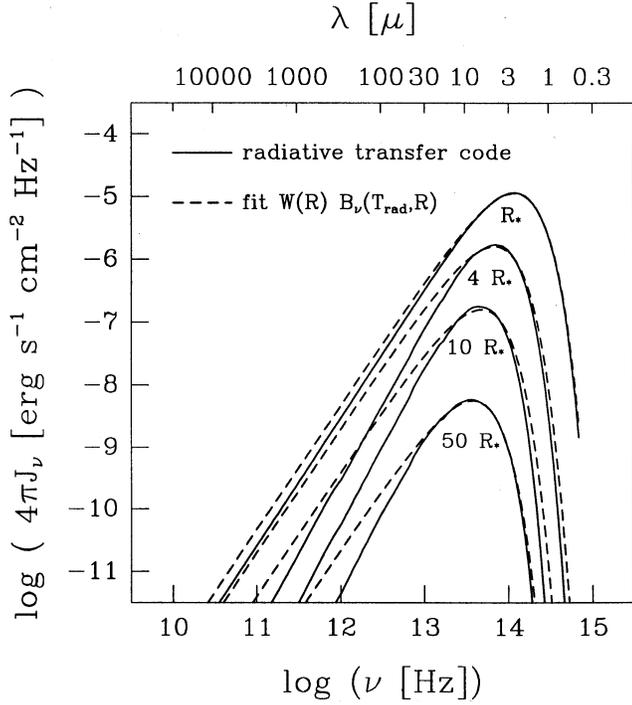
$$E_{\text{g}}(T_{\text{gas}}, T_{\text{PAH}}) + H_{\text{PAH}}(T_{\text{rad}}) = C_{\text{PAH}}(T_{\text{PAH}}). \quad (35)$$

The results obtained for some PAHs in the envelope of IRC+10216 described by the WDS model are presented in Fig. 5. As already noticed by Cherchneff et al. (1991), PAH temperatures are much lower than the gas temperature.

Fig. 6 shows the heating rates in the envelope (lower diagram) and the relative contribution of collisions with gas particles for heating (upper diagram) in the case of various PAHs. The larger the PAH, the smaller is the part of collisions compared to the part of absorption in the heating process. However, absolute values of collisional heating increase with PAH molecular size, as well as the total heating rates (see lower diagram of Fig. 6).

Fig. 6 also shows that heating rates have higher values near the star where both collisions and radiation are more abundant. Near the star, however, collisions dominate over absorption of stellar radiation for the heating of all PAHs. In contrast, at distances from the star greater than 2 stellar radii, absorption of stellar emission is the main heating process.

In the studies of Cherchneff et al. (1991, 1992) the two heating processes have not been treated simultaneously. Fig. 7 presents the temperatures that one would obtain by considering only one of the heating mechanisms for pyrene molecules taken as an example (a similar result is obtained for all PAHs). In the region near the star, collisional heating alone provides a good approximation of PAH temperatures. On the other hand, heating by absorption of radiation from the star and the dust layer provides good values of the PAH temperatures for distances greater than 2 stellar radii. At distances greater than  $2R_{\star}$ , PAH temperatures are therefore much higher than those assumed by Cherchneff et al. (1992) who only considered collisional heating. This allows PAHs to stay longer in the temperature window



**Fig. 4.** Mean specific intensity  $J_\nu$  as a function of frequency  $\nu$  at various distances from the star centre for the WDS model of the IRC+10216 envelope. The fit by a diluted blackbody field  $W(R) B_\nu(T_{\text{rad}}, R)$  is also represented.

(1000-800 K) favourable to their formation and growth. To conclude, we note that the determination of PAH temperatures in the whole envelope imperatively requires to take into account both heating processes simultaneously.

## 5. Growth of PAHs in circumstellar envelopes

### 5.1. Chemical reactions

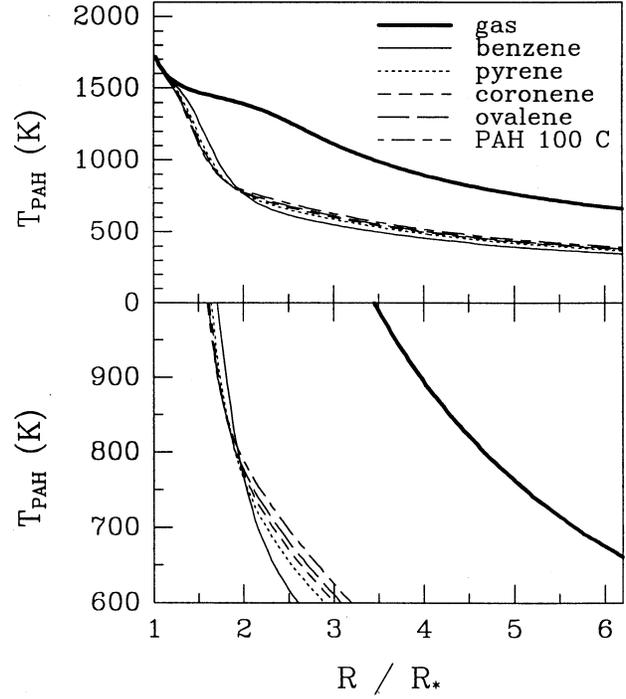
The reactions of hydrogen abstraction from PAH molecules and addition of acetylene on the formed PAH radicals are the basic chemical reactions in the process of PAH growth in circumstellar environments (Keller 1987; Gail & Sedlmayr 1987a; Frenklach & Feigelson 1989, Cherchneff et al. 1992). Unfortunately, no experimental data concerning these chemical reactions for PAHs larger than benzene is available in the literature. Applying these results to larger PAHs is still relatively uncertain and requires the introduction of some modifications with respect to the case of benzene.

The reaction of hydrogen abstraction has a rate given by the modified Arrhenius expressions introduced in Allain et al. (1996b):

$$\text{for } T \geq 1000 \text{ K}, \quad (36)$$

$$k_{\text{H}}^{\text{abs}} = 4.15 \cdot 10^{-10} \left( \frac{N_{\text{C}}}{6} \right)^{\frac{1}{2}} \exp\left(-\frac{8060}{T}\right) \text{ cm}^3 \text{ s}^{-1},$$

$$\text{for } T < 1000 \text{ K},$$



**Fig. 5.** Temperatures of some PAHs as a function of distance from the star in the model of WDS for IRC+10216. The lower panel presents the curves in more detail.

$$k_{\text{H}}^{\text{abs}} = 5 \cdot 10^{-12} \left( \frac{N_{\text{C}}}{6} \right)^{\frac{1}{2}} \exp\left(-\frac{4080}{T}\right) \text{ cm}^3 \text{ s}^{-1}.$$

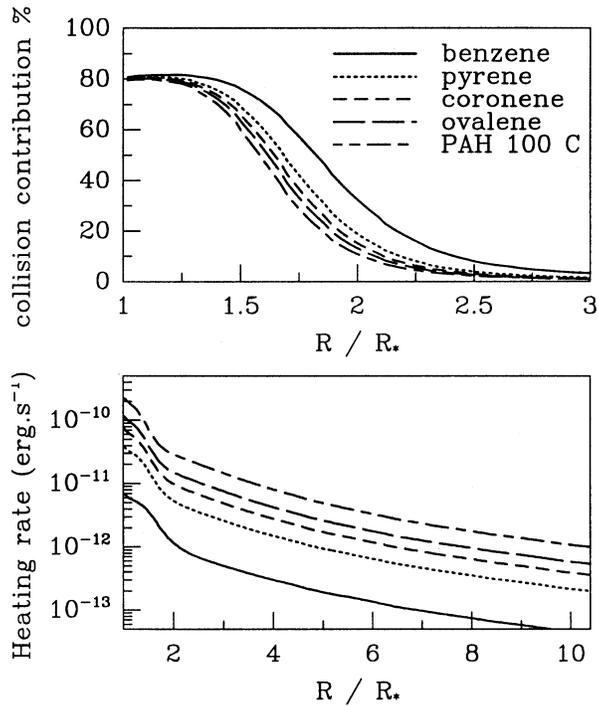
The factor  $(N_{\text{C}}/6)^{\frac{1}{2}}$  accounts for the increasing number of hydrogen atoms at the edge of PAHs for increasing PAH molecular size. The efficiency of the hydrogen abstraction reaction may be defined as the ratio of the reaction rate to the collision rate. The values of the efficiency for a PAH with 50 carbon atoms are plotted in the upper diagram of Fig. 8 as a function of temperature for the temperature range observed in late type star envelopes. The efficiency is less than 1% for temperatures lower than 2000 K and rapidly decreases with decreasing temperature.

Fahr & Stein (1989) have obtained a rate for the reaction of addition of acetylene to the radical phenyl. From their results we derive the following expression of the Arrhenius law:

$$k_{\text{C}_2\text{H}_2}^{\text{add}} = 6.6 \cdot 10^{-11} \exp\left(-\frac{5090}{T}\right) \text{ cm}^3 \text{ s}^{-1}. \quad (37)$$

We assume that this rate also gives valid results for the addition of acetylene to PAH radicals larger than phenyl. However, this may prove incorrect when the addition of acetylene leads to the formation of a new ring, as for instance in the formation of naphthalene from phenylacetylene. There are unfortunately no experimental data for the rate of such reactions. We therefore also use the result of Eq. (37) in this case.

Using Eq. (37) we can calculate the efficiency of the acetylene addition reaction as for the case of hydrogen abstraction. The result is plotted in Fig. 8 for a PAH radical with 50 carbon



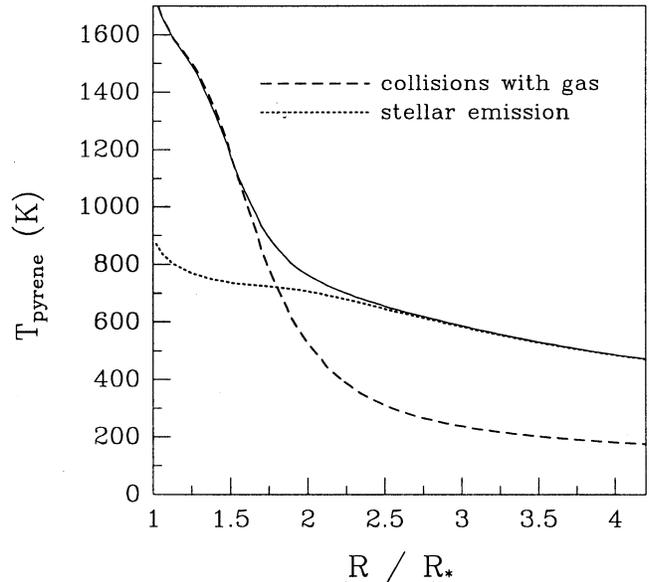
**Fig. 6.** Upper diagram: Relative contribution of collisions for the heating of PAHs in the envelope of IRC+10216 as a function of distance from the star. Lower diagram: Heating rates of PAHs in the envelope as a function of distance from the star.

atoms as a function of temperature. For temperatures lower than 2000 K the efficiency is less than 1% and decreases with temperature down to  $10^{-6}$  at 500 K. These values are comparable to the experimental efficiency measured by Wehrer et al. (1983) for the decomposition of acetylene on carbon.

The low efficiency of PAH chemical reactions with hydrogen and acetylene could constitute a severe hindrance for their realization in some astrophysical environments. In order to study this question in the special case of CSEs, we have represented in the lower diagram of Fig. 8 the rates of the processes of hydrogen abstraction from PAH molecules,  $n_{\text{H}}k_{\text{H}}^{\text{abs}}$  and of addition of acetylene on PAH radicals,  $n_{\text{C}_2\text{H}_2}k_{\text{C}_2\text{H}_2}^{\text{add}}$ , for a PAH with 50 carbon atoms as a function of temperature in a C-star envelope described by the WDS model. The densities of atomic hydrogen and of acetylene have been obtained from the kinetic calculation presented in Sect. 5.5.

The inverse of the chemical rates  $1/n_{\text{H}}k_{\text{H}}^{\text{abs}}$  and  $1/n_{\text{C}_2\text{H}_2}k_{\text{C}_2\text{H}_2}^{\text{add}}$  provide the characteristic timescales for reaction of typical circumstellar PAHs with hydrogen and acetylene, respectively. We have compared the chemical timescales to the characteristic timescale for the dynamical changes of the physical parameters in the envelope. This timescale is simply stated as being equal to  $R/v$ , where  $v$  is the gas velocity in the envelope and  $R$  the distance from the star. The inverse of the dynamical timescale is plotted in Fig. 8.

We can infer from Fig. 8 that in the inner part of the envelope the chemical reactions have the smallest timescales. They are therefore the quickest processes until the temperature and



**Fig. 7.** Determination of the temperature of pyrene molecules as a function of distance from the star. The solid curve shows the temperature obtained by taking into account both collisions and absorption of stellar emission for the heating. The other curves present the results obtained by considering separately each heating process. This calculation has been done for the WDS model for IRC+10216.

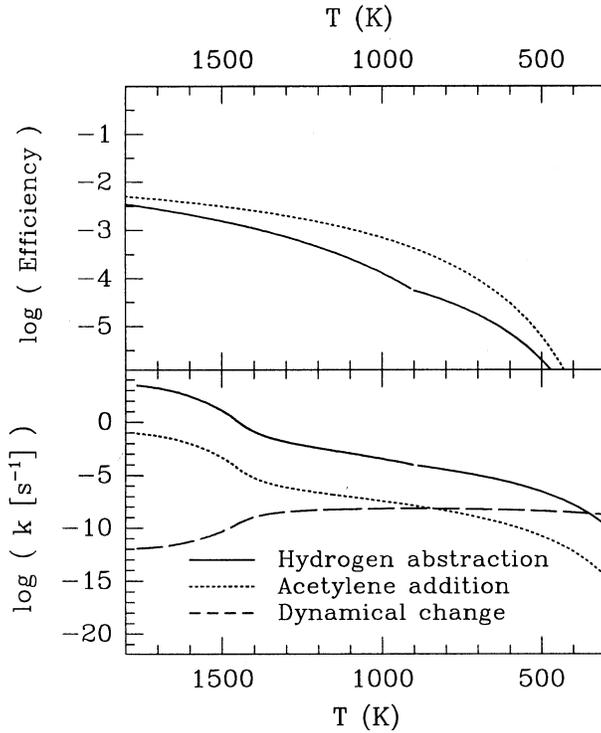
densities have dropped to values where the chemistry is frozen due to rapid dynamic evolution of the shell physical properties. The freezing-out of chemistry occurs for temperatures lower than 800-600 K which correspond to a distance to the centre of the star greater than 5 stellar radii. If one considers that the reaction temperatures are mainly governed by the PAH temperatures (Cherchneff et al. 1992), the reactions may be frozen out for distances larger than 3 stellar radii. We finally conclude that the chemical reactions of hydrogen abstraction from PAHs and acetylene addition to PAH radicals can take place within a distance of a few stellar radii from the star although their efficiencies are lower than 1%.

## 5.2. Growth rate of PAHs in circumstellar envelopes

We know of only two studies taking into account the growth of large PAHs ( $N_{\text{C}} > 18$ ) by addition of acetylene in CSEs (Frenklach & Feigelson 1989, Cadwell et al. 1994). However, these authors have performed their calculation for PAHs larger than naphthalene without taking into consideration the various temperatures of PAHs and under the assumption that the chemical reaction rates for larger PAHs are all equal to those of benzene. We propose here some simple arguments to describe more adequately the growth of PAHs in CSEs.

PAHs can grow by addition of acetylene when they have a radical site at their edge. To describe the growth of a given PAH we therefore introduce the following growth rate:

$$k_{\text{C}_2\text{H}_2}^{\text{gr}} = p_{\text{rad}} n_{\text{C}_2\text{H}_2} k_{\text{C}_2\text{H}_2}^{\text{add}}, \quad (38)$$



**Fig. 8.** Upper panel: Efficiency of hydrogen abstraction and acetylene addition for a PAH with 50 carbon atoms as a function of temperature. Lower panel: Rates for hydrogen abstraction and acetylene addition for a PAH with 50 carbon atoms and dynamical changes as a function of gas temperature in a typical C-giant envelope [WDS model for IRC+10216] (see text for the definition of the rates).

where  $p_{\text{rad}}$  represents the probability for the considered PAH to have a radical site (Keller 1987). In Eq. (38)  $k_{\text{C}_2\text{H}_2}^{\text{add}}$  is the rate already presented in Eq. (37) for the addition of acetylene to the phenyl radical.

The probability  $p_{\text{rad}}$  can be obtained approximately from the expression:

$$p_{\text{rad}} \simeq N_{\text{H}} \frac{n_{\text{PA}\blacklozenge}}{n_{\text{PA}\blacklozenge} + n_{\text{PAH}}}, \quad (39)$$

where  $n_{\text{PA}\blacklozenge}$  and  $n_{\text{PAH}}$  are the densities of PAHs having one radical site, and as a molecule, respectively, while  $N_{\text{H}}$  is the number of hydrogen atoms at the edge of the PAH. The fraction in Eq. (39) provides the probability to be a radical site for a carbon atom bound to a hydrogen atom at the edge of the PAH carbon skeleton. To establish Eq. (39) we have implicitly assumed that all hydrogen atoms at the edge of a PAH molecule are equivalent and simply multiply by  $N_{\text{H}}$  the probability relative to a carbon atom at the edge. The number of hydrogen atoms increases with the length of the edge and, for compact PAHs, may be estimated as:

$$N_{\text{H}} \simeq \sqrt{6N_{\text{C}}}. \quad (40)$$

The reaction of hydrogen abstraction is more rapid than the dynamical change in the region of the envelope where acetylene

addition is effective (see Fig. 8) and therefore remains at chemical equilibrium in the region where acetylene addition occurs efficiently. This point is confirmed by the kinetic calculation presented in Sect. 5.5. Hence, by use of the law of mass action we can deduce the radical to molecule density ratio for a given PAH:

$$\frac{n_{\text{PA}\blacklozenge}}{n_{\text{PAH}}} = \frac{k_{\text{H}}^{\text{abs}}}{k^r} \frac{n_{\text{H}}}{n_{\text{H}_2}} \quad \text{with} \quad (41)$$

$$\frac{k_{\text{H}}^{\text{abs}}}{k^r} = \exp\left(-\frac{\Delta G_{\text{PA}\blacklozenge}^0 + \Delta G_{\text{H}_2}^0 - \Delta G_{\text{PAH}}^0 - \Delta G_{\text{H}}^0}{RT}\right) \quad (42)$$

where  $k^r$  denotes the reverse reaction to hydrogen abstraction. In Eq. (42) the difference of the standard free enthalpies,  $\Delta G_{\text{PA}\blacklozenge}^0 - \Delta G_{\text{PAH}}^0$ , has been estimated by using the group additivity theory of Benson (1976).

The temperature in Eq. (42) is a reaction temperature, which depends on the temperatures of the hydrogen molecules and of the PAH. For such a reaction involving two species A and B we define the following chemical reaction temperature  $T_{\text{r}}$ :

$$T_{\text{r}} = \frac{s_{\text{A}}T_{\text{A}} + s_{\text{B}}T_{\text{B}}}{s_{\text{A}} + s_{\text{B}}}, \quad (43)$$

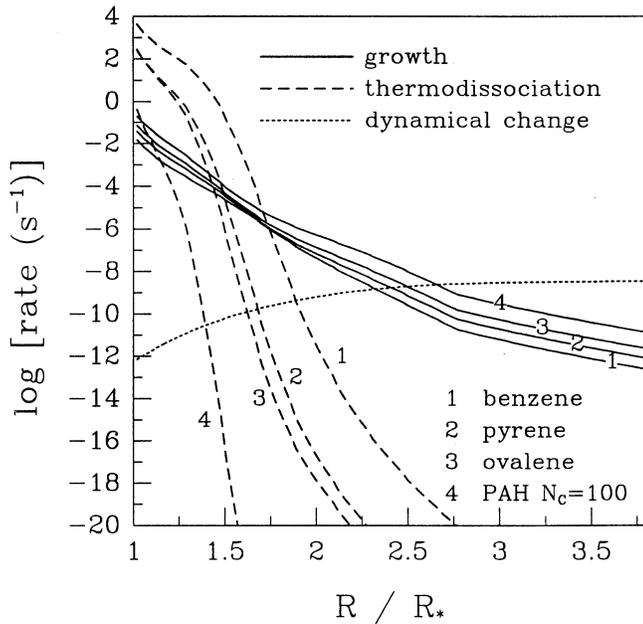
where  $T_{\text{X}}$  represents the temperature of species X, while  $s_{\text{X}}$  is its number of vibrational degrees of freedom, equal to  $3N - 6$  for a PAH with  $N$  atoms and to  $3N - 5$  for linear molecules ( $\text{H}_2$ ,  $\text{C}_2\text{H}_2$ ). By using Eq. (43) we assume that the vibrational energy of the reactive species is redistributed over the vibrational modes of both species during the reaction. This treatment of the reaction temperature seems to be more realistic than that proposed by Cherchneff et al. (1992), who assumed that reactions always occur at the PAH temperature when PAHs are involved. However, a theoretical study of this question is still required for future work on PAH chemistry in CSEs.

Combining Eqs. (39) to (43) enables the calculation of the growth rate of a given PAH by addition of acetylene in circumstellar environments, taking into account both the size and the temperature of the PAH. The results for some PAHs are presented in Fig. 9 as a function of distance from the star centre in the WDS model for IRC+10216. The growth rate increases with molecular size and is nearly two orders of magnitude greater for a PAH with 100 carbon atoms than for benzene. For a given PAH the growth rate decreases with decreasing PAH temperature and acetylene density and, consequently, with distance from the star. For distances greater than 3 star radii the growth rate of PAHs is lower than the dynamical change rate in the envelope so that the growth process freezes out.

### 5.3. Thermodestruction of PAHs

In the region near the star where temperatures have higher values, PAHs may dissociate by the reverse reaction to the growth process. An estimate for the rate of this thermodissociation process can be obtained by the following expression:

$$k^{\text{diss}} = \int_0^{\infty} k(E)\rho(E)\rho(E)dE, \quad (44)$$



**Fig. 9.** Rate of growth by acetylene addition and rate of thermoejection of acetylene for some PAHs as a function of distance from the star centre in the envelope of IRC+10216 modeled by WDS.

where  $E$ ,  $k(E)$ ,  $\rho(E)$  and  $p(E)$  are the internal energy of the PAH, its dissociation rate, its density of states and its probability for having the internal energy  $E$ , respectively.

The density of states can be approximated by the semi-empirical expression of Whitten & Rabinovitch (1963):

$$\rho(E) = (E + aE_z)^{s-1} \left[ s! \prod_{i=1}^s h\nu_i \right]^{-1}, \quad (45)$$

where  $\nu_i$  are the vibrational frequencies of the molecular modes and  $s$  their number, while  $a$  is a correction factor ( $0 < a < 1$ ) that varies with  $E$  according to an empirical law given by Forst (1973). For the calculations we use the same set of vibrational frequencies as in Allain et al. (1996a). We furthermore assume that the probability  $p(E)$  is of a Boltzmann type and write:

$$p(E) = \frac{\exp\left(-\frac{E}{kT_{\text{PAH}}}\right)}{\int_0^\infty \rho(E) \exp\left(-\frac{U}{kT_{\text{PAH}}}\right) dE}. \quad (46)$$

The dissociation rate in Eq. (44) is estimated by RRK theory using the parameters presented in Allain et al. (1996b) for the loss of an acetylene molecule.

The thermodissociation rates  $k_{\text{C}_2\text{H}_2}^{\text{diss}}$  calculated according to Eq. (44) are plotted in Fig. 9 for some PAHs in the circumstellar shell of IRC+10216 described by the WDS model. Fig. 9 confirms that thermodissociation dominates over growth in the region near the star.

The thermodissociation rate rapidly decreases with molecular size. PAHs with 100 carbon atoms and more are already stable against thermodissociation at  $1.1 R_*$ , whereas benzene

molecules are stable only for distances greater than  $1.9 R_*$ . At a given position in the envelope, we call critical PAH the smallest PAH for which the growth rate is greater than the thermodissociation rate. Near the star, the critical PAH contains at least 100 carbon atoms, while for distances greater than 2 stellar radii the critical PAH is as small as benzene.

The concept of a critical PAH along the PAH chemical pathway has been developed by Keller (1987), Gail & Sedlmayr (1987a) and Goeres (1993). For PAHs smaller than the critical PAH the chemistry can probably be correctly described by equilibrium calculations. PAHs larger than the critical PAH grow under kinetical equilibrium and may be correctly described by moment equations similar to those used by Gail & Sedlmayr (1988) to describe the growth of dust particles.

Additionally, we note that for PAHs larger than benzene the thermodissociation rate is lower than the typical rate for infrared emission ( $10^2 - 10^3 \text{ s}^{-1}$ ) (see Léger et al. 1989b, Jochims et al. 1994). This partially justifies that we have neglected thermoejection processes in the cooling process of circumstellar PAHs (see Sect. 4).

#### 5.4. Efficiency of PAH growth processes

Although some work has been devoted to the question of the growth process of PAHs up to macroscopic size, the exact pathway from PAHs to large macromolecules is still unknown. According to Allamandola et al. (1989) and more recently Cadwell et al. (1994), the growth may proceed via coagulation of PAHs. On the other hand, Keller (1987) and Frenklach & Feigelson (1989) have considered growth of PAHs by reaction with acetylene and hydrogen.

In order to study quantitatively, the hypothesis concerning the growth of PAHs in circumstellar envelopes, we define characteristic timescales for the growth of a pyrene molecule ( $N_C = 16$ ) up to a large PAH with 100 carbon atoms. For the growth process via acetylene addition we define:

$$\tau_{\text{C}_2\text{H}_2}^{\text{add}} = \sum_{N_C=16,18,\dots,100} \frac{1}{\tilde{k}_{\text{C}_2\text{H}_2}^{\text{gr}}(N_C)}. \quad (47)$$

In Eq. (47) we have introduced a net growth rate  $\tilde{k}_{\text{C}_2\text{H}_2}^{\text{gr}}$  defined by:

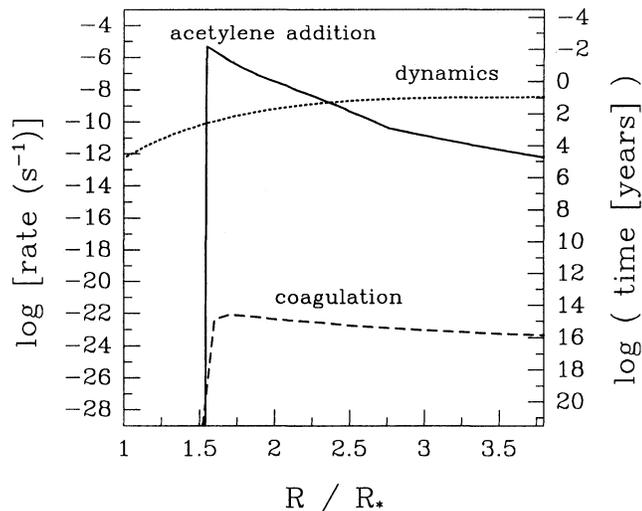
$$\tilde{k}_{\text{C}_2\text{H}_2}^{\text{gr}} = \text{Max}(0, k_{\text{C}_2\text{H}_2}^{\text{gr}} - k^{\text{diss}}), \quad (48)$$

where  $k_{\text{C}_2\text{H}_2}^{\text{gr}}$  is defined according to Eq. (38) and  $k^{\text{diss}}$  is the thermodissociation rate.

In the case of coagulation, we define a timescale by considering the growth by successive additions of pyrene molecules:

$$\tau_{\text{C}_{16}\text{H}_{10}}^{\text{coag}} = \frac{N_{\text{coll}}}{\alpha_s A^{\text{pyr}} v_{\text{th}}^{\text{pyr}} n^{\text{pyr}}}, \quad (49)$$

where  $A^{\text{pyr}}$ ,  $v_{\text{th}}^{\text{pyr}}$  and  $n^{\text{pyr}}$  represent the surface, thermal velocity and density of pyrene molecules, respectively. The factor  $\alpha_s$  is a sticking coefficient which is unknown and set here equal to unity.  $N_{\text{coll}}$  represents the number of collisions necessary to obtain a



**Fig. 10.** Rates for growth of a pyrene molecule up to a PAH with 100 carbon atoms by acetylene addition and by coagulation of pyrene molecules as function of distance from the star centre in the envelope of IRC+10216 modeled by WDS.

PAH with 100 carbon atoms from pyrene molecules. In agreement with our assumption that each colliding pyrene molecule sticks onto the growing PAH, we deduce a value of 5 for  $N_{\text{coll}}$ . We note that this assumption corresponds to the best efficiency for coagulation. The density of pyrene molecules in Eq. (49) has been obtained from the kinetic calculation presented in Sect. 5.5.

Fig. 10 shows the values obtained for these timescales in the envelope of IRC+10216. The timescale for coagulation is several orders of magnitude greater than the timescale for acetylene addition. The large difference would probably not be changed by a more exact calculation of coagulation based on the Smoluchowski equation (Cadwell et al. 1994). Moreover, coagulation processes are probably too slow to take place in the envelope since the coagulation timescale is much larger than the time for dynamical changes in the envelope. On the other hand, growth of large PAHs via addition of acetylene is rapid enough to take place in the first stellar radii of the shell. We therefore conclude that small PAHs probably grow up to large size preferentially via addition of acetylene molecules in the inner part of C-star CSEs.

### 5.5. Nucleation rate of PAHs

The previous results confirm that PAHs can favourably grow in the circumstellar envelopes of C-stars, probably up to macroscopic size. It has already been suggested by Keller & Sedlmayr (1983), Keller (1987), Gail & Sedlmayr (1987a) and Allamandola et al. (1989) that PAH formation constitutes the first step in the chemical pathway to dust in C-star shells. Unfortunately, the approach developed in the previous sections does not allow us to estimate the abundance of PAHs which form in the envelope and, therefore, does not allow to test quantitatively the hypothesis of PAHs as seed particles for dust. An alternative way to study the formation of PAHs is to solve the kinetic equations

of a chemical reaction network which takes into account all the species involved in PAH formation. Such calculations have already been performed by Frenklach & Feigelson (1989) and Cherchneff et al. (1992). We use this approach here to evaluate the nucleation rate of dust particles via PAHs.

In the present calculations we use the networks of Frenklach & Feigelson (1989) and Cherchneff et al. (1992) with the following modifications: (i) the reactions of PAHs with acetylene are described by the coefficient rate of Eq. (37), (ii) the reverse reaction of the reaction of formation of acenaphthylene from the naphthyl radical (reaction 100 of Frenklach & Feigelson (1989), which was artificially omitted by Frenklach & Feigelson (1989) for the sake of their computing procedure, is introduced, (iii) the set of reactions to pyrene is corrected (since one acetylene molecule is needed to form pyrene from anthracene and not two!), (iv) the formation of corannulene, which is constituted by a five carbon atom ring surrounded by five fused 6-membered aromatic rings, is implemented, (v) for distances greater than  $R^{\text{gr}} = 1.6R_*$  we have added to the set of reactions the growth reaction of pyrene and corannulene to take into account the growth of larger PAHs.

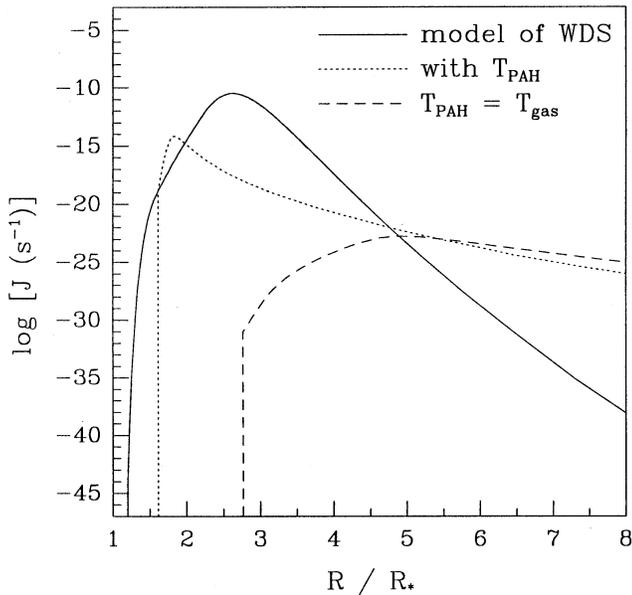
For distances greater than  $R^{\text{gr}} = 1.6R_*$  pyrene and corannulene indeed grow more rapidly than they eject acetylene (see Fig. 9). Hence, pyrene and corannulene molecules are consumed by the PAH growth process and their densities are thereby diminished. The above modification (v) accounts for this diminution. Since PAHs larger than pyrene and corannulene also grow faster than they dissociate, we can moreover neglect the increase of pyrene and corannulene densities due to the dissociation of larger PAHs. On the other hand, at distances smaller than  $R^{\text{gr}}$ , pyrene and corannulene eject acetylene rather than grow and we can therefore omit the growth reaction of these species. For distances smaller than  $R^{\text{gr}}$ , some PAHs larger than pyrene and corannulene may also dissociate rather than grow and thereby enhance the densities of pyrene and corannulene. With the present reaction network we cannot take into account the influence of those larger PAHs.

Some reactions in the chemical network involve species with different temperatures. The same procedure as in Eq. (43) has been used for the reaction temperature  $T_r$  in order to calculate the rate coefficients of the forward and reverse reactions. As did Cherchneff et al. (1992) we have also performed the calculation by setting all reaction temperatures equal to the gas temperature. In this case the distance  $R^{\text{gr}}$ , where pyrene and corannulene grow more rapidly than they dissociate, is equal to  $2.75 R_*$ .

To estimate the formation rate of large PAHs,  $J_{\text{PAH}}$ , we have calculated the flux of PAHs growing from pyrene and corannulene molecules to larger molecular sizes, according to the following relations:

$$R \leq R^{\text{gr}} : \quad J_{\text{PAH}} = 0 \quad (50)$$

$$R > R^{\text{gr}} : \quad J_{\text{PAH}} = k_{\text{C}_2\text{H}_2}^{\text{gr},\text{pyr}} n^{\text{pyr}} + k_{\text{C}_2\text{H}_2}^{\text{gr},\text{cor}} n^{\text{cor}} \quad (51)$$



**Fig. 11.** Formation rate of PAHs (i) including PAH temperatures; (ii) with reaction temperatures set equal to the gas temperature, and (iii) dust nucleation rate used in the WDS model.

where  $k_{\text{C}_2\text{H}_2}^{\text{gr,pyr}}$  and  $k_{\text{C}_2\text{H}_2}^{\text{gr,cor}}$  represent the rates for addition of acetylene defined in Eq. (38) for pyrene and corannulene, respectively, while  $n^{\text{pyr}}$  and  $n^{\text{cor}}$  are the corresponding PAH densities. Fig. 11 shows the results we have obtained for the PAH formation rate by solving the kinetic reaction network.

The results presented in Fig. 11 correspond to the calculation carried out at gas temperature and to the calculation including PAH temperatures. The introduction of PAH temperatures leads to a displacement of the maximum value of the PAH formation rate nearer to the star and to an enhancement of nine orders of magnitude for the maximum of the PAH formation rate. This result is in qualitative agreement with the results of Cherchneff et al. (1992). We consider that this phenomenon is a crucial point for the study of circumstellar PAHs. The nucleation rate calculated by Cadwell et al. (1994), who did not take into account this effect, would probably be considerably changed by introducing the PAH temperatures.

To test the hypothesis of PAHs as seed for the dust particles, we have compared the PAH formation rate to the dust nucleation rate. We have reported in Fig. 11 the nucleation rate used by WDS to describe the formation of dust particles. In the model of WDS the condensation of carbon grains is described by classical nucleation theory according to the equations given in Gail & Sedlmayr (1984) and extended to heteromolecular, homogeneous growth of the dust particles (Gail & Sedlmayr 1988). The PAH formation rate reaches its maximum nearer to the star than the dust nucleation rate of WDS. However, the maximum values obtained with the PAH chemistry are 4 orders of magnitude lower than the rate obtained by WDS. This could suggest that the present PAH formation path is not sufficient to produce the amount of dust capable of driving the stellar wind. Nevertheless, the self-consistency of the envelope model of WDS makes

the dynamical structure very dependent on the dust nucleation rate. Introducing another nucleation rate would indeed induce other temperature and pressure profiles. The new profiles in turn would affect the concentration of the condensating species and the value of the nucleation rate. As a consequence, a stellar wind could also develop for an apparently lower nucleation rate. For that reason any conclusion from the previous comparison remains fragile.

Some additional criticism must be addressed to the present kinetic description of the PAH chemistry. The chemical pathway in the network is based on study of terrestrial gas flame chemistry and there may exist other more efficient routes for PAH formation in the case of circumstellar envelopes, for which no kinetic data are now available (see for instance the proposal of Goeres 1993). Moreover, as already pointed out by Goeres (1993) a correct description of PAH formation with a chemical network should include species up to the critical cluster size. Near the star the critical cluster contains about 100 carbon atoms, which is much more than the larger PAHs considered in the network ( $N_C = 20$ ). Finally, our theoretical approach of chemical reactions involving partners with different temperatures probably needs some improvement. Consequently, it seems with the present results difficult to draw any definite quantitative conclusion about the role of PAHs in the formation of dust particles. However, it is qualitatively confirmed that PAHs, due to their low temperatures, are potentially a good candidate as seeds for dust nucleation in C-star CSEs.

## 6. Discussion

The chemical reactions of PAHs with hydrogen atoms and acetylene molecules have proved to be rapid enough to enable the formation and growth of PAHs in carbon-star envelopes (Keller 1987; Frenklach & Feigelson 1989; Cherchneff et al. 1992). Although these reactions have efficiencies lower than one percent, their characteristic timescales indeed are smaller than the timescale for the dynamical change of the physical parameters in the envelope. These reactions ensure a rapid and efficient growth of PAHs up to large molecular size. This growth via acetylene addition proceeds quicker than growth via coagulation of PAHs in the region near the star.

Generally, growth processes are considerably favoured by differential drift velocities between the growing species and the gas reacting species. Dominik et al. (1989) and more recently Krüger & Sedlmayr (1994) have for instance investigated the influence of drift velocity of dust grains in their study of the structure of carbon-star envelopes. They have shown that the efficiency of dust growth and consequently the structure of the envelope actually depend on dust grain drift. In the case of PAHs, the drift velocities of some thousand  $\text{cm}\cdot\text{s}^{-1}$  we have obtained are much smaller than the gas thermal velocity. Thus, the PAH drift velocities do not lead to any modifications of the chemical reaction rates involving PAHs and can therefore be neglected in the study of PAH growth in CSEs.

In contrast, PAH temperatures have a strong influence on the PAH growth process. Cherchneff et al. (1991, 1992) first

estimated the temperatures of PAHs in carbon-star envelopes and investigated their influence on PAH chemistry. They have shown that the yield of formation of small PAHs ( $N_C < 20$ ) is enhanced by several orders of magnitude when one introduces temperatures for PAHs lower than the gas temperature. Because of their lower temperatures, PAHs indeed reach the temperature range ( $800 \text{ K} \leq T \leq 1000 \text{ K}$ ) favourable to their formation nearer to the star than when they are assumed to be at gas temperature. Near the star, the density is much greater and the growth of PAHs is therefore more effective. However, Cherchneff et al. (1992) have considered only heating of PAHs via collisions with the gas and used a simple model of CSE. Their yield for PAH formation is therefore somewhat uncertain. In the present study, we have introduced heating via absorption of stellar emission and shown that this heating process is important at distances greater than  $\simeq 1.5R_*$ . Hence, PAHs stay longer in the favourable temperature range and thereby grow more efficiently than estimated by Cherchneff et al. (1992).

In the model of Gail & Sedlmayr (1987b) and WDS for C-stars, the onset of dust formation occurs at a distance from the star where the gas temperature has dropped to a value of about 1300 K. Gail & Sedlmayr (1987a) have shown that, at such temperatures, the efficiency of PAH formation is not high enough to induce a dust nucleation rate and consequently a dust formation which allows to drive a stellar wind. These results seem to be in contradiction to the picture of PAHs as seeds for the formation of dust grains. The lower temperatures of PAHs compared to the gas temperature may provide an explanation of this discrepancy. Near the star PAHs may indeed have temperatures lower than 1000 K and therefore favourably grow, while the gas temperature remains at higher values. The formation rate of PAHs calculated using a chemical reaction network is considerably increased when one takes into account PAH temperatures. The study of PAHs as possible seeds for dust particles has therefore to be carried out more precisely. Compared to SiC, which has also been proposed as seed particle (Cadwell et al. 1994) but for which no convincing thermodynamical data exist, and to purely carbon particles, whose nucleation described according to classical nucleation theory is still discussed (Donn & Nuth 1983, Keller 1987), PAHs indeed constitute a promising candidate which should be introduced in models of dust formation.

However, the question of a dust nucleation rate based on PAH chemistry deserves a careful analysis. The formation rate calculated from PAH chemistry has indeed a high dependence on the reaction rates and chemical pathway used to describe the formation and growth of PAHs. The data used in the present paper are derived from laboratory experiments whose physical conditions are far from those of circumstellar environments. Most of these experiments have been furthermore performed with benzene, which is not a characteristic PAH. More experimental data concerning the reactions of PAHs with acetylene and hydrogen are presently needed to have a better understanding of the chemical pathway from acetylene to PAHs and dust grains. Moreover, the PAH chemistry is based on reactions involving partners with different temperatures for which no reliable theoretical description exists. The situation is furthermore

complicated by the presence of shock waves in the envelopes of C-stars (Fleischer et al. 1992) which have not been taken into account in the present paper. Cherchneff (1991) and Cherchneff (1995) have qualitatively shown that PAH formation rate could be enhanced under the pressure and temperature conditions of the shocks developing near the star. Finally, we note that the introduction of a nucleation rate based on the PAH chemistry in a self-consistent model of carbon-star envelopes is a difficult task which nevertheless requires further investigation.

## 7. Conclusion

We have studied the interaction of gas particles with PAHs, regarded in this paper as large and flat plates. This modelization enables the calculation to be carried out of collision rates of PAHs with gas particles and of the momentum and energy exchange rates from gas particles to PAHs. The results have been applied to the case of C-star envelopes where PAHs can form and grow. The results of the self-consistent models of C-star envelopes of Winters et al. (1994) have been used to provide reliable estimates of the temperature and density profiles and of radiative transfer in the envelope.

The reaction rates of the chemical reactions involved in PAH formation and growth are shown to be high enough to ensure a rapid growth of PAHs, although the efficiencies of these reactions do not exceed some per-cent. These reaction rates are not enhanced by the drift velocity of some thousand  $\text{cm.s}^{-1}$  affecting PAHs in the envelope.

The temperatures of PAHs have been determined by balancing their heating via collisions with gas particles and absorption of stellar emission and their cooling via emission from the rotational and vibrational levels of PAHs. The PAH temperatures are lower than the gas temperature and enable an efficient formation and growth of PAHs in the circumstellar envelopes of C-stars. The PAH formation rate is large enough to support the idea that PAHs could constitute the first step in the formation of dust grains.

Dust particles have a crucial role in circumstellar envelopes because they partly drive the stellar wind and therefore influence the structure of the shells where PAHs form. The study of the growth of PAHs and dust is consequently closely coupled with that of the structure of the C-star shells. A complete treatment of the whole problem, now far from being obtained, provides the only possibility to accurately determine both the structure of carbon-star envelopes and the nature of circumstellar PAHs.

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