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Photodestruction of PAHs in the interstellar medium

I. Photodissociation rates for the loss of an acetylenic group

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Abstract. We have developed a model for interstellar polycyclic aromatic hydrocarbons (PAHs) in order to estimate their rate of photodissociation in the interstellar medium. These photoreactions include the loss of atomic and molecular hydrogen and the loss of the acetylene molecule. We have studied the stability of PAHs in the regions of high UV radiation where the infrared emission bands attributed to PAHs are observed (reflection nebulae, planetary nebulae, active galactic nuclei, HII regions...) by comparing the rate of acetylene loss to the rate of accretion of carbon to PAHs. This comparison shows that only PAHs with more than 50 carbon atoms may survive the UV radiation field of these regions, whereas smaller PAHs such as coronene or ovalene are destroyed within a few years.

Key words: ISM:molecules – molecular processes – ultraviolet:ISM

1. Introduction

Since it was proposed that polycyclic aromatic hydrocarbons (PAHs) could be the carriers of the so–called unidentified infrared (UIR) emission bands at 3.3, 6.2, 7.7, 8.6 and 11.3 μm (Léger & Puget 1984; Allamandola *et al.* 1985), the interest in interstellar PAHs has been steadily developing. From the flux of the UIR bands it has been deduced that PAHs are probably the most abundant molecules in the interstellar medium (ISM) after H_2 and CO (Léger & d'Hendecourt 1985). Their influence on the chemistry of interstellar gas has therefore been discussed (Lepp & Dalgarno 1988; Lepp *et al.* 1988, Millar 1992). PAHs have also been introduced in models of interstellar dust in order to account for the extinction and emission of the ISM (Puget & Léger 1989; Désert *et al.* 1990).

However, there has been less work on the processes of formation and destruction of PAHs, which is a crucial point in order to confirm their presence in the ISM. It is now well established that PAHs form in large quantities in the envelopes of C–giants (Keller & Sedlmayr 1983; Keller 1987; Frenklach & Feigelson 1989; Cherchneff *et al.* 1992; Goeres 1993; Cadwell *et al.* 1994; Cherchneff & Tielens 1994) where the chemistry of their formation is known. The growth and sputtering of PAHs have also been studied in shocked regions but the lack of exact chemical data leads to contradictory results concluding that PAHs are either a transient species or an ubiquitous component in interstellar clouds (Duley & Williams 1986; Brown *et al.* 1989, Flower *et al.* 1990). Another proposal by Herbst (1991) provides models for *in situ* formation of large hydrocarbon species in dense interstellar clouds. Nevertheless, all of these studies have been done in regions where the UIR bands are not observed because the UV radiation field is too weak to excite PAHs and make them reemit in the IR.

The regions where the UIR emission bands are seen (reflection nebulae, planetary nebulae, active galactic nuclei, H_{II} regions...) are usually associated with a strong UV radiation field, which may also be an important factor for destruction of PAHs via photodissociation. A recent study on unimolecular photoreactions of PAHs has been done by Jochims *et al.* (1994) which provides the rates of photodissociation of PAHs for given values of their excitation energy. These results argue against the theoretical and semi–empirical results which have been used so far to estimate the photostability of PAHs (Barker 1983; Omont 1986; Allamandola *et al.* 1989; Léger *et al.* 1989a; Buch 1989) and prove that for the typical energy of photons in the ISM only PAHs with more than 30 – 40 carbon atoms may have infrared radiative rates larger than the photodis-

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sociation rates and can therefore survive the interstellar UV field.

To subsist, these PAHs nevertheless have to undergo a rate of growth by accretion of carbon atoms or ions greater than the rate of photodissociation integrated over the interstellar UV spectrum. The determination of such an integrated photodissociation rate is a difficult task because it has to take into account all the possible processes following the absorption of a photon: ionization, dissociation, IR and visible luminescence. It is however worth calculating because it is the only way to estimate the size of the interstellar PAHs and their density independently from the observational determinations and hence could improve our understanding of the existence of interstellar PAHs.

2. Photophysics and photochemistry of interstellar aromatic molecules

In this section we first make some comments on the state of knowledge concerning the photophysics and photochemistry of interstellar PAHs. We then propose a model for these PAHs which describes in a simplified way their behaviour using some relations deduced from both theory and experiment. In the last subsection we apply this model to determine the yields of the more important processes following the absorption of a photon by a PAH in the interstellar medium.

2.1. Photophysics

Omont (1986) has shown that in the ISM the rates of collision of the most abundant particles with a typical PAH are never larger than 10^{-4} s^{-1}. Since the smallest rates of PAHs unimolecular processes are of the order of 10^2 s^{-1} (Allamandola *et al.* 1989; Léger *et al.* 1989a; Jochims *et al.* 1994) they are highly isolated in space. Léger & Puget (1984) have first shown that they can however reach transitory vibrational temperatures up to 1000 K, whereas it has been demonstrated that their rotational temperature always remains around 100 K (Rouan *et al.* 1992). In the interstellar medium PAHs therefore have the possibility to evolve as free molecules from states of high vibrational excitation. Accounting for these results we use for the description of interstellar PAHs a step ladder model that only specifies the electronic and vibrational states of the species. Figure 1 represents the case of an aromatic molecule whose electronic states can be singlets or triplets.

UV photon absorption is in many interstellar situations the dominant excitation process of such a molecule. When absorption occurs, the molecule is in most cases in the lowest singlet electronic state, S_0, from which it reaches an upper level. The main absorption transitions of PAH molecules are S_0—S_1, S_0—S_2, S_0—S_3,...which are spin allowed and the very strong far-UV band around 16 eV due to the $\sigma \rightarrow \sigma^*$ and the $\sigma \rightarrow \pi^*$ transitions (Koch & Otto 1972,1976; Pantos *et al.* 1978) and to direct ionization (Verstraete *et al.* 1990).[See for instance the recent spectra of Joblin (1992) obtained in the gas phase at low pressure].

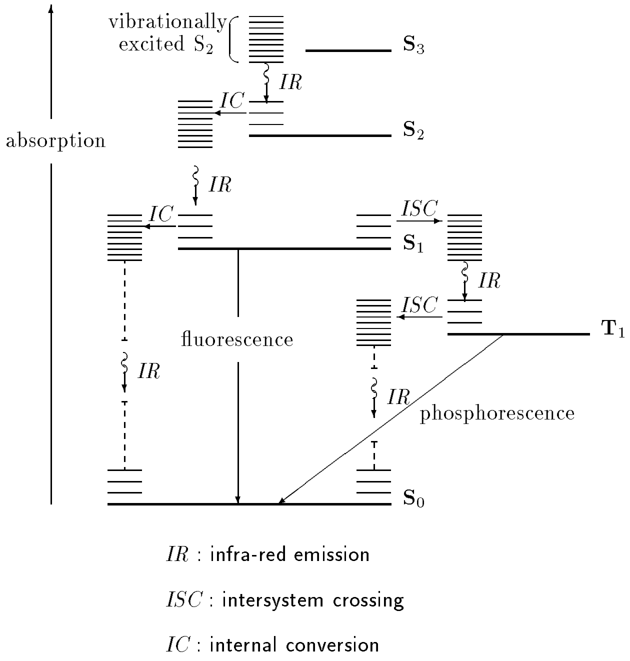

Fig. 1. Radiative and radiationless decay processes in a typical PAH molecule.

The processes following photoabsorption are electronic and vibrational transitions, ionization and photodissociation. The photophysics of PAHs and especially the transition processes have been extensively described in the literature (Birks 1970). The transitions are either radiative, described as fluorescence when they take place between states of same multiplicity and phosphorescence between states of different multiplicity, or radiationless. The radiationless transitions take place between isoenergetic vibrational levels of different electronic states and are described as internal conversion (IC) between states of same multiplicity or intersystem crossing (ISC) otherwise. After absorption of a photon, S_p—S_{p-1} ,..., S_2—S_1 internal conversions usually occur rapidly ($10^{-12}-10^{-10}$ s) and result in a practically complete conversion of the absorbed energy to vibrationally excited levels of the S_1 and S_0 electronic states.

2.2. Photochemistry

Several theoretical calculations have been performed to study the photodissociation of PAH molecules. The results obtained by Barker (1983), Tielens *et al.* (1987) and Allamandola *et al.* (1989) using QRRK (Quantum

Rice, Ramsperger, and Kassel theory) calculations have not been confirmed by the more recent experimental results of Jochims *et al.* (1994). These experimental results also argue against the model of Buch (1989) who predicted direct photodissociation of C—H bonds for all PAHs at energies less than 13.6 eV by absorption to a repulsive σ^* molecular orbital. The experiment shows on the contrary that for large PAHs rapid intramolecular redistribution of the absorbed energy among the vibrational modes considerably limits the yield of such a dissociation process. Omont (1986) has used a modified RRKM theory (Rice, Ramsperger, Kassel and Marcus theory) to estimate the rate of loss of hydrogen and carbon atoms. To obtain numerical results he introduced into the calculation data from experiments not directly carried out on PAHs. A similar approach has been more recently adopted by Léger *et al.* (1989a) who proposed to use the following expression given by Forst (1973) for the dissociation rates:

$$k(E) = k_0 \frac{\rho(E-E_0)}{\rho(E)} \qquad \text{for } E > E_0 \ ,$$
$$k(E) = 0 \qquad \text{for } E \le E_0 \ , \qquad (1)$$

where E represents the internal energy of the molecule, ρ its density of states and E_0 is the sum of the dissociation energy and the zero point energy E_z. The function $\rho(E)$ can be expressed using the Whitten-Rabinovitch approximation (Whitten & Rabinovitch 1963) in the form:

$$\rho(E) = (E + aE_z)^{s-1}\left[s! \prod_{i=1}^{s} h\nu_i\right]^{-1} , \qquad (2)$$

where ν_i are the vibrational frequencies of the modes and s their number, while a is a correction factor ($0 < a < 1$) that varies with E according to an empirical law given in Whitten & Rabinovitch (1963). Equations (1) are only valid if the rate of dissociation for a molecule thermalised at temperature T has the form of the Arrhenius law:

$$k(T) = k_0 \ \exp\left(-\frac{E_0}{RT}\right) , \qquad (3)$$

Table 1. Parameters for the RRK expression.

loss channel	$E_0(eV)$	$k_0(s^{-1})$ $^{(a)}$
H	2.8	1 (16)
H_2	2.9	1 (16)
C_2H_2	2.9	1 (15)

(a) Powers of ten are written inside the brackets

providing the constant k_0 and E_0 of Eq. (1). From indirect experimental evidence, Léger *et al.* (1989a) (who call this process thermo–photodissociation) have proposed to use the values $k_{0_H} = 2.4\ 10^{14}\ s^{-1}$ and $E_{0_H} = 4.5$ eV for the loss of a hydrogen atom and $k_{0_C} = 10^{17}\ s^{-1}$ and $E_{0_C} = 8$ eV for the loss of a carbon atom.

More recently Jochims *et al.* (1994) have obtained experimental results for the dissociative ionization of PAH molecules. This study led to the determination of the internal energy of the ion corresponding to the astrophysically critical rate of dissociation $10^2\ s^{-1}$ below which the species will preferentially relax by infrared emission. The results obtained were considered to be valid for neutral PAHs since the intramolecular dynamics and dissociation energies are closely similar for monocationic and neutral PAHs, as illustrated by the fact that vibrational frequencies are little modified in these two species which differ only by removal of a single π electron from a "sea" of conjugated π electrons (Leach 1987).

Jochims *et al.* (1994) explored experimentally three main channels corresponding to the loss of an hydrogen atom, a hydrogen molecule and an acetylene molecule. Their results have proved to be correctly interpreted on the basis of the simple Rice, Ramsperger, and Kassel (RRK) theory (for more details see for instance Forst (1973)). The rate of disintegration for a molecule of energy E is then given by the expression:

$$k(E) = k_0 \left(1 - \frac{E_0}{E}\right)^{3N-7} \qquad \text{for } E > E_0 \ ,$$
$$k(E) = 0 \qquad \text{for } E \le E_0 \ , \qquad (4)$$

where N is the number of atoms of the molecule. k_0 and E_0 are determined from the results of the experiment and are given in Table 1 for the loss of H, H_2 and C_2H_2. We note that in the RRK model, the parameter E_0 is only approximately related to the bond dissociation energy (Forst 1973) and it was used as a fitting parameter by Jochims et al. (1994).

We have plotted in Fig. 2 the rates of loss of carbon atoms calculated from the so–called thermo–photodissociation model and from RRK theory for benzene, naphthalene, anthracene, pyrene and coronene. In both cases the evolution of the rates with the size of the molecule are the same, leading to the conclusion that larger molecules are more stable against photodestruction. There is however a large discrepancy in the numerical values of the results which indicates that the rates from the thermo–photodissociation theory are by several orders of magnitude lower than those obtained with the RRK theory. This is probably due to the values of the parameters k_0 and E_0 used for the thermo–photodisociation. This point shows that theoretical considerations based on experimental observations not directly based on reactions with PAHs may lead to large uncertainties in the results. On the contrary, values of the constants in the RRK model have been

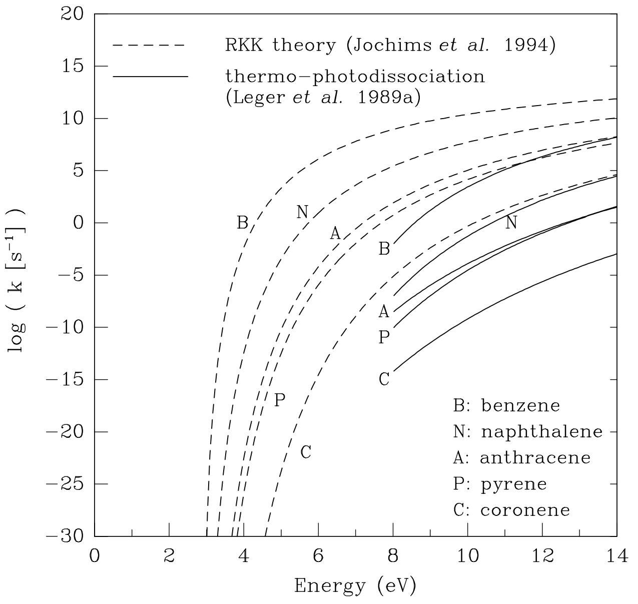

Fig. 2. Rates of destruction for various PAHs molecules calculated from RRK and thermo–photodissociation theories.

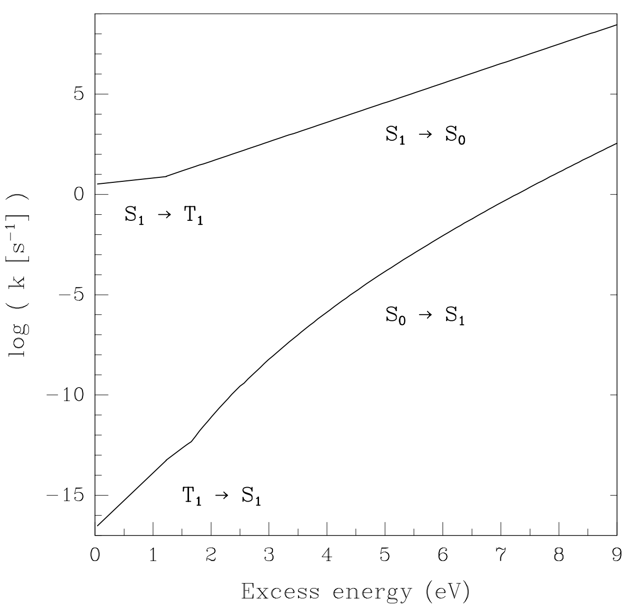

Fig. 3. Rates of radiationless processes and reversal processes for the molecule of naphthalene.

obtained to fit the recent experiments of Jochims *et al.* (1994) performed on PAHs. We therefore use the RRK results for our calculations in the remainder of this article. Another advantage of the RRK theory for the sake of our study is its simplicity compared to the calculation of the thermo–photodissociation rate, which supposes the use of the vibrational frequencies of the molecule (3N-6 for a molecule possessing N atoms!). Furthermore, the lack of data about these vibrational modes, especially for PAHs containing more than 8 rings, prevents us from using thermo–photodissociation calculations for these PAHs.

2.3. A model for the study of interstellar PAHs

The model for interstellar PAHs presented in this section is based on an ensemble of equations which integrates the present knowledge on PAHs in order to describe,in a reliable and simple way, the behaviour of interstellar PAHs in the ISM after absorption of a photon.

As suggested in Sect. 2.1, the only electronic levels considered in the model are S_1, S_0 and T_1. The transitions involving upper levels are supposed to bring quasi–instantaneously the species to the level S_1 by internal conversion. The other transitions of the molecules (S_1–S_0, S_1–T_1 and T_1–S_0 radiationless transitions, S_1 fluorescence and T_1 phosphorescence) have been taken into account using the rates of Birks (1970) and more recent data when they exist. The references of the data we use for the calculations are presented in Table 2. The decay rates have been mainly determined from the lifetime $\tau_{\rm f}$ and the quantum yield of fluorescence $\Phi_{\rm f}$ of PAHs. The expressions for the radiative $k_{\rm r}$ and non-radiative $k_{\rm nr}$ transitions are simply:

$$k_{\rm r} = \frac{\Phi_{\rm f}}{\tau_{\rm f}} ,$$
$$k_{\rm nr} = \frac{1 - \Phi_{\rm f}}{\tau_{\rm f}} . \qquad (5)$$

Unfortunately, these rates have often been obtained in solution and, in such a medium, a molecule excited by photoabsorption dissipates its vibrational excitation energy to its neighbours and thereby comes rapidly (typically 10^{-11} s) into thermal equilibrium with its environment. The values of the decay rates obtained in solution can therefore only be used for PAHs having no vibrational energy left in their S_1 and/or T_1 electronic states. To study the evolution of the rates with excess vibrational energy, we use the results of experiments on PAH vapors at low pressure and/or in molecular beams when they are available and some semi-empirical calculations otherwise.

For the radiationless transitions we use the results described in the extensive reviews of Avouris *et al.* (1977) and Lim (1985). To simplify the model, we always assume simple laws (linear or exponential) for the dependence of the rate on excess energy, which is in good agreement with both theory and experiment. For the non-radiative transition $S_1 - S_0$ of most PAHs we deduce for instance from Lim (1985) the following semi-empirical result:

$$k_{\rm nr} = k_0 \exp\left(\alpha E_{\rm vib}\left[{\rm cm}^{-1}\right]\right) \qquad (6)$$

with

$$\alpha = 2\ 10^{-2} + 4.38\ 10^{-8} \left(E_{\mathrm{S_1-S_0}} \left[\mathrm{cm}^{-1}\right] - 25500\right) \ , \quad (7)$$

where k_0, E_{vib} and $E_{\mathrm{S_1-S_0}}$ represent the rate for no excess energy over the state $\mathrm{S_1}$, the excess energy and the energy of the transition $\mathrm{S_1} - \mathrm{S_0}$, respectively. Figure 3 shows the evolution of the non-radiative rates in the case of a naphthalene molecule. Concerning the radiative transitions of vibrationally excited PAHs, we use the yields of fluorescence and phosphorescence available in the literature, especially from molecular beam experiments (see for instance the results of Hermine (1994)). When no experimental data are available, we assume that the rates of fluorescence and phosphorescence are constant up to the quenching of luminescence set at the electronic levels $\mathrm{S_2}$, and $\mathrm{T_2}$.

The IR properties of large PAHs are adapted from the model PAH considerations of Léger *et al.* (1989b). For some smaller PAHs in the gas phase the Einstein coefficients of vibrational transitions have been directly determined from measurements of integrated absorption coefficient (Bishop and Cheung 1982) or from laser-induced dissociation studies (Dunbar *et al.* 1987; Klippenstein *et al.* 1993). For PAHs having less than N = 25 atoms we have also collected the values of the 3N-6 frequencies in the literature determined either from experiment or from theoretical calculations. For computational purposes they have been grouped according to their physical origin. More precisely, all the modes around 3.3 μm which correspond to stretching modes of the C–H bonds have been considered together as well as the bending modes of the C–H bonds around 11.3 μm, the stretching modes of the C–C bonds around 6.2 μm, the bending modes of the C–C bonds around 8.6 μm and finally the typical polycyclic skeleton modes around 7.7 μm. The Einstein coefficients corresponding to these IR transitions have also been modified to take into account the excess vibrational energy of the PAH. When this excitation energy is high, the emitting mode may indeed have n quanta with $n > 1$ and its Einstein coefficient may therefore change. From the harmonic approximation we deduce:

$$A^{\mathrm{n,n-1}} = n\ A^{1,0} \ , \quad (8)$$

where $A^{\mathrm{n,n-1}}$ represents the Einstein coefficient for the $n \rightarrow (n-1)$ transition. The number of quanta of the emitting mode is calculated by assuming a complete energy distribution between all normal modes. The most probable population numbers can be calculated from the equation:

$$E_{\mathrm{ex}} = \sum_{i=1}^{3N-6} \frac{h\nu_i}{\exp\left(\frac{h\nu_i}{kT^*}\right) - 1} \ , \quad (9)$$

where E_{ex} is the excess energy, T^* a parameter that is defined as a vibrational temperature and ν_i the frequency of the mode i. The occupation probability of a particular mode is then given by a Bose-type function:

$$n = \left[\exp\left(\frac{h\nu_i}{kT^*}\right) - 1\right]^{-1} . \quad (10)$$

The correction to $A^{1,0}$ is larger for the smaller molecules which have fewer modes over which the absorbed energy can be distributed. The corrections to the Einstein coefficients are however always less than a factor 10 in the case of benzene. They can therefore be neglected with a good approximation for PAHs having more than 25 carbon atoms, for which the vibrational frequencies of all the modes are not available.

For the ionization of the molecule we use the value of the first ionization potential (IP) from Eilfeld and Schmidt (1981). As confirmed in the study of Verstraete *et al.* (1990) concerning the ionization cross-section σ_{ion} of isolated pyrene and coronene molecules, we assume that the photoionization yield $Y_{\mathrm{ion}} = \sigma_{\mathrm{ion}}/\sigma_{\mathrm{absorption}}$ does not depend on the number of carbon atoms of the molecule. In general Y_{ion} shows a steep increase after the first ionization potential up to a value of 0.75 at the Lyman limit. We use the following linear interpolation for the ionization yield of PAH molecules:

$$\begin{aligned}
Y_{\mathrm{ion}} &= 0.0 && \text{for } E < \mathrm{IP} \ , \quad (11)\\
Y_{\mathrm{ion}} &= \frac{0.10}{8.90 - \mathrm{IP}} \left[(E/\mathrm{eV}) - \mathrm{IP}\right] && \text{for } E/\mathrm{eV} \in [\mathrm{IP}, 8.9] \ ,\\
Y_{\mathrm{ion}} &= 0.25\,(E/\mathrm{eV}) - 2.125 && \text{for } E/\mathrm{eV} \in [8.9, 11] \ ,\\
Y_{\mathrm{ion}} &= 0.0596\,(E/\mathrm{eV}) - 0.03 && \text{for } E/\mathrm{eV} \in [11, 13.6] \ .
\end{aligned}$$

Table 2 shows that there exists a systematic evolution of the ionization potential with the size of the molecule. Verstraete *et al.* (1990) have proposed the following expression, which we use for larger PAHs whose ionization threshold is unknown

$$\mathrm{IP} = 4.8 + \frac{10.9}{a \ \ (\text{Å})} \ \ \mathrm{eV} \ , \quad (12)$$

where a is the largest linear size of the molecule and corresponds to the radius in the case of compact PAHs. We use the following relation of Omont (1986) for the radius of such a PAH molecule containing N_{C} carbon atoms:

$$a = 0.9\ N_{\mathrm{C}}^{1/2} \ \ \text{Å} \ . \quad (13)$$

No real evidence exists in the laboratory for inverse internal conversion (IIC) from a vibrational level to another corresponding to an upper electronic state, but this process may be important in the ISM. This has been proposed by Léger *et al.* (1988) who predict a recurrent fluorescence which they name Poincaré fluorescence, due to the possibility for a molecule in very high vibrational levels of the ground state to return to the state $\mathrm{S_1}$. The IIC

Table 2. Physical data on PAH molecules.

molecule	benzene C_6H_6	naphthalene $C_{10}H_8$	anthracene $C_{14}H_{10}$	pyrene $C_{16}H_{10}$	coronene $C_{24}H_{12}$
$IP\ (eV)$	$9.24^{(a)}$	$8.15^{(a)}$	$7.41^{(a)}$	$7.41^{(a)}$	$7.29^{(a)}$
$S_1\ (eV)$	4.72	3.97	3.42	3.34	2.95
$S_2\ (eV)$	6.08	5.77	3.72	3.71	3.51
$T_1\ (eV)$	3.66	2.64	1.82	2.08	2.37
$fluorescence\ rate\ (s^{-1})$	$2.2\ (6)^{b}$	1.0 (7)	4.9 (7)	$6.2\ (5)^{(c)}$	$2.5\ (6)^{(d)}$
$phosphorescence\ rate\ (s^{-1})$	1.0 (−15)	2.0 (−2)	1.1 (−7)	5.9 (1)	5.9 (1)
$S_1 \rightarrow T_1\ rate\ (s^{-1})^{(e)(f)}$	$7.8\ (6)^{(b)}$	$2.5\ (3)^{(g)}$	1.1 (7)	3.0 (4)	2.1 (6)
$S_1 \rightarrow S_0\ rate\ (s^{-1})^{(e)(f)}$	4.0 (4)	$2.0\ (5)^{(h)}$	1.0 (6)	3.0 (5)	4.0 (5)
$T_1 \rightarrow S_0\ rate\ (s^{-1})^{(e)(f)}$	2.9 (−2)	3.9 (−1)	2.2 (1)	2.0 (0)	1.2 (1)
$UV - absorption\ spectrum$	(i)	(j)	(i)	(i)	(i)
$IR - modes$	$(k)\ (l)\ (m)$	$(k)\ (l)$	$(l)\ (n)$	$(k)\ (o)\ (p)$	$(k)\ (o)\ (q)$

Data without indication are taken from Birks (1970), (a) Eilfeld and Schmidt (1981), (b) Spears & Rice (1971), (c) Werhoven *et al.* (1975a,1975b), (d) Bermudez & Chan (1986), (e) Avouris *et al.* (1977) and references therein, (f) Lim (1985) and references therein, (g) Fisher *et al.* (1971), (h) Hsieh *et al.* (1974), (i) Joblin (1992), (j) Koch *et al.* (1972), (k) Cyvin (1982), (l) Cyvin *et al.* (1984), (m) Bishop & Cheung (1982), (n) Evans & Scully (1964), (o) Cyvin *et al.* (1979), (p) Bree *et al.* (1971) and (q) Léger *et al.* (1989b)

is introduced in the model and its rate $k_{\rm IIC}$ is deduced from the rate of the corresponding IC, $k_{\rm IC}$, by application of detailed balance (Léger *et al.* 1988):

$$k_{\rm IIC} = k_{\rm IC}\ \frac{\rho(E - \Delta E)}{\rho(E)}\ , \tag{14}$$

where E is the vibrational energy of the molecule, ρ the density of states and ΔE the energy gap between the two electronic levels involved in the transition. Figure 3 gives the results obtained in the case of the non-radiative transitions of naphthalene. As already noticed by Léger *et al.* (1988) the effect of IIC increases rapidly with the internal energy. Our calculations have also proved that, for two molecules presenting similar rates of IC, the importance of IIC could be greater in the case of the smaller molecule. Introducing IIC processes leads to some modifications of the fluorescence and phosphorescence properties. As did Léger *et al.* (1988) we define rates of Poincaré luminescence, by mutiplying the probability to emit a photon by phosphorescence or fluorescence with the rate at which the molecule returns to the excited emitting modes:

$$\begin{aligned} k_{\rm fluo}^{\rm Poincare} &= (k_{\rm S_0 \rightarrow S_1} + k_{\rm T_1 \rightarrow S_1})\ \frac{k_{\rm fluo}}{\sum k_{\rm i}}\ , \\ k_{\rm phos}^{\rm Poincare} &= (k_{\rm S_0 \rightarrow T_1} + k_{\rm S_1 \rightarrow T_1})\ \frac{k_{\rm phos}}{\sum k_{\rm i}}\ , \end{aligned} \tag{15}$$

where $k_{\rm fluo}$, $k_{\rm phos}$ and $\sum k_{\rm i}$ represent the rates of fluorescence, phosphorescence and the sum of all the processes which the molecule can undergo, respectively. However, as in the case of Fig. 3, the IIC rates have relative low values for the smaller values of excess energy where visible and UV luminescence have the greatest yields. This largely limits the importance of Poincaré fluorescence and phosphorescence.

2.4. Redistribution of the absorbed energy

In this section we use the previous model to analyse the distribution of energy in a PAH having absorbed a photon. The energy ranges between 0 and 13.6 eV, which are the typical astrophysical values in HI region of the ISM. Using the references and data of Table 2 we have computed the total rate of luminescence (visible and UV fluorescence, phosphorescence and infrared emission) $k_{\rm lum}(E)$ as a function of energy, taking into account all the modifications introduced by the excess energy and the Poincaré luminescence (Eqs. (8) (10) (15)). From the determination of photodissociation rates $k_{\rm diss}$ (Eq. (4)) and from the yield of ionization $Y_{\rm ion}$ (Eq. (11)), we are then able to estimate the yields of each process, assuming that there are no relaxation processes other than luminescence, photodissociation and ionization after the absorption of a photon. We can hence write:

$$\begin{aligned} Y_{\rm fluo}(E) &= \frac{k_{\rm fluo}(E)}{k_{\rm tot}}\ , \\ Y_{\rm phos}(E) &= \frac{k_{\rm phos}(E)}{k_{\rm tot}}\ , \end{aligned}$$

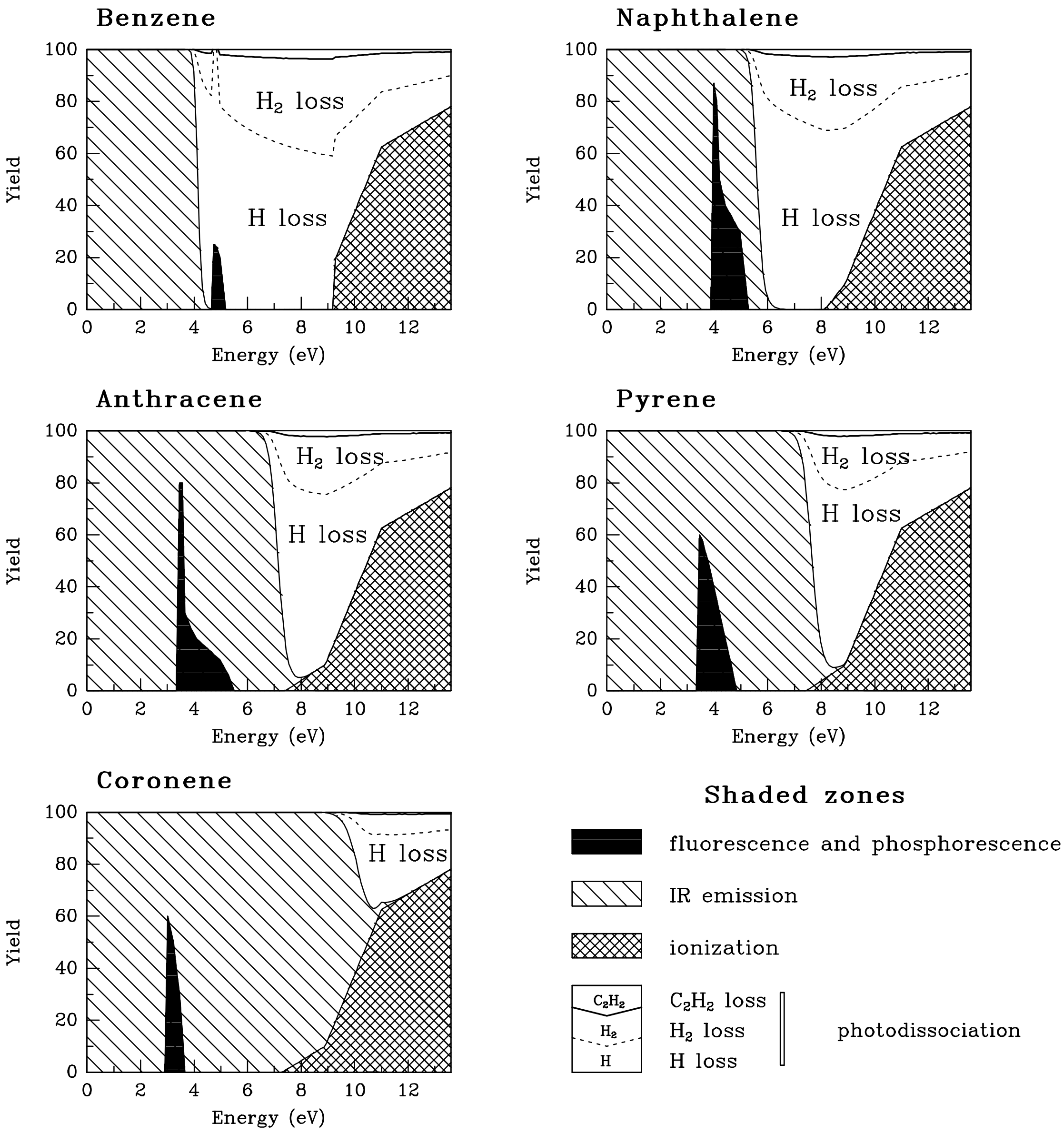

Fig. 4. Distribution of the energy in some PAH molecules after the absorption of a photon.

$$
\begin{aligned}
Y_{\mathrm{IR}}(E) &= \frac{k_{\mathrm{IR}}(E)}{k_{\mathrm{tot}}} , \\
Y_{\mathrm{H\ loss}}(E) &= \frac{k^{\mathrm{RRK}}_{\mathrm{H\ loss}}(E)}{k_{\mathrm{tot}}} , \\
Y_{\mathrm{H_2\ loss}}(E) &= \frac{k^{\mathrm{RRK}}_{\mathrm{H_2\ loss}}(E)}{k_{\mathrm{tot}}} , \\
Y_{\mathrm{C_2H_2\ loss}}(E) &= \frac{k^{\mathrm{RRK}}_{\mathrm{C_2H_2\ loss}}(E)}{k_{\mathrm{tot}}} , \qquad (16)
\end{aligned}
$$

where

$$
\begin{aligned}
k_{\mathrm{IR}}(E) &= A_{3.3\mu\mathrm{m}} + A_{6.2\mu\mathrm{m}} + A_{7.7\mu\mathrm{m}} + A_{8.6\mu\mathrm{m}} + A_{11.3\mu\mathrm{m}} , \\
k_{\mathrm{lum}}(E) &= k_{\mathrm{IR}}(E) + k_{\mathrm{fluo}}(E) + k_{\mathrm{phos}}(E) , \\
k_{\mathrm{diss}}(E) &= k^{\mathrm{RRK}}_{\mathrm{H\ loss}}(E) + k^{\mathrm{RRK}}_{\mathrm{H_2\ loss}}(E) + k^{\mathrm{RRK}}_{\mathrm{C_2H_2\ loss}}(E) , \qquad (17) \\
k_{\mathrm{tot}} &= k_{\mathrm{lum}}(E) + k_{\mathrm{diss}}(E) + k_{\mathrm{ion}}(E) , \\
k_{\mathrm{ion}} &= Y_{\mathrm{ion}} k_{\mathrm{tot}} .
\end{aligned}
$$

Figure 4 shows that luminescence is the dominating process for all PAHs after absorption of a photon having less than 6 eV. This emission appears practically only as infrared emission although some high yields of fluorescence are observed in the vicinity of the first excited singlet state.

A striking feature is the increasing importance of infrared emission with the size of the molecule. Since the yield of ionization remains almost constant for all PAHs, this means that the larger the molecule, the smaller is its

Table 3. Minimum energy for a yield of acetylene loss greater than 0.01.

molecule	C_6H_6	$C_{10}H_8$	$C_{14}H_{10}$	$C_{16}H_{10}$	$C_{24}H_{12}$
Energy (eV)	4.96	5.72	7.23	7.77	-

photodissociation yield. The energy for which the yield of acetylene loss is larger than 1.0 % also increases with the size of the molecule as listed in Table 3. The yield of acetylene loss for a coronene molecule is always less than 0.8%. This may be the reason why this reaction channel has not been observed for coronene with the experimental set–up used by Jochims *et al.* (1994).

3. Photodissociation rates of PAHs in the ISM

In the first subsection we present the expressions we use for the interstellar UV radiation field. The calculations of photodissociation rates are presented in the following two subsections.

3.1. Interstellar radiation field

Estimates of the intensity of the background interstellar radiation field of the ISM and of the solar neighbourhood have been made by Habing (1968), Witt and Johnson (1973), Jura (1974), Draine (1978), Gondhalekar *et al.* (1980) and Mathis *et al.* (1983).

Draine (1978) has proposed an analytic expression for the angle-averaged photon flux $\lambda^3 u_\lambda / 4\pi h^2 c$ where u_λ is the radiative energy density.

$$\frac{N_1(E)}{4\pi} = 6.919\ 10^3 (E/\mathrm{eV})^3 - 2.152\ 10^5 (E/\mathrm{eV})^2 + 1.658\ 10^6 (E/\mathrm{eV}) \quad \text{photons cm}^{-2}\text{s}^{-1}\text{eV}^{-1}\ . \quad (18)$$

$N_1(E)$ represents the photon flux integrated over all directions. Equation (18) gives valid results over the range 5 – 13.6 eV. However, the energies of interest for the study of PAH photodissociation range from the threshold of fragmentation at 2.8 eV to the Lyman limit at 13.6 eV. To extend the expression (18) to lower energies, we use the observational results of Witt and Johnson (1973), which has been used by Draine (1978), and obtain the following expression for the total flux over the range 2.8 – 5.2 eV:

$$N_1(E) = 4.89085\ 10^6 (E/\mathrm{eV})^4 - 9.133074\ 10^7 (E/\mathrm{eV})^3 + 6.36590\ 10^8 (E/\mathrm{eV})^2 - 1.96811\ 10^9 (E/\mathrm{eV}) + 2.28706\ 10^9 \quad \text{photons cm}^{-2}\text{s}^{-1}\text{eV}^{-1}\ . \quad (19)$$

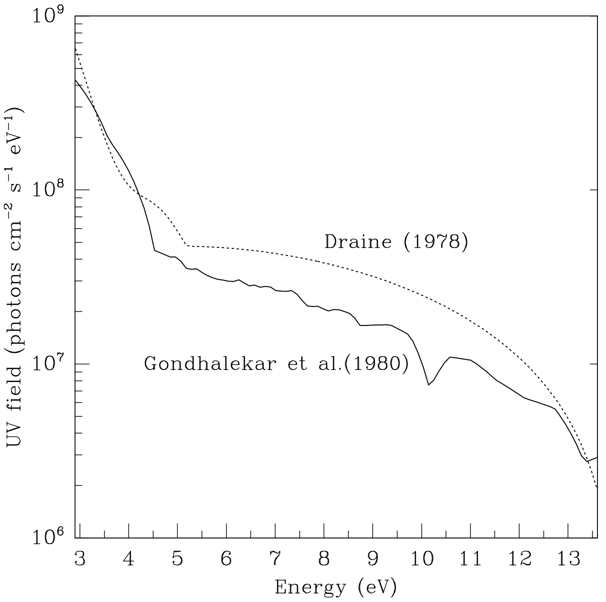

Fig. 5. Intensity of the interstellar radiation field.

The expressions (18) and (19) provide us a first set of values N_1 for the photon flux in the ISM. As did van Dishoeck (1988), we also use another set N_2 of more recent data. Gondhalekar *et al.* (1980) have indeed indicated an interstellar UV radiation field over the range 4.5 – 13.3 eV which is somewhat smaller than the previous estimates of Draine. However, they have used the first observations made over the whole sky and should therefore provide a realistic value of the total interstellar radiation field. The theoretical estimate of Mathis *et al.* (1983) appears to be in good agreement with the results of Gondhalekar *et al.* (1980) and has been used to extend the latter interstellar radiation field to the range 2.8 – 13.6 eV. The two sets of values are reported in Fig. 5.

3.2. Photodissociation rates

In order to compute the rate of a process (i) for a given species (s) in the ISM, one needs to know the yield $Y^{(i)}_{(s)}$ of the involved process, the absorption cross–section $\sigma_{(s)}$ of the species and the photon flux N, as a function of the energy E. The photodissociation rate is then given by the following relation:

$$k^{\mathrm{ISM}}{}^{(i)}_{(s)} = \int_{E=E_0}^{E=13.6eV} Y^{(i)}_{(s)}(E)\sigma_{(s)}(E)N(E)dE\ . \quad (20)$$

Table 4. Photodissociation rates of PAH molecules in the ISM (unit = s^{-1}).

	H loss		H_2 loss		C_2H_2 loss	
	Set 1$^{(a)}$	Set 2$^{(b)}$	Set 1	Set 2	Set 1	Set 2
benzene	4.76 (−9)	2.89 (−9)	2.51 (−9)	1.50 (−9)	2.51 (−10)	1.49 (−10)
anthracene	6.17 (−9)	3.40 (−9)	2.15 (−9)	1.19 (−9)	2.14 (−10)	1.89 (−10)
pyrene	3.73 (−9)	2.05 (−9)	1.28 (−9)	7.13 (−10)	1.29 (−11)	7.13 (−11)
coronene	2.56 (−9)	1.49 (−9)	7.61 (−10)	4.55 (−10)	7.61 (−11)$^{(c)}$	4.55 (−11)$^{(c)}$
ovalene	2.07 (−10)	1.78 (−10)	5.58 (−11)	4.85 (−11)	5.59 (−12)$^{(c)}$	4.85 (−12)$^{(c)}$
PAH 50 C	2.27 (−16)	2.31 (−16)	3.51 (−17)	3.61 (−17)	3.49 (−18)$^{(c)}$	3.56 (−18)$^{(c)}$

(a) radiation field from Draine (1978), (b) radiation field from Gondhalekar *et al.* (1980), (c) results extrapolated from the experiments of Jochims *et al.* (1994)

Table 5. Photoionization rates of PAH molecules in the ISM (unit = s^{-1}).

molecule	Set 1$^{(a)}$	Set 2$^{(b)}$
benzene	2.01 (−9)	1.23 (−9)
anthracene	4.63 (−9)	2.79 (−9)
pyrene	3.84 (−9)	2.34 (−9)
coronene	7.53 (−9)	4.54 (−9)
ovalene	8.43 (−9)	5.09 (−9)
PAH 50 C	9.79 (−9)	6.24 (−9)

(a) radiation field from Draine (1978), (b) radiation field from Gondhalekar *et al.* (1980)

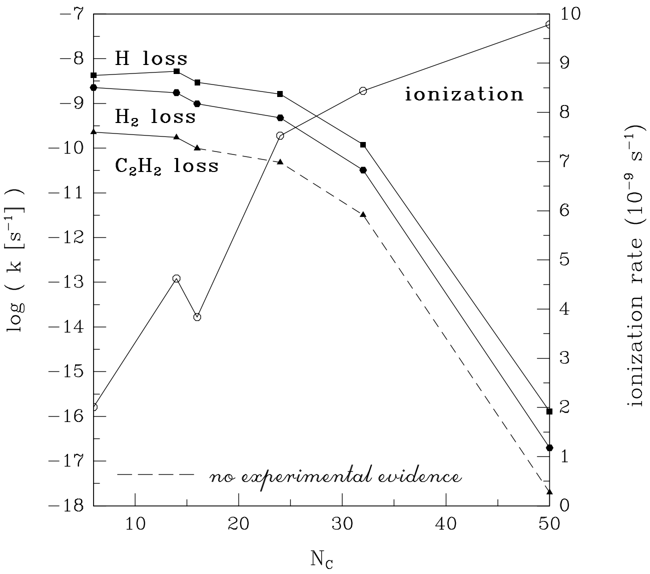

Fig. 6. Photodissociation and photoionization rates of PAH molecules in the ISM.

Using the yields defined in Eq. (16) and the photon flux of Sect. 3.1 we compute the rate of photodissociation and photoionization of benzene, anthracene, pyrene and coronene, using the spectra of Joblin (1992) for the UV–absorption cross–sections. To examine the effect of size we also calculate these rates for ovalene and for PAH molecules containing up to 100 carbon atoms. For ovalene and larger PAHs the yields of photodissociation were computed without taking into account IIC rates and the modifications of the Einstein coefficients for IR emission. For PAHs larger than ovalene we also omit phosphorescence and adopt a typical rate of 10^7 s^{-1} for fluorescence and the following expression of Robertson (1986) for an estimate of the energy of the first excited state

$$E_{S_1-S_0} = \frac{2\beta}{N_{\rm ring}} , \qquad (21)$$

where $N_{\rm ring}$ is the number of rings of the molecule and 2β a transition energy equal to 4.8 eV deduced from experiment. The UV absorption cross–section of ovalene is taken from Joblin (1992) and for the larger PAHs from Verstraete & Léger (1992). The results obtained for the two sets of interstellar field are listed in Tables 4 and 5. The two sets of results differ by a factor 1.6 with larger values for the radiation field of Draine (1978).

To have a better view of the size effect on the photoreactions we plot in Fig. 6 the rates as a function of the number of carbon atoms of the molecules for the values

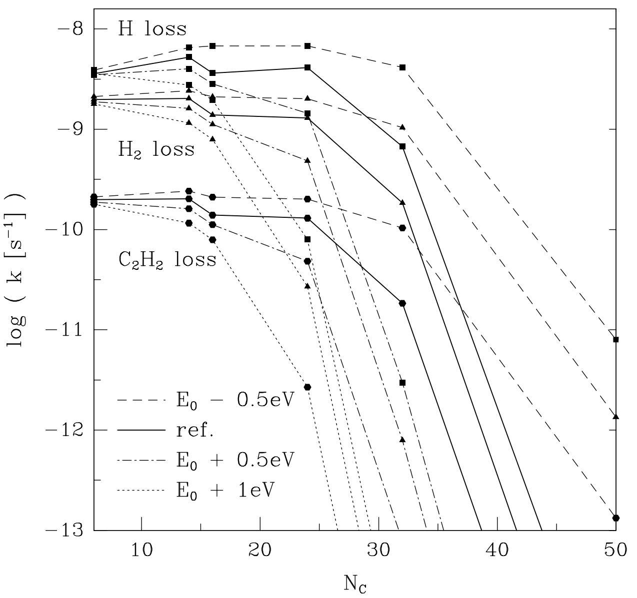

Fig. 7. Dissociation rates in the ISM from RRK calculations with various values of the parameter E_0
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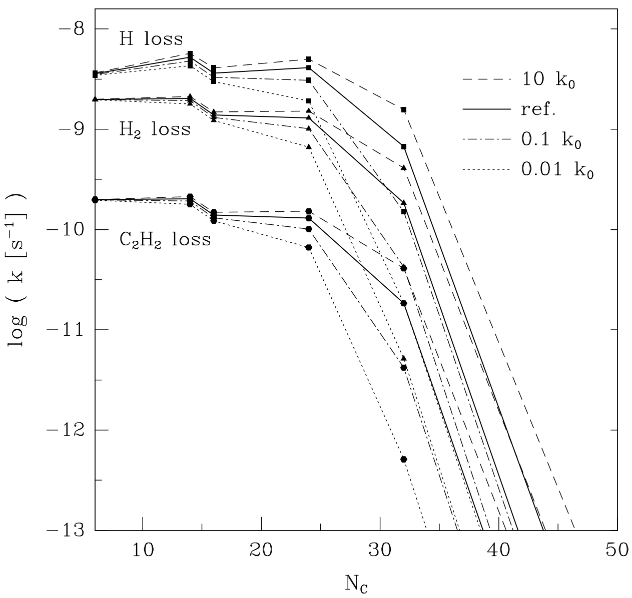

Fig. 8. Dissociation rates from RRK calculations with various values of the parameter k_0
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of photon flux given by Gondhalekar *et al.* (1980). From Fig. 6 we observe a slight increase of the photoionization rate with the size of the molecule. This can be easily explained when one considers that the yield of ionization is practically the same for all PAHs whereas the cross-sections of absorption vary roughly as $N_{\rm C}$ (Verstraete *et al.* 1991). The explanation for the lower rate of pyrene ($N_{\rm C}$ = 16) compared with the rate for anthracene ($N_{\rm C}$= 14) may be found in the compact form of the pericondensed molecule of pyrene to be compared with the linear shape of the catacondensed molecule of anthracene. The decrease of the photodissociation rates with size is *a priori* more difficult to predict. Larger PAHs have indeed larger absorption cross–sections and are therefore more likely to be photodissociated but the yields of photodissociation for large PAHs are much lower than for small PAHs. As has already been shown by Jochims *et al.* (1994), Fig. 6 confirms that large PAHs are more stable against photodissociation. For PAHs having $N_{\rm C}$ > 50 carbon atoms the results of photodissociation and photoionization are well reproduced by the following analytical expressions:

$$k^{(i)}_{\rm loss}(N_{\rm C}) = k^{(i)}_{\rm loss}(50)\, 10^{-0.3373(N_{\rm C}-50)} ,$$
$$k^{(i)}_{\rm ion}(N_{\rm C}) = k^{(i)}_{\rm ion}(50) \left(\frac{N_{\rm C}}{50}\right) , \qquad (22)$$

where (i) represents a given choice for the interstellar field and reaction channel.

Since the parameters entering into the expression (4) of the RRK theory are not a direct result of the experiment but constants determined to fit the experimental results, it is worth testing the sensitivity of our results to these parameters. For the present purpose we have used only the set of data from Gondhalekar *et al.* (1980) for the radiation field. We have made two series of calculations. The first was achieved by simultaneously modifying E_0 values for the three loss channels by increments ranging from -0.5 eV to +1 eV and keeping the values for the parameter k_0 unchanged. In the second calculation E_0 values remained at their original values but we multiplied k_0 by a factor ranging from 0.01 to 10 common to the three reactions. The results of these two series of calculation are displayed in Figs. 7 and 8. As is obvious from Eq. (4), the variation of $k^{\rm ISM}$ with E_0 and k_0 increases with the number of carbon atoms. This result was expected after inspection of Eq. (4). However, for molecules with less than 20 carbon atoms these variations remain smaller than an order of magnitude for a variation of E_0 of 1 eV and a variation of two orders of magnitude of k_0. For larger molecules the results of the calculations have to be taken with care since they are very sensitive to the parameters and since there has not always been real laboratory evidence for the photoejection of acetylene molecules from PAHs larger than pyrene (Jochims *et al.* 1994).

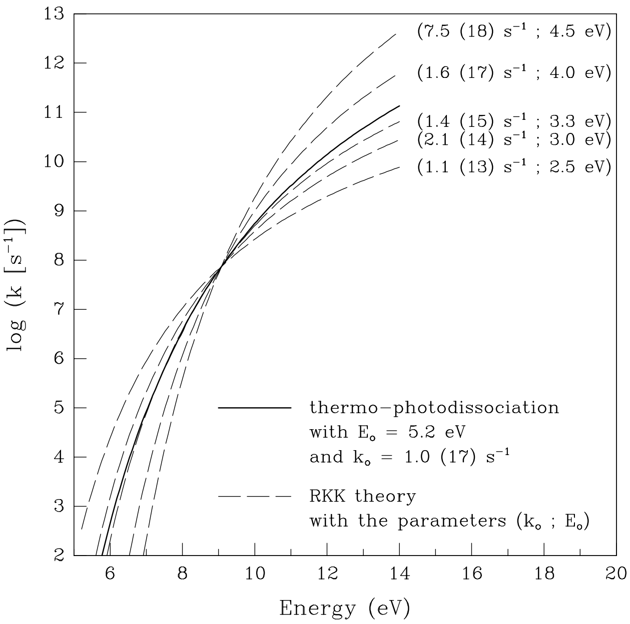

Fig. 9. Rate of photolysis of the φ — C_2H bond calculated by the thermo–photodissociation and RRK models.

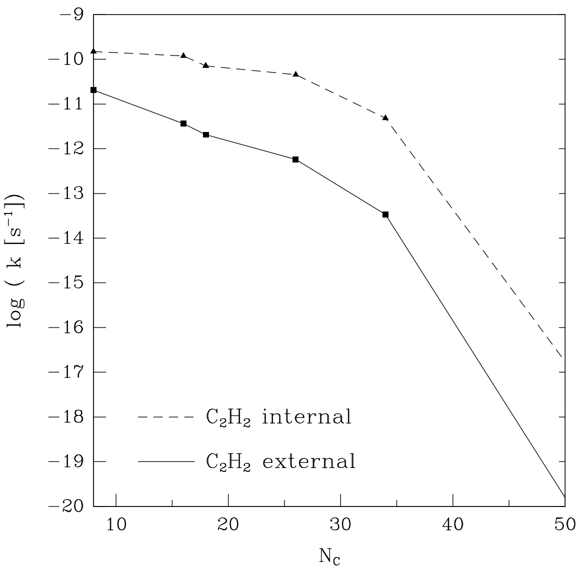

Fig. 10. Rate of photolysis of the φ — C_2H bond as a function of the number of carbon atoms of the PAH molecule bearing the acetylenic group.

3.3. The case of an acetylenic group attached to a PAH structure

In the previous sections we have investigated the rates for the loss of an acetylene molecule from a compact PAH molecule. From the network of Frenklach & Feigelson (1989) and Cherchneff *et al.* (1992) who have studied the formation of PAHs in carbon star shells it can be seen that many species in the envelope of the star are composed of a PAH with an acetylenic group attached to its carbon skeleton (the simplest example of such molecules is phenylacetylene). It is therefore of interest to study the loss of the acetylenic group from these molecules. No experimental data addressing this question has been found in the literature. We have therefore used a theoretical approach similar to that already given in Sect. 2.2.

We first concentrate on the case of phenylacetylene. We use the expression (1) from the thermo–photodissociation theory to determine the rate of photolysis of the benzene-ethynyl group bond because the parameters entering in Eq. (1) may be easily evaluated. For this purpose we follow the approach of Benson (1976) and assume that the reaction of dissociation for a molecule thermalised at temperature T has the form of the Arrhenius law. We estimate the frequency factor to be $k_0 = 10^{17}$ s^{-1}, taking the same value as that for similar reactions. To determine the activation energy E_0 we observe that the reverse reaction is a radical–radical recombination reaction which has no barrier energy. The activation energy of the dissociation reaction is therefore simply equal to the enthalpy of the dissociation reaction.

$$E_0 = \Delta H_{\rm r} = \Delta H_{\rm f}(\varphi\bullet) + \Delta H_{\rm f}(\equiv\bullet) - \Delta H_{\rm f}(\varphi-\equiv)\ , \quad (23)$$

where φ and $\equiv$ represent the phenyl and ethynyl groups, respectively. $\Delta H_{\rm f}$ corresponds to the energy of formation which can be deduced using the group additivity theory of Benson (1976), from which we obtain the value of 5.2 eV for the activation energy E_0. The vibrational modes of phenylacetylene have also to be evaluated in order to use the theory of thermo–photodissociation. They have fortunately already been calculated by Palmő *et al.* (1986), Pietilă *et al.* (1987) and Csàszàr *et al.* (1989) who have developed various force fields. We use the more recent results which are in better agreement with the observations of King & So (1970). Using all these data we compute the rate of photolysis of the φ — C_2H bond as a function of the internal energy of the molecule. The results are displayed in Fig. 9.

There is no data in the literature concerning vibrational states of larger PAHs bearing an ethynyl group. We therefore use the RRK theory for these molecules. In order to determine the parameters E_0 and k_0 entering in the expression (4) we first fit the curve provided by thermo–photodissociation calculations of phenylacetylene for the dependance of the rate with internal energy. As shown in Fig. 9 this is correctly achieved in the domain of interest for the pair of values:

$$E_0 = 3.3 \text{ eV}, \qquad k_0 = 1.4\, 10^{15} \text{ s}^{-1}. \tag{24}$$

We then assume that these values also give correct values for larger PAHs as has been observed by Jochims *et al.* (1994) for the loss of an acetylene molecule from compact PAHs. To compute the rate of dissociation in an astrophysical environment one has to integrate, over the energy, the yield corresponding to this process multiplied by the number of absorbed photons for a given energy (see Eq. (20)). Unfortunately, much of the data needed concerning PAH molecules having an acetylenic group is not available. For the calculations, we have therefore assumed that the rates for fluorescence, phosphorescence and ionization of PAHs bearing an acetylenic group are equal to that of the corresponding PAHs without side chains. The UV absorption cross–section and the IR Einstein coefficient of the PAHs with an acetylenic group have been evaluated from the data of the corresponding PAHs without side chain by scaling to the number of carbon atoms (for instance in the case of the cross–section of acetylcoronene we write $\sigma(C_{24}H_{12}\text{–}C_2H) \simeq 26/24\ \sigma(C_{24}H_{12})$). This may be the crudest approximation of the calculation and may introduce the largest errors, especially for the smallest molecules whose structures are markedly changed by the addition of an acetylenic group. We also assume that the photodissociation processes can be calculated with the RKK theory using the same constants E_0 and k_0 as for compact PAHs for the loss of hydrogen and acetylene from the compact part of the PAHs. To simplify the following discussion we will call internal acetylene such a molecule and refer to external acetylene when considering the loss of the attached acetylenic group. Figure 10 shows the results obtained for the loss of internal and external acetylene of PAHs having up to 50 carbon atoms, calculated for the radiation field of Gondhalekar *et al.* (1980).

The rates obtained for the loss of an external acetylenic group are relatively smaller than the rate corresponding to the loss of an internal acetylene molecule although the constants E_0 and k_0 are quite similar. This might be explained by the difference of the photodissociation reactions involved in the two processes. For the photolysis of the external acetylenic bond the vibrational energy has to be transfered to one bond of the molecule whereas the loss of an internal acetylenic group involves the vibrations of the carbon skeleton and may take place at various sites in the PAH. However, in both situations the evolution of the rate of photodissociation with the size of the PAH plotted in Fig. 10 shows no unexpected results and confirms the stability of larger PAHs against photodestruction.

4. Astrophysical implications

The results concerning the photoejection rate of an acetylene molecule provide an estimate of the characteristic time τ^{UV} of destruction of PAHs in interstellar regions where UV photodissociation is the most important cause of destruction. If we introduce the factor χ to describe a medium with a radiation field χ times larger than the mean interstellar field (for example a typical value for a planetary nebula is $\chi = 10^4$), we obtain for the destruction time:

$$\tau^{UV}{}_{PAH} = \frac{1}{\chi\ k^{ISM}{}^{C_2H_2}_{PAH}}, \tag{25}$$

where $k_{PAH}^{ISM\ C_2H_2}$ is the value for the loss of acetylene from a PAH in the ISM with $\chi = 1$. We list in Table 6 the corresponding destruction times for some small PAH molecules in the ISM.

The growth time of PAHs is given by:

$$\tau^{gr} = \frac{1}{n_{<H>}\ X(C)\ k_C}, \tag{26}$$

where $n_{<H>}$, $X(C)$ and k_C represent respectively the total hydrogen density, the carbon abundance and reaction rate for accretion of carbon particles (carbon atoms or cations). The PAHs whose growth time is smaller than the characteristic time of photodestruction tend to grow. The accretion of carbon dominate over acetylene molecule loss so that the PAHs resist the radiation field. In contrast, the PAHs having $\tau_{PAH}^{UV} < \tau^{gr}$ lose acetylene more rapidly than they accrete carbon and are therefore destroyed in a time of the order of τ_{PAH}^{UV}. The smallest size of surviving PAHs is obtained for equality of τ_{PAH}^{UV} and τ^{gr}. To have a more quantitative idea we have plotted in Fig. 11 the locations of this minimal size in the $\log(\chi)$, $\log(n_{<H>})$ plane. We have adopted the values of 3.10^{-4} for the carbon abundance and 10^{-12} s^{-1} for k_C from Omont (1986). Some modifications of the value of k_C could arise from the different nature of the accreting carbon particles. However, this would only slightly change Fig. 11. It is worth noting that the value of k_C we choose is also in

Table 6. Destruction times of small PAH molecules in the ISM ($\chi = 1$).

molecule	$k^{ISM}{}^{C_2H_2}_{PAH}$ (s^{-1})$^{(a)}$	$\tau^{UV}{}_{PAH}$ (years)
benzene	1.49 (−10)	213
anthracene	1.89 (−10)	168
pyrene	7.13 (−11)	442
coronene	4.55 (−11)$^{(b)}$	692
ovalene	4.85 (−12)$^{(b)}$	6.50 (3)
PAH 50 C	3.56 (−18)$^{(b)}$	8.91 (9)

(a) data using the radiation field of Gondhalekar *et al.* (1980),
(b) value not observed experimentally

Table 7. Physical properties of various astrophysical regions.

medium	Object	$n(\mathrm{cm}^{-3})$	χ
Planetary nebula	NGC 7027[(a)]	7 (4)[(b)]	4.6 (5)
$\mathrm{H_{II}}$ region	Orion Bar[(c)]	1 (5)[(d)]	4.3 (3)
Reflection Nebula	NGC 7023[(e)]	4 (3)[(f)]	2.5 (3)
Galactic nucleus	M82[(g)]	1 (4)[(h)]	2.9 (3)
Diffuse medium	Galactic plane[(i)]	6 (-1)[(j)]	1 (0)

References to the observations and physical conditions (a) Cohen *et al.* (1986), (b) Allamandola *et al.* (1989), (c) Bregman *et al.* (1989), (d) Tielens and Hollenbach (1985a, 1985b), (e) Sellgren *et al.* (1985), (f) Chokshi *et al.* (1988), (g) Willner *et al.* (1977), (h) Wolfire *et al.* (1988), (i) Giard *et al.* (1988) and (j) Allen (1973)

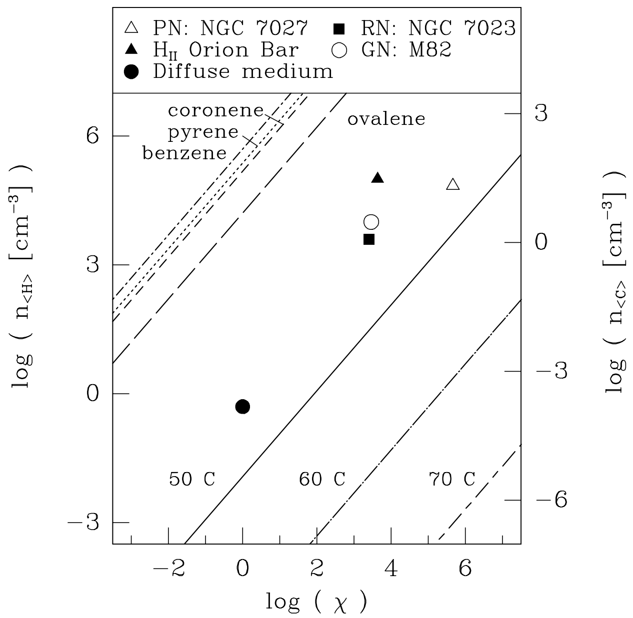

Fig. 11. Locations of the minimal size (number of carbon atoms) of PAHs in the plane $\log(\chi)$–$\log(n_{<\mathrm{H}>})$. The astrophysical environments mentioned are discussed in the text.

agreement with the rate of Frenklach & Feigelson (1989) for a PAH ring closure by addition of acetylene.

From Fig. 11 it is clear that for increasing values of χ and decreasing values of $n_{<\mathrm{H}>}$ the minimal size of surviving PAHs gradually increases. We have also plotted in Fig. 11 the positions of some media where the UIR emission bands attributed to PAHs have been observed. The physical parameters of these media are presented in Table 7 with references to the observations. We have restricted our choice to some regions already studied by Omont (1986) and by Allamandola *et al.* (1989). As already mentioned the coefficient χ is the scaling factor to be multiplied to the radiation field of Gondhalekar *et al.* (1980) to describe the various environments. Allamandola *et al.* (1989) and Omont (1986) have used another unit for the intensity of the incident radiation field, namely the average interstellar UV field of Habing (1968) integrated between 6 and 13.6 eV and an average interstellar UV field (10^7 photons $\mathrm{s^{-1}\ cm^{-3}\ sr^{-1}}$), respectively. The differences in the values of χ with that of these authors are therefore due to our choice of the UV interstellar radiation field. We have also included in Table 7 the diffuse medium where the band at 3.3 μm has been observed (Giard *et al.* 1988).

Figure 11 demonstrates that for all media showing the UIR bands the minimal size of surviving PAHs is between 40 and 50 carbon atoms. This result is slightly larger than the results of Jochims *et al.* (1994) who compared the rate of photodissociation obtained from RRK theory to the rates of IR radiation. They concluded that, after absorption of a photon of energy 13.6 eV, PAHs having more than 30 – 40 carbon atoms should undergo relaxation via IR emission rather than photodissociation and therefore are likely to subsist in the ISM. Our approach is different: we propose here values for the rate of photoejection of an acetylene group integrated over the photon energy available in the ISM and compare this rate with the rate of the reverse process of carbon addition. Our results demonstrate that under the conditions of the interstellar radiation field, PAHs containing less than 50 carbon atoms have energy integrated photodissociation rates larger than the carbon accretion rate and are therefore eventually destroyed by the UV radiation field. This is independent of the fact that, according to Jochims et al. (1994), the larger of these PAHs ($N_C = 30 - 50$) may have photodissociation rates lower than IR emission rates for some values of the internal energy. Another point to note is that the size of 50 carbon atoms is in very good agreement with the value obtained for the size of interstellar PAHs from the UIR intensity observations (Allamandola *et al.* (1989)).

For the calculations we have considered only fully hydrogenated molecules. However, it is thought that a large fraction of PAHs are ionized and partially dehydrogenated (Léger & d'Hendecourt 1985; van der Zwet & Allamandola 1985; Tielens *et al.* 1987; Allamandola *et al.* 1989; Geballe *et al.* 1989; Léger *et al.* 1989a,1989b; Verstraete *et al.* 1990). Cations are surely less stable against photodissociation than their parent molecules because they cannot lose energy through ionization as easily as the neutral PAHs. As has been shown by Leach (1986) one needs about 11 – 13 eV to ionize a PAH cation whereas the ionization potential of neutral PAHs is about 7 eV. It is also evident that dehydrogenated PAHs are less stable against photodissociation because of the lowering of the number of vibrational modes over which they can redistribute the energy and through which they can relax via IR emissions. The value of 50 carbon atoms we obtain for the smallest surviving

PAHs is therefore a lower limit and will have to be revised to account for the exact physical state of interstellar PAHs. There is unfortunately little knowledge concerning the physical and chemical properties of PAH cations and dehydrogenated PAHs and it makes their study difficult. A forthcoming paper will address this question.

One advantage of having integrated photodissociation rates is that they may be used in the conservation equation of PAHs and therefore may help to provide estimates of the density of PAHs in the ISM. These rates are crucial for small PAHs ($N_C < 50$) for which the interstellar UV radiations are a very effective cause of destruction. Only an intensive formation *in situ* may indeed make possible their presence in UV exposed regions. Unfortunately, the rates of formation of such processes are rather uncertain, partly because the processes are largely unknown. Most of the proposed mechanisms evoke PAH formation by sputtering of dust in shocked regions (Omont 1986; Duley and Williams 1986; Waters *et al.* 1989; Brown *et al.* 1989, Flower *et al.* 1990). Herbst (1991) has proposed a model for the formation of hydrocarbon molecules having 30 carbon atoms in dense region. Both types of proposal unfortunately suffer from large uncertainties and a lack of experimental data and therefore prevent us from making a definitive assessment. It is however questionable whether the molecules of ovalene and coronene often presented as prototypes of interstellar PAHs and all the smaller PAHs are present in the ISM. We have shown here that in all media showing the UIR bands these molecules are indeed destroyed on a timescale of some years (see Eq. (25) and the values of χ in Table 7). Due to the lower UV radiation field in the diffuse medium this timescale is larger there (about 10^3 years).

The case of large PAHs ($N_C > 50$) is different because they can survive the interstellar UV field in all situations. Their destruction may happen through oxidation reactions (Duley & Williams 1986) or strong shocks (Omont 1986; Flower *et al.* 1990). Latter (1991) has concluded that the lifetime of such PAHs is probably as large as 10^8 years, which is also the timescale for the galactic rotation and somewhat larger than the lifetime of a typical molecular cloud. He proposed that PAHs formed in the envelopes of C–giants are distributed in the ISM where the UIR are observed and showed that the yield of formation of PAHs calculated by Frenklach & Feigelson (1989) could explain the abundances of PAHs deduced from the observations. However, more recent calculations of Cherchneff *et al.* (1992) argue that the yield of formation calculated in more realistic envelope models is at best not as high as 10^{-4} times the yield of Frenklach & Feigelson (1989). This puts into question the results of Latter (1991). Nevertheless, recent calculations by Cherchneff & Tielens (1994) show that the formation yield of PAHs may be enhanced in the shocks of circumstellar red giants envelopes. Cadwell *et al.* (1994) show that this yield could also be enhanced following deposition of PAHs on grains. These new results are encouraging and show that further quantitative study into the formation and destruction of interstellar PAHs is required to make valid estimates of the density of PAHs in the ISM.

5. Conclusion

We have proposed a model for interstellar PAHs which includes the most recent knowledge about the behaviour of these molecules in space using both theoretical and experimental results. This model has enabled us to calculate the integrated rates of photodissociation corresponding to the loss of atomic and molecular hydrogen and of acetylene molecules.

Comparing the rate of photoejection of acetylene to the rate of accretion of carbon particles to PAHs we have deduced that in all the media showing the UIR emission bands only PAHs having more than 50 carbon atoms can survive the interstellar UV radiation field. In media exposed to strong UV radiation fields (reflection nebulae, planetary nebulae, galactic nuclei, H_{II} region) the time of destruction of PAHs as large as ovalene ($N_C = 32$) and smaller is not longer than a few years. As it is doubtful that any process could form PAHs more rapidly in these media we question the presence of small PAHs ($N_C <$ 50) where the UIR bands are seen. Moreover, as a large fraction of PAHs is ionized and probably partially dehydrogenated the actual rates of photodissociation may be even larger and may therefore lead to a larger minimal size for the surviving PAHs and a quicker destruction of small PAHs. On the contrary PAH molecules having more than 50 carbon atoms can survive the interstellar medium in all the media we have investigated. They may also possibly grow by accretion of carbon atoms or ions. However, it is at present impossible to estimate their density because there are too many uncertainties concerning their formation and destruction processes.

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