

The ionisation state of PAHs in interstellar environments

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Abstract. We present an ionisation model for Polycyclic Aromatic Hydrocarbon (PAH) molecules from which we determine the various size dependant ionisation states expected in different space environments. Maps of ionisation regimes are derived. They allow the estimate of the ionisation fraction of PAH for any given set of parameters (electron density, flux factor and temperature) assuming a typical PAH size of 50 carbon atoms. Moreover, a particular astronomical case is considered: the variation in ionisation states with depth in a typical dense cloud illuminated by a bright B1.5V star.

Key words: molecular data – molecular processes – ISM: molecules – ISM: general

1. Introduction

Stellar light absorbed by interstellar dust is mainly redistributed in two different ways. The first one (dominating) is reemission of energy in the thermal infrared. The second is the photoelectric mechanism that leads to the heating of the interstellar gas. Heated interstellar matter gives also rise to bands observed in the infrared in a great variety of objects (reflection nebulae, planetary nebulae, active galaxies...), always at the same wavelengths (3.28, 6.2, 7.7, 8.6, 11.3, 12.7 μm) (Willner 1984). In the mid eighties, it was proposed that carbonaceous aromatic species could be responsible for these so-called 'Unidentified Infrared Bands' (Leger & Puget 1984, Allamandola, Tielens and Barker 1985). These molecules could account for 10-20% of interstellar carbon, ranking them as the third molecular species in abundance after H_2O and CO molecules.

The Diffuse Interstellar Bands (DIBs) are features extending from the near infrared (11560 cm^{-1}) to the visible (23952 cm^{-1}). The number of bands detected has risen rapidly, from 39 to 80 proposed by Herbig respectively in 1975 and 1988 to 64 more plus 69 possible by Jenniskens & Désert (1994). Their spectral positions suggest that the transitions involved are electronic transitions but their widths (0.3 Å to 37 Å) exclude atomic transitions or transitions in radicals like CH.

The suggestion that follows these two different parts of the interstellar spectrum is the proposition that the PAH cations/radicals are among the best candidates for the DIBs identification (Leger & d'Hendecourt 1985, Allamandola et al. 1985, Crawford et al. 1985). This comes from the consistency of the PAH model because:

- PAHs are abundant in the Interstellar Medium (ISM), as it is shown by infrared spectroscopy (Leger 1995).
- When ionised, the PAHs present strong visible transitions that could account for the DIBs (and we expect to find conditions in the ISM where they are ionised).
- The largest of them can survive UV irradiation (Allain et al. 1996).
- The DIBs have recently been shown to exhibit rotational structure (Sarre et al. 1995, Ehrenfreund & Foing 1996), consistent with large molecular species.

Various ionisation models for PAHs have been developed since the last decade (Omont 1986, d'Hendecourt and Leger 1987, Verstraete et al. 1990, Bakes and Tielens 1996, Salama et al. 1996). We present here further investigations in these ionisation model to determine whether PAHs are positively, negatively charged or neutral in various environments. This could explain the variations in intensities seen in many lines of sight which have led to the search for the correlation of the DIBs and to constrain the possible families among them.

The model presented here takes into account recent absorption cross-section for PAHs, determined in laboratory by Joblin (1992), and a size dependent sticking coefficient. The latter was, up to now, generally assumed to be unity (Bakes & Tielens 1994) for PAHs except for those (few) measured in laboratory (Salama et al. 1996). The introduction of this parameter allows us to find size dependent recombination rates that are in good agreement with the experiments. We find, for example, a recombination rate of $4.10^{-7}\text{ cm}^{-3}\text{ s}^{-1}$ for a PAH^+ with 15 carbon atoms and a kinetic temperature of 10 K for the gas. Experiments of Abouelaziz et al. (1993) have derived a recombination rate of $1.10^{-6}\text{ cm}^{-3}\text{ s}^{-1}$ for C_6H_6^+ and $3.10^{-7}\text{ cm}^{-3}\text{ s}^{-1}$ for $\text{C}_{10}\text{H}_8^+$. We then use recombination rates for PAHs that are considerably lower for PAHs with $N_C < 25$ than those used in precedent models.

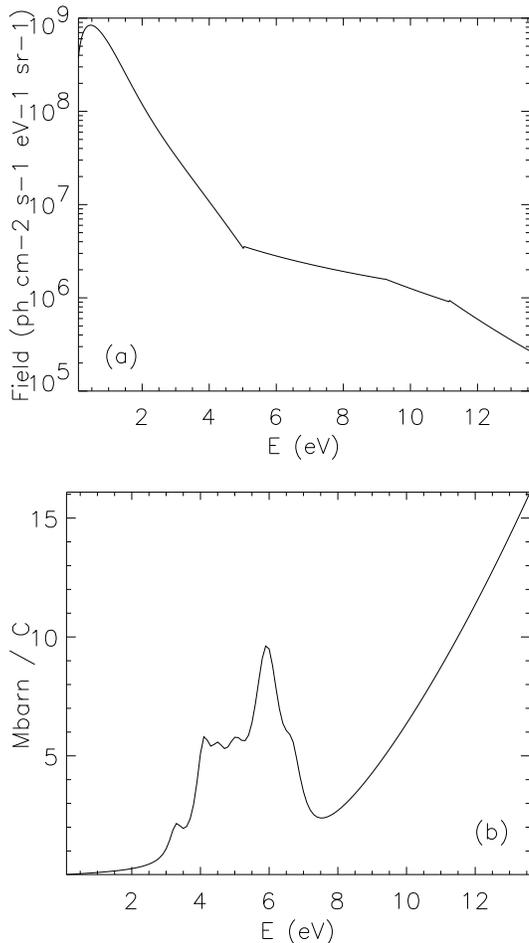


Fig. 1. **a** Interstellar radiation field used in our calculations. **b** Absorption cross-section in MegaBarn per carbon atom ($=10^{-24} \text{cm}^2/\text{C}$) for a PAH mixture as a function of energy.

2. The model

The goal of such an ionisation study is to discuss the PAH model on a large wavelength range (infrared to visible). PAHs are observed in UV excited regions through their IR emission. In other environments, such as in diffuse cloud medium, these molecules should exhibit other transitions (absorption) in the UV-visible, associated with their ionisation state. Hence, the model presented here is important in order to obtain a better knowledge on the ionisation state of PAHs of various sizes in different ISM environments.

The model, based on the Draine & Sutin (1987) formalism, and on the study of Bakes & Tielens (1994) is established at equilibrium, i.e. in conditions where the ionisation rate equals the recombination rate. We first briefly discuss the photoionisation, then recombination and equilibrium. We then apply the model to different media, define the ionisation regimes and finally we discuss the particular case of a dense cloud illuminated by a bright star.

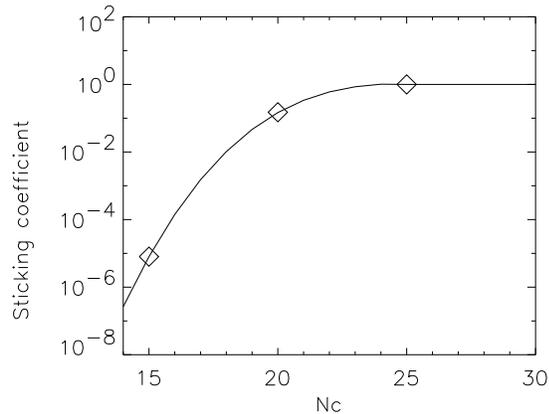


Fig. 2. Electron sticking coefficient as a function of carbon atoms (N_c) in the PAH molecule.

Table 1. Physical properties of the characteristic environments in the ISM (see Fig. 3).

Environment	figure	N_{e-} (cm^{-3})	F	T (K)
Dense H_2 UV	3a	20	1(3)	3(2)
Dense molecular core	3b	1(-2)	1(-5)	1(1)
Diffuse Warm medium	3c	1(-5)	1	1(4)
Diffuse medium	3d	7.5(-2)	1	1(2)
Reflection nebula	3e	1(-1)	1(3)	1(3)
Dense molecular cloud	3f	1(-3)	1(-2)	2(1)

2.1. Photoionisation of PAHs

The photoionisation rate of PAHs is given by (d'Hendecourt and Leger 1987, Bakes and Tielens 1994):

$$\tau_{ph}(Z) = N_c \times F \int_{IP(Z, N_c)}^{13.6eV} 4\pi\Phi(E)\sigma_{ph}(E, Z)dE \quad (1)$$

where $IP(Z, N_c)$ is the ionisation potential of a PAH of charge Z with N_c carbon atoms, $\Phi(E)$ is the photon flux distribution after Mathis et al. (1988), (Fig. 1a), and $\sigma_{ph}(E, Z)$ is the photoionisation cross-section of the molecule in the Z charge state at energy E per carbon atom. F is a flux factor with which one can modulate the interstellar flux intensity.

The ionisation potential $IP(Z, N_c)$ of a PAH is given by (Smith 1961, Bakes and Tielens 1994, Moskovitz 1991, Makov et al. 1988). $\sigma_{ph}(E, Z, N_c)$ is the product of the absorption cross-section $\sigma_a(E)$ and the photoelectric yield $\eta(E, Z, N_c)$. In this model the experimental measurements found in Joblin (1992) are taken into account (Fig. 1b). $\eta(E, Z, N_c)$ comes from Draine (1978, Eq. (1) and (2)) using a typical value for l_a of 100 Å and 10 Å for l_e .

Hereafter, we assume a disk shape for the molecule.

2.2. Recombination of PAHs

The recombination rate which balances the ionisation in this model is given by Draine & Sutin (1987, Eq. (3.1)). Since we use the spherical interaction potential, we must apply a correction

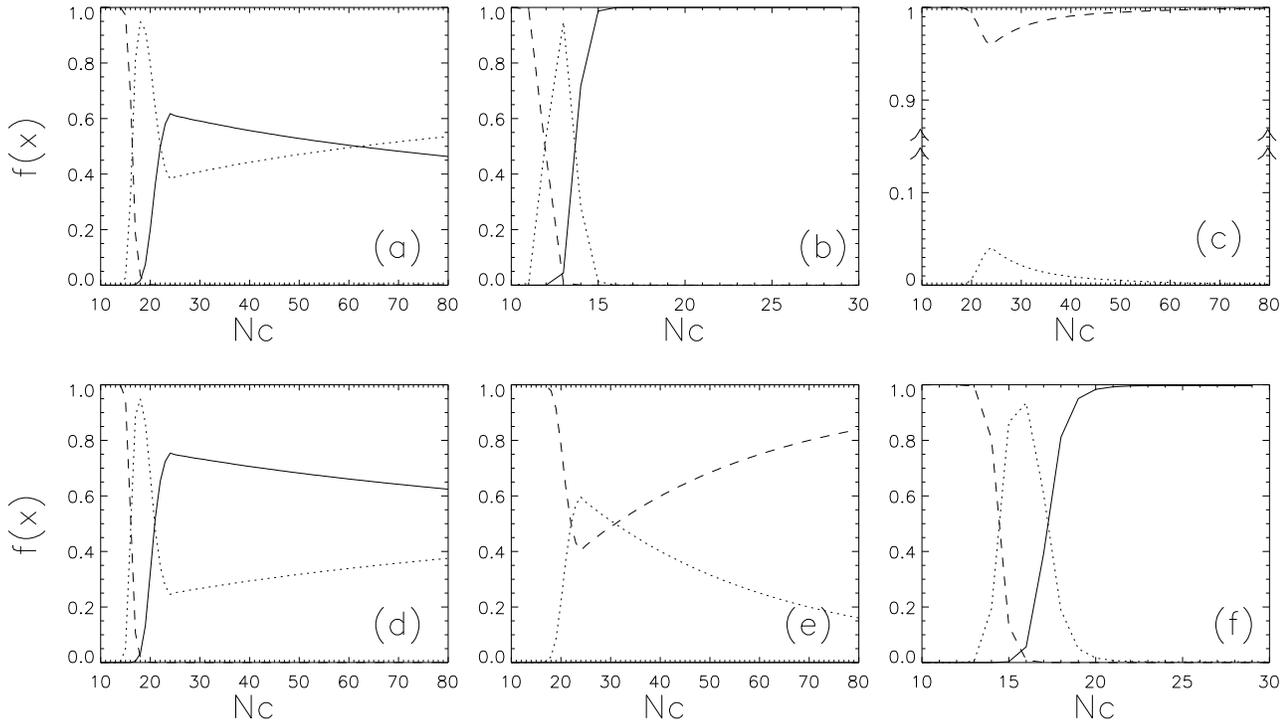


Fig. 3a–f. Ionisation fraction of anions (solid line), neutrals (dotted line) and cations (dashed line) in various environments: **a** Dense H₂ UV rich medium **b** Dense molecular core **c** Diffuse Warm medium **d** Diffuse medium **e** Reflection nebula **f** Dense molecular cloud. See text for further explanation.

on the absorption cross section for the disk shape, $Y_C = \frac{\sigma_{disk}}{\sigma_{sphere}}$. Verstraete et al. (1990) showed that Y_C versus the energy of the recombining electron was ≈ 0.8 in the energy range we are dealing with (from $\approx 10^{-2}$ eV for the diffuse medium at 80 K to ≈ 1 eV for the warm medium at 8000K). The electron sticking coefficients taken are those of Tielens (1993). They were derived on the basis of Christophorou et al. (1994) experiments and estimates of the PAH electron affinities. A curve was fitted on the behaviour shown in the resultant calculation, shown in Fig. 2., as a function of the number of carbon atoms.

Taking into account the evolution of the sticking coefficient, we reproduce the behaviour of PAHs experimental recombination rates measured by Abouelaziz et al. (1993) for any compact PAH containing N_C carbon atoms.

In particular it prevents the recombination rate from getting too high as this is often criticized in the models and fulfill the requirements of the model: producing a general trend for compact PAHs. Furthermore we chose to concentrate on compact PAHs for at least three reasons:

- Although pentacene has a high electron affinity (like all the catacondensed species, the polarisability varying as N_C^3 as opposed to $N_C^{3/2}$ for compact PAHs (Davies 1952, Omont 1986)) implying a behaviour concerning the sticking coefficient of almost the one of a 100C atoms PAH, the use of a spherical interaction potential for such an elongated species to derive the ionisation states in Salama et al. (1996) seems less appropriate.
- The catacondensed species are much less stable than the com-

pact one (Birks 1970).

- Models on the growth of PAHs does not favour specifically elongated species (Frenklach and Feigelson 1989).

2.3. Ionisation equilibrium

τ_{ion} and τ_{rec} established, it appears then possible to calculate the equilibrium charge of the PAHs. If we consider the molecules of charge Z , the ionisation equilibrium is governed by (Draine and Sutin 1987):

$$f(Z)\tau_{ph}(Z) = f(Z+1)\tau_{rec}(Z+1), \quad (2)$$

where $f(Z)$ is the probability of finding a PAH in the charge state Z .

Using this equation iteratively one obtains $f(Z > 0)$, $f(Z < 0)$ as a function of $f(0)$ which is given by the normalisation condition:

$$\sum_{-\infty}^{+\infty} f(Z) = 1. \quad (3)$$

The molecules cannot reach infinite charge. The maximum (Z_{max}) and minimum (Z_{min}) charges are given by:

$$IP(Z_{max}, N_C) = 13.6\text{eV} = 4.4 + \frac{(Z_{max}+1/2) \times e^2}{C} \quad (4)$$

Actually, if the n^{th} ionisation potential of the PAH exceeds the hydrogen threshold, there is no way for the molecule to get to

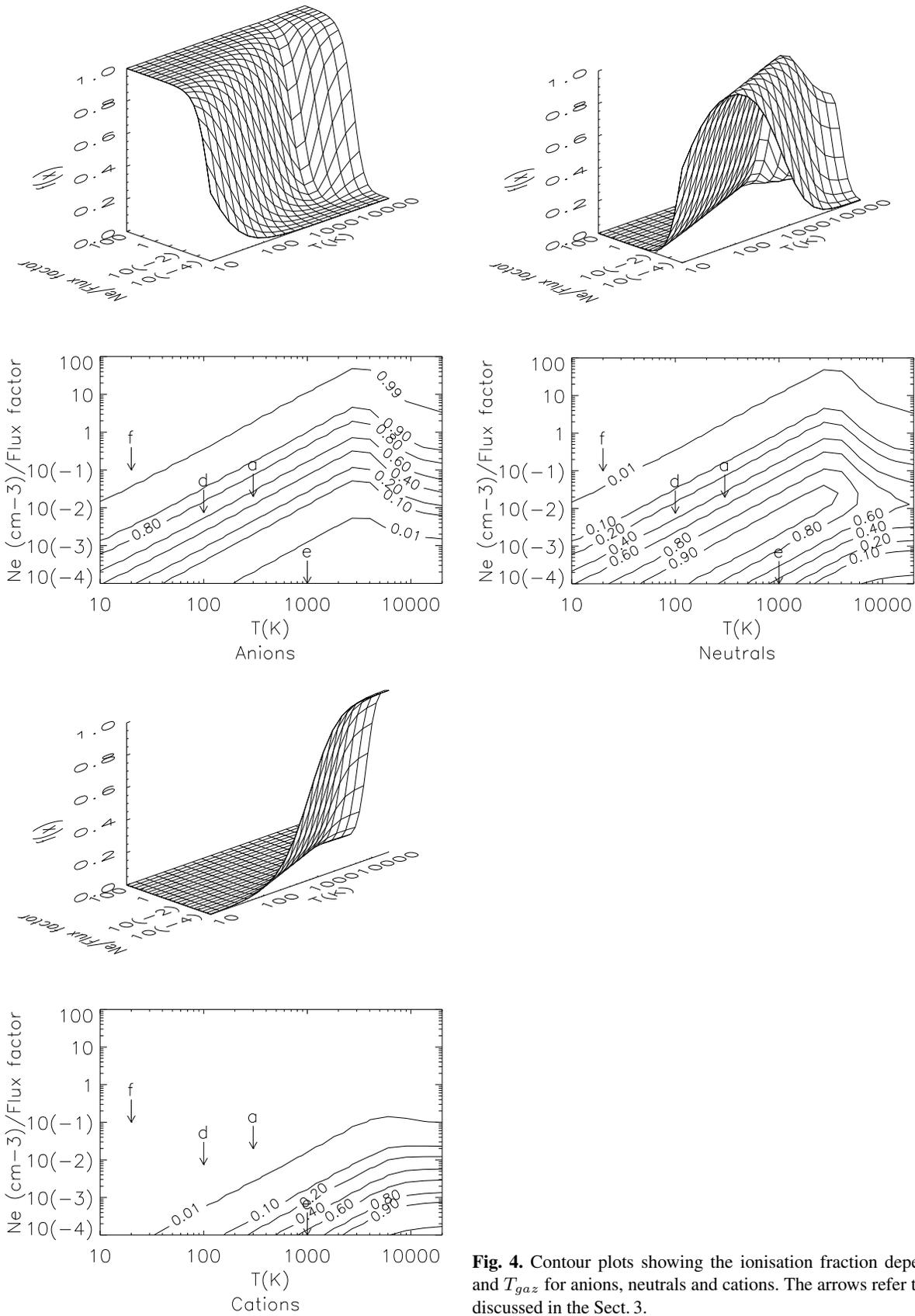


Fig. 4. Contour plots showing the ionisation fraction dependence with N_e/F and T_{gaz} for anions, neutrals and cations. The arrows refer to different regimes discussed in the Sect. 3.

another state (except by cosmic radiation) because the flux is cut at these energies.

$$IP(Z_{min}, N_c) = 0eV = 4.4 + \frac{(Z_{min}+1/2) \times e^2}{C}. \quad (5)$$

If $IP(Z, N_c)$ goes lower than zero, the PAH will “autoionise” quickly, thus returning to the initial upper state (each electron colliding with the PAH spontaneously detaching itself).

3. Ionisation in various environments

Application of the model to different environments gives rise to various ionisation states shown in the Figs. 3a to 3f. The values of N_{e-} , T and F taken to describe the environment are those given in Verstraete et al. (1990). In these figures we can see the importance of the sticking coefficient that rules the ionisation states of the smallest PAHs and the steep variations one sees in the $N_c \leq 25$ range are due to the fall of the sticking coefficient with decreasing N_c . Indeed, the decrease in density of states of the molecule with N_c imply a lowering in the radiative decay rate for the excited PAH^{-*} intermediate product after the electron capture. The re-ejection of the electron is thus favoured as the decay is responsible for the anion stabilisation.

The diffuse interstellar medium shows negatively charged and neutral species for large species with a fractionation in favour of negative PAHs, but which decreases with size. If we place the interstellar PAHs in the 60 carbon atoms range we then expect to have $f(anion) \approx 0.65$ and $f(neutral) \approx 0.35$ in agreement with the work of Salama et al. (1996).

Concerning reflection nebulae, it is clear that the dominant species is the positively ionised form if we only look at large species that can survive this environment. This is clearly explained by the UV flux density.

This does not however imply that in HII regions (with an high UV flux density) the PAHs should be in the cation form as in such medium the gas is ionised and the electron density is much higher than 3.10^{-4} .

There is not much to discuss about the diffuse warm medium which, in the model, is completely ionised and could contribute highly to the destruction of PAHs via the photodissociation process. Furthermore, no molecules are seen in this hot environment.

In the case of the outer part of a molecular cloud the dense part is negatively ionised but to a greater extent. We come back to this case in the next section.

For the dense H₂-UV medium we see a trend that is not too far from the one of the diffuse medium, this will be discussed later. As was already inferred for the diffuse medium in Salama et al. (1996) and omitted in previous works, the evolution of the sticking coefficient with PAH size rules their size dependant ionisation state. This is clearly shown here for typical interstellar environments. This have certainly not a great influence in media where small PAHs are destroyed (the evolution for large PAH being quite smooth) but is important to consider in other media (UV protected or low energy spectral distribution).

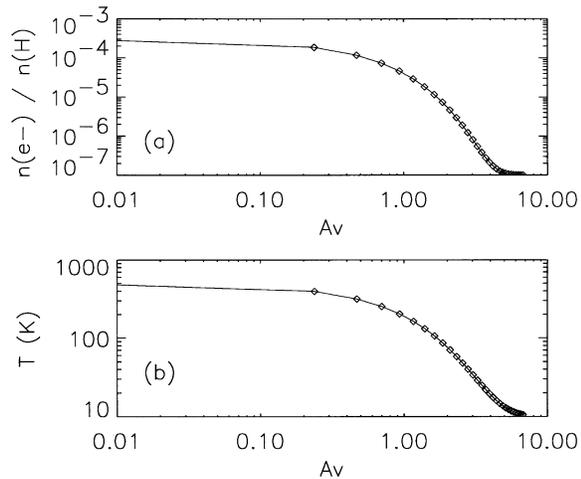


Fig. 5a and b. Variation of **a** N_{e-}/N_H and **b** of the gas kinetic temperature with the penetration in the cloud, as a function of A_V .

4. Ionisation regimes

The next step, with such a model, is to generate charts that give us directly the information on the ionisation state in any environment. The important parameters to be varied are the N_{e-}/F ratio and the kinetic temperature T . The Fig. 4 show the ionisation fractionation for a 50 carbon atom PAH toward these parameters. The number of carbon atoms was chosen after the determination made by Geballe et al. (1994) of the average size of interstellar PAHs using the intensity ratio of the $3.3\mu\text{m}$ feature and its overtone at $1.68\mu\text{m}$. On these plots, the arrows indicate the status of four of the six media we discussed in the previous section. Two are missing because for the dense molecular core, $N_{e-}/F = 10^3$ and for the Diffuse warm medium, $N_{e-}/F = 10^{-4}$. Two kinds of environments are fully positively ionised: the diffuse warm medium and the reflection nebulae. On the other hand the diffuse medium and dense H₂-UV medium display neutral and negative ionisation states. This could be interesting to discuss because some diffuse interstellar bands could arise from negatively ionised PAHs. Indeed, they produce similar spectra to the positively ionised PAHs (Salama et al. 1996), but slightly shifted towards the red. The trend of the ionisation is, however, to produce more neutrals as the number of carbon atoms in the PAH increases. In regard to the dense cloud and outer part of a molecular cloud, it is seen that the *majority of the PAHs are in the negative form*.

These charts should not however be applied to HII regions where the hardness of the incident spectral incident energy distribution would not be taken into account.

5. An example: ionisation in a dense cloud

In this section, we apply our model to a practical case such as the behaviour of the ionisation states when one penetrates a dense cloud illuminated by a bright star.

We thus choose to take a star like HD 37903 in NGC2023 i.e. a spectral type B1.5V star with a radius of $\approx 3.510^{11}\text{cm}$ and

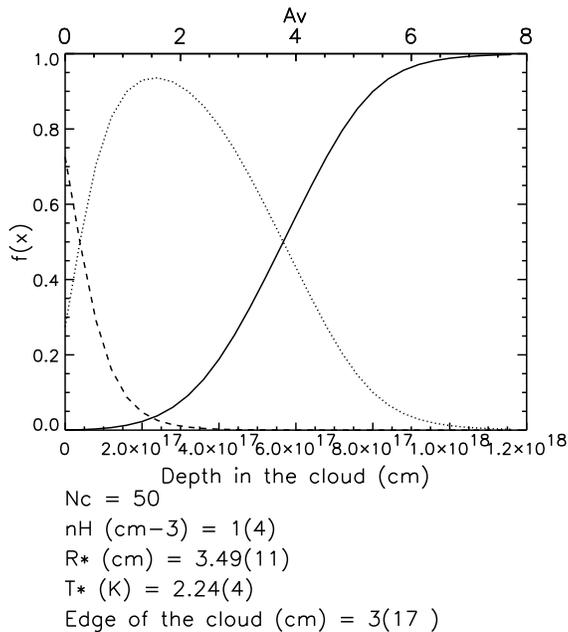


Fig. 6. Ionisation fraction for a 50 carbon atoms PAH as a function of the penetration in a cloud of density $N_H = 10^4 \text{ cm}^{-3}$ located at 3.10^{17} cm (≈ 0.1 parsec) of a B1.5V star. The front of the cloud shows a cation enhancement (dashed line) followed by the neutral maximum (dotted line) and the anions in the well shielded part of the cloud (solid line). The negative charge of the cloud will be almost entirely on PAHs if we assume 10% of the interstellar carbon in such molecules.

we place a cloud at 310^{17} cm from the star. The mean size of the PAH is assumed to be $N_c = 50$. The density of the cloud, taken as constant is $N_H = 10^4 \text{ cm}^{-3}$. We also choose to put in this modelisation the variation of N_{e^-}/N_H with the penetration in the cloud (Fig. 5a). Therefore we decided to take, for the internal part of the cloud ($A_V > 3$), an ionisation due entirely to cosmic ionisation at a level of $N_{e^-}/N_H = 10^{-7}$. On the outer part of the cloud we used a fractionation due to carbon ionisation so $N_{e^-}/N_H = 310^{-4}$ and the transition zone is an exponential attenuation with A_V of the edge electron fraction, explained by the flux decrease. Furthermore, we took, for the kinetic temperature behaviour, the variation with A_V from the model of Le Bourlot et al. (1990), Fig. 5b. The first result obtained is the delimitation of ionisation areas that shows the PAH ionisation spatial structure in the cloud (Fig. 6). The main difference introduced with the case treated by Salama et al. (1996) in a *diffuse cloud* is that clearly we delimitate zones where the charge states are concentrated. We also answer to the question of the balance between the attenuation of the flux when penetrating in the cloud (which increase the anion fraction) and the diminution of the electron density (which favours the cations). If we assume that the PAH abundance is around 10% of the interstellar carbon, it can be seen that as we go further into the cloud, more and more PAHs become negative, to such an extent that a large part of the cloud's negative charge could be in these molecules. This can have a great influence on the cloud chemistry as was already pointed out by Lepp & Dalgarno (1988).

The $PAHs^-$ could react more easily with their environment and offer new reaction schemes for molecular formation, including PAH derivatives (organometallics, PAH Oxides) and induce molecular formation through attachment to them.

6. Conclusion

We have reconsidered the ionisation state of compact PAHs in various environments and produced easily usable ionisation regimes maps. The main consequences of this study are the following:

(i) PAHs are positively charged in regions of high UV excitation such as reflection nebulae.

(ii) PAHs are mostly neutral and/or negatively charged in the Diffuse Interstellar medium depending on the average size assumed.

Consequently, variations in the UIR features arising from reflection nebulae should be expected when better spatial resolution observations become available, such as evidenced by Joblin et al. (1996). ISO will certainly provide tests for this prediction by comparison with anion, neutral and cation IR experimental (Moutou et al, 1996) and theoretical (Langhoff 1996, Pawzat et al. 1997) spectra behaviour. For the DIBs, if due to such species, they could arise from anions, the spectroscopy of which should be measured in laboratory to provide further investigation in this complex problem. They would produce spectra similar to the cations, shifted towards the red. The PAHs are mainly neutral and/or negatively charged in the Diffuse medium.

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