

Photo-thermo-dissociation

I. A general mechanism for destroying molecules

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Summary. We call photo-thermo-dissociation (PTD) of an isolated molecule, the process when a photon is absorbed by an electronic transition, the energy is transferred to the vibrations (hot molecule) and then an atom or a fragment is ejected. We present a statistical physics treatment that goes beyond the thermal approximation and fully takes into account the isolation of the system. A model is given that permits an explicit calculation of the ejection rates of hydrogen and carbon fragments from aromatic molecules as a function of their size and internal energy. Then, the lifetime of species against PTD in different astronomical radiation fields will result when a precise dynamical evolution of their internal energy can be established.

Key words: interstellar medium: molecules – interstellar medium: reflection nebulae – atomic and molecular processes – atomic and molecular data

1. Introduction

Direct photo-dissociation (PD) of a molecule occurs when the absorption of a photon induces a transition from a binding to a repulsive electronic state. This process is efficient for breaking molecules but relies on the existence of suitable potential curves (see, for instance, Duley and Williams, 1984). We call photo-thermo-dissociation (PTD) of an isolated molecule or a cluster of atoms the process in which a photon is absorbed by an electronic transition, the energy is transferred to nuclear vibrations (hot molecule) by internal conversion and then an atom or a molecular fragment is ejected after some time. This mechanism is quite general for highly isolated species and the physical conditions in space are favorable for it because species are much more isolated than under laboratory conditions and it can take a long time (~ 3 s) for a molecule to cool down after the absorption of a photon (Léger and d'Hendecourt, 1987). Clearly direct PD and PTD can coexist in the interstellar medium and are cumulative.

The importance of PTD was first pointed out in the astrophysical field by Léger and Puget (1984, LP thereafter). They showed that very small grains undergoing impulsive heatings (Sellgren, 1984) could not survive if they were made of silicates

but could stand if made of graphitic material. A further study led them to propose that these species were large polycyclic aromatic hydrocarbon (PAH) molecules. A most striking consequence of this PAH hypothesis is the suggestive fit between the expected IR emission spectrum of these molecules and the formerly called “unidentified” IR emission features observed in the interstellar medium. It has also *predicted* (Puget et al., 1985) that : (i) the IRAS cirrus clouds should emit in the 12 μ m band, (ii) the diffuse IR emission of the Galaxy should contain the aromatic 3.3 μ m feature. Both predictions have been verified (Boulanger et al., 1985; Giard et al., 1988). Puget et al. (1985) and Omont (1986) have determined an approximative minimum size of PAH molecules under PTD.

The aim of the present paper is to make a more precise study of PTD using a statistical treatment of the molecule that takes into account the isolation of the system in the interstellar medium instead of a thermal approximation that assumes a coupling with a thermostat.

2. Evolution of a molecule after the absorption of a UV photon

2.1. Absorption and redistribution of the energy

Isolated molecules can be described by the step ladder model (Bixon and Jortner, 1968) that specifies the electronic and vibrational states of the system. Figure 1 represents the case of an ion which is relevant for PAH molecules because these species are expected to be ionized in the astronomical environments where they are presently well observed (Allamandola et al., 1985; Omont, 1986; d'Hendecourt and Léger, 1987, Table 1). The electronic states can be doublets¹ ($D_0, D_1, D_2 \dots$) (Leach, 1987) and the vibrational states are characterized by the different modes which are excited.

For a large molecule, the vibrational density of states (ρ) is a steeply increasing function of the vibrational energy (U), it corresponds to the number of ways of distributing this energy between the different modes of the molecule.

The processes following the absorption of a UV photon are also reported in Fig. 1. They have been described in the literature (Birks, 1970; Bixon and Jortner, 1968; Avouris et al., 1977;

¹ This is the case for fully hydrogenated species but partially hydrogenated ones (radicals) can have higher multiplicity.

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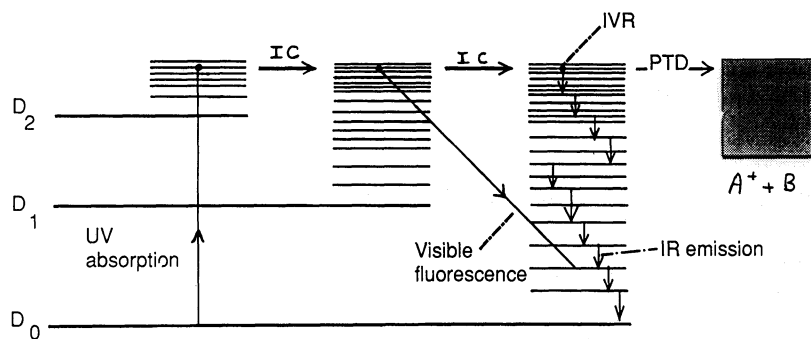


Fig. 1. Step ladder model of a large ion (AB)⁺. The energy levels of the system are represented that involve an electronic part (doublets $D_0, D_1, D_2 \dots$) and a vibrational part. The spacing between vibrational levels reduces as vibrational energy increases. The present diagram is schematic and the density of states rapidly becomes huge. The different abbreviations correspond to processes which are described in the text and are: IC = internal conversion, IVR = internal vibrational redistribution, PTD = photo-thermo-dissociation, the latter leading to a fragmentation ($A^+ + B$) with a continuous density of states. The transitions with energy change correspond to photon absorption or emission, the horizontal ones are internal to the molecule and non radiative. Electronic state with other multiplicities (quartets . . .) are not represented for reasons explained in the text

Tramer and Voltz, 1979) including recent developments (Léger et al., 1988) and are only briefly summarized with an indication of their characteristic times. The UV absorption transition (D_0, U_0) to (D_n, U_n) and the other transitions are followed by rapid internal vibrational redistribution ($10^{-12} - 10^{-10}$ s) which allows the use of statistical physics (Oref and Rabinovitch, 1979; Parmenter, 1982). From (D_n, U_n) the molecular ion undergoes fluorescence transitions ($\approx 10^{-7}$ s) or internal conversion (IC) ($\approx 10^{-12} - 10^{-8}$ s) to lower electronic states (D_p, U_p) until it arrives at the ground electronic state D_0 with a high vibrational energy. We have omitted the electronic levels with different multiplicity (quartets, . . .) for the sake of simplicity and because they do not have a conceptually essential rôle in ions (see Leach, 1987). So, after typically 10^{-8} s, the molecule spends most of its time in a hot electronic ground state (D_0) which corresponds to the solid state physics description of a very small gain heated by the absorption of a UV photon.

2.2. Channels for energy decay

For an isolated hot ion, the routes for energy decay are: IR emission, visual fluorescence and dissociation. The first process can be called IR fluorescence as it follows a UV absorption.

Because the internal vibrational redistribution in middle size and large molecules is effective in time (10^{-10} s) several orders of magnitude shorter than the energy decay (Oref and Rabinovitch, 1979; Parmenter, 1982), a statistical description of the system is adequate during its cooling. The ion is in an internal thermodynamical equilibrium (ITE) although it is not in local thermodynamical equilibrium (LTE) with the interstellar gas because of too weak external interactions (collisions and radiation).

How large a molecule must be for the preceding assertion to stand? The criterion is whether the density of states ρ is high enough (say 10^3 states per cm^{-1}) to allow efficient internal conversion and internal vibrational redistribution. Studies show that H_2O at internal energy $U = 11,000 \text{ cm}^{-1}$ (0.9 eV) does not fulfil the criterion and can have cyclic evolution whereas C_6H_6 at $U \sim 18,000 \text{ cm}^{-1}$ (1.5 eV) clearly does (Stannard and Gelbart, 1981). The limit is probably lower than 5 atoms for energies of several eV as we are concerned.

We do not discuss the possibility for the system to be locked in a metastable excited electronic state as it had been proposed

by Allamandola et al. (1985). For closed shell ions, this is not relevant because the first excited state has generally the same spin state (doublet) as the fundamental (Leach, 1987) and no such metastable states exist.

The cooling rate by IR emission can be evaluated as a function of the emissivity of the molecule. It is quite slow: $k_{\text{IR}} \sim 0.3 \text{ s}^{-1}$ at $T \approx 1000 \text{ K}$ (Léger and d'Hendecourt, 1987). The existence of another energy decay channel has recently been pointed out for isolated systems: the Poincaré fluorescence (Léger et al., 1988). In addition to the initial possibility of visual fluorescence, this recurrent fluorescence can give a decay several orders of magnitude faster than IR emission. Because this fluorescence depends strongly upon the molecule size and the position of its first electronically excited state (ΔE), the determination of the actual dynamical evolution of the internal energy of a molecule has not yet been done.

2.3. Photo-thermo-dissociation (PTD)

At each step of the cooling process, the vibrational energy is redistributed among the different modes of the system and the hot ion can eject an atom or a fragment. LP (1984) have used a thermal approximation to study this dissociation but a more accurate approach can be developed by using the theory of unimolecular processes (Robinson and Hollbrooks, 1972; Forst, 1973) and is performed thereafter.

3. Statistical physics of an isolated molecule

LP estimated the rate of carbon ejection from a graphitic cluster by calculating the temperature reached by the system after the UV absorption and using the rate of ejection from bulk graphite at this temperature. The main weakness of such an approach is to consider an isolated system (microcanonical) with fixed energy U_0 as a system in contact with a thermostat (canonical) with fixed temperature T . It is instructive to point out the limits of validity of this approximation.

3.1. Microcanonical treatment

For an isolated system, all the statistical information is contained in the density of states function $\rho(U)$ giving the number of

accessible levels per unit of energy. If the molecule is described as a set of (s) harmonic oscillators ($h\nu_i$) (see Sect. 4.1), the vibrational density of states can be calculated by counts or approximated by the semi-empirical expression (Whitten and Rabinovitch, 1963; Forst, 1973):

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

where E_z is the sum of the oscillator zero point energies, $E_z = \sum_{i=1}^s (1/2) h\nu_i$; and a is an empirical correction factor ($0 < a < 1$) whose expression is given in Appendix A1. The limiting cases $a=0$ and $a=1$ are referred to as the classical and semi-classical approximations.

This density of states is shown in Fig. 2 for a set of vibrational modes representative of an interstellar PAH (dehydrogenated coronene, see Sect. 4.1).

When statistical redistribution is achieved, in a molecule with a total energy U_0 , the probability that a given mode contains an energy B , is proportional to $\rho^*(U_0 - B)$, the density of states for the system, but the considered mode, taken at the remaining energy $U_0 - B$. The ratio of the probability that this mode is found with energy B to the probability to find it in its ground state is then:

$$p_{\text{micro}}(B) = \rho^*(U_0 - B) / \rho^*(U_0), \quad (2)$$

this results simply from the ergodic assumption.

It must be noticed that the number of modes s being large, the curve $\rho^*(U)$ is very similar to $\rho(U)$. Owing to the logarithmic scale of Fig. 2, the logarithm of the probability ratio p_{micro} appears as the difference in ordinates between points M and N . This will make very clear the limit of validity of the thermal approximation.

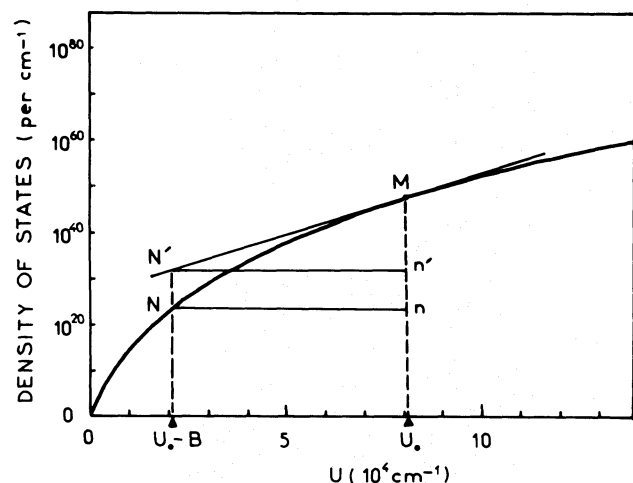


Fig. 2. Density of vibrational states for a typical PAH ion. The set of modes used is the n_2 column of Table 1 (dehydrogenated coronene). Mn and Mn' are graphic representations of the logarithm of the ratios of the probabilities that a given mode is found at an energy level $B = 7$ eV to the probabilities to find it in its ground state for the microcanonical and canonical systems respectively with total energy $U_0 = 10$ eV

3.2. Thermal (canonical) approximation

We call thermal (or canonical) approximation for an isolated system (0) the use of the associated canonical system (2) which has the same physical components but is connected to a thermostat at temperature T such that

$$\langle U_2(T) \rangle = U_0, \quad (3)$$

where U_2 and U_0 are the internal vibrational energies of systems (2) and (0), respectively. The average is taken over the time because for a canonical system the temperature is fixed but the internal energy fluctuates².

In the rest of the paper when we write the "temperature" of an isolated system, we mean "the temperature of the associated canonical system".

An important result of statistical physics is that this temperature is given by

$$(k_B T)^{-1} = \partial / \partial U [\ln(\rho(U))]. \quad (4)$$

The probability ratio $p_{\text{therm}}(B)$, corresponding to $p_{\text{micro}}(B)$ is given by the Boltzmann factor:

$$p_{\text{therm}}(B) = e^{-B/k_B T}. \quad (5)$$

This ratio appears in Fig. 1 simply as the ordinate difference between points M and N' taken on the tangent to the curve. The approximation made is clear: the thermal model will give the correct answer if the curve $\ln(\rho(U))$ has not deviated too much from its tangent at the energy $U_0 - B$. In other words, as long as the energy B which is localized in the considered mode remains small compared to U_0 , the remaining modes of the molecule acts as a reservoir at temperature T .

3.3. Validity of the thermal approximation

A quantitative criterion for the validity of the approximation is given by a second order development taking into account the curvature of $\ln[\rho(U)]$:

$$\ln p_{\text{micro}}(B) \simeq -\frac{B}{kT} \left[1 + \frac{B}{2C^*T} \right],$$

where C^* is the specific heat of the molecule (without the mode) at temperature T .

For many practical purposes (IR emission for instance), it is better to compare the total probability $P_{\text{micro}}(B)$ and $P_{\text{therm}}(B)$ to find an energy B in a given mode rather than the probability ratios $p_{\text{micro}}(B)$ and $p_{\text{therm}}(B)$ defined above.

For the microcanonical system, in the denominator of Eq. (2), $\rho^*(U_0)$ is replaced by $\rho(U_0)$, the total number of accessible states:

$$P_{\text{micro}}(B) = \rho^*(U - B) / \rho(U). \quad (6)$$

For canonical systems, this probability is obtained by a normalization to z_0 , the partition function of the mode:

$$P_{\text{therm}}(B) = z_0^{-1} \cdot e^{-B/k_B T}, \quad (7)$$

with $z_0^{-1} = 1 - e^{-h\nu_0/k_B T}$ in the case of a harmonic oscillator.

² A thermostat, at temperature T , if connected with the system (0), would exchange energy as time goes with a zero mean value.

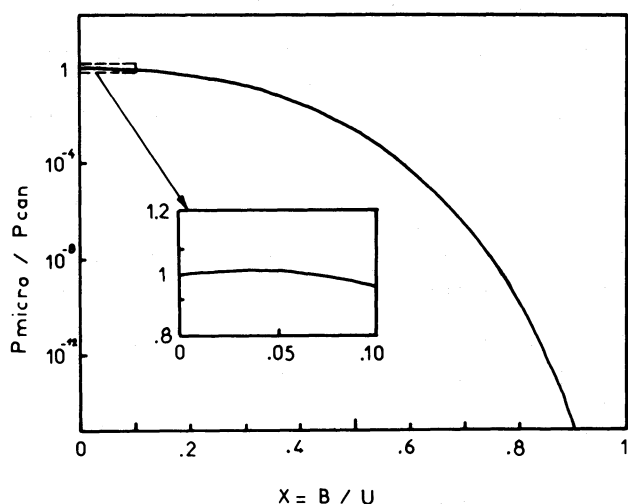


Fig. 3. Test of the validity of the thermal approximation. The ratio of the probabilities for having an energy B in a mode of a system with total energy U as given by the microcanonical expression (6) and the thermal approximation (7) is plotted versus B/U . The values of B/U are quantized but the curve has been interpolated. It is calculated for the set of modes that give the density of states of Fig. 2. The two models give similar probabilities at small B/U which validates the thermal approximation in this regime (usual case for IR emission). At large B/U they are completely different and the thermal approximation should not be used (case for TD)

Figure 3 reports the ratio of the exact to the approximated probabilities as a function of the fraction of the total energy which is localized in the mode: $x = B/U_0$, for the same molecule as in Fig. 2.

As expected the two probabilities are similar at small x . This validates the thermal approximation for the calculation of IR emission from hot PAHs (IR fluorescence) as long as the internal energy of the molecule is much higher than the emitted photon energy. For instance, the emission of a photon at 3000 cm^{-1} from a molecule with the above parameters corresponds to $x = 3.7 \cdot 10^{-2}$ and the thermal approximation gives the correct answer within 1%.

This point is important and was not correctly appreciated in the past when criticisms were addressed to the thermal approximation (Allamandola et al., 1985). Several experiments also support the concept of thermal emission by isolated hot molecules (Gottfried et al., 1984; Wild et al., 1985). For the very specific cases of IR emission where x is not small (emission of the last IR photons), the microcanonical treatment (Sect. 3.2) should be used but this is a marginal situation.

At large x , the two probabilities differ by orders of magnitude and the thermal approximation should *not* be used. This is the case for PTD where typical values are $B = 5 - 8 \text{ eV}$ and $x \sim 0.5 - 0.8$. The physical reason of the failure appears: the internal energy of the associated canonical system fluctuates with time which favors its transient accumulation in one mode and leads to an overestimate of the corresponding dissociation rate. It is obvious for the probability to localize an energy (B) greater than the total energy (U_0) of the molecule: the thermal approximation gives $e^{-B/k_B T}$ instead of the correct value which is clearly zero.

Therefore, the PTD rate will be calculated in the framework of unimolecular reactions.

4. Rate of thermo-dissociation (TD)

In the theory of unimolecular reactions, it is assumed that the molecule does not react unless its internal energy U is greater than a critical value B and that, above this threshold, the reaction rate $k(U)$ depends only on U . This is the case if the internal energy redistribution is fast enough and if tunnelling for energy less than B is negligible. A model for the determination of $k(U)$ is the transition state theory developed by Bohr and Wheeler (1939) for nuclear physics and used in the same form in the RRKM theory (Forst, 1973; Robinson and Holbrook, 1972). However, the description of the transition state (e.g. a very large amplitude vibrational state) involves parameters difficult to determine. Forst (1972) has shown that a very simple expression can be derived from an inverse Laplace transform of the Arrhenius law (see Appendix A2):

$$k(U) = \begin{cases} A \rho(U-B)/\rho(U), & U > B \\ 0, & U < B, \end{cases} \quad (8)$$

provided the reaction rate of the molecule, when thermalized at temperature T (canonical limit), has the familiar Arrhenius form:

$$k_{\text{th}}(T) = A e^{-B/k_B T} \quad (9)$$

over the whole temperature range. This derivation of $k(U)$ is quite general as it depends only on a mathematical inversion and does not require any assumptions on the nature of the transition state. Barker (1982) has shown the similarity between the results of this approach and the RRKM one.

Now, we estimate the different quantities entering in (8) and (9).

4.1. Density of vibrational states and specific heat for PAHs

The function $\rho(E)$ can be deduced from the set of the molecule vibrational modes ($h\nu_i$) as explained in Sect. 3.1. However, the knowledge of all the modes is required and not only that of the easily measured IR or Raman active ones. This usually implies the use of a vibrational model of the system.

For large hydrogenated PAHs, with hydrogen to carbon ratio close to 0.5, we use the mode distribution derived from the model by Cyvin (1982) and Cyvin et al. (1984) for coronene, with a normalization to the number of modes ($s = 3N - 6$). For dehydrogenated PAHs, we use the same set but with subtraction of the CH stretching and bending modes. Table 1 and Fig. 4 give the histograms of these two distributions. When PAH molecules with H/C ratio sensibly less than 0.5 are considered (e.g. partially dehydrogenated species), an interpolation between the two histograms can be used.

The density of states function $\rho(U)$ is then calculated using the Whitten and Rabinovitch's approximation (Eq. (1)).

The internal specific heat of a PAH also results from the mode distribution. In the harmonic approximation, one reads (Reif, 1965):

$$C(T) = k_B \sum_{i=1}^{3N-6} \left(\frac{\theta_i}{T} \right)^2 \frac{e^{\theta_i/T}}{(e^{\theta_i/T} - 1)^2}, \quad (10)$$

where k_B is the Boltzmann constant; $\theta_i = h\nu_i/k_B$; N and $s = 3N - 6$ are the molecule number of atoms and modes, respectively. The specific heat curves resulting from the mode distributions of Table 1 are reported in Fig. 5 for PAHs with $H/C = 0.5$ and dehydrogenated species. The specific heat, as measured for

Table 1. Simplified distribution of the vibrational modes of large PAHs with H/C ratio equal to 0.5 (n_1), and dehydrogenated PAHs (n_2). The modes have been taken from the model by Cyvin (1982) and Cyvin et al. (1984) for coronene $C_{24}H_{12}$ and gathered in 100 cm^{-1} bins. For dehydrogenated species, the 36 CH stretching and bending modes have been withdrawn in the 3000, 1150 and 850 cm^{-1} ranges. The total number of modes of an N atom molecule is $3N - 6$ so that the mode distribution of a hydrogenated PAH or dehydrogenated one is obtained from the above values with a *scaling* by $(3N - 6)/102$ or $(3N - 6)/66$, respectively. For PAHs with different H/C ratio see text. Using similar mode distributions for different large molecule sizes is a reasonable approximation but for the lowest modes (Omont, 1986)

$h\nu_i$ (cm^{-1})	n_1	n_2	$h\nu_i$ (cm^{-1})	n_1	n_2
3050	12	0	950	11	9
1650	5	5	850	10	0
1550	5	5	650	7	7
1450	9	9	550	7	7
1350	2	2	450	5	5
1250	2	0	350	9	9
1150	7	0	250	1	1
1050	6	3	150	4	4
Total			102	66	

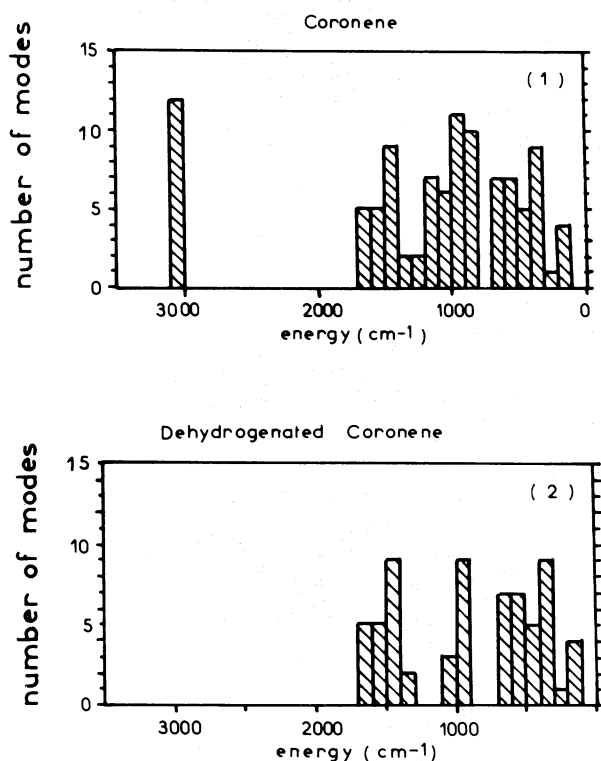


Fig. 4. Histograms of the two distributions of Table 1

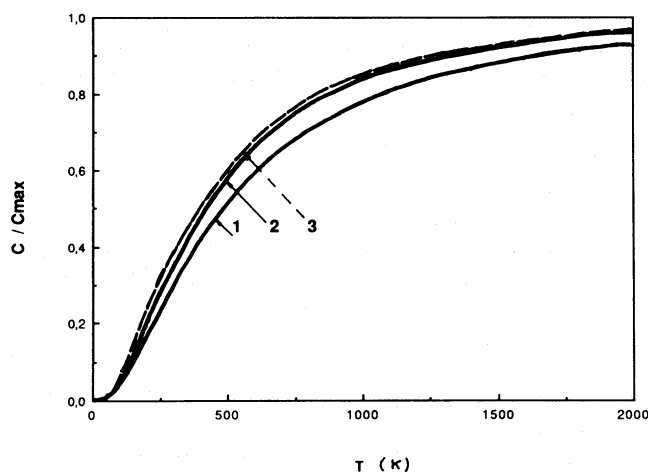


Fig. 5. Internal specific heat per molecule, $C(T)$, divided by its maximum value, $C_{\max} = (3N - 6)k_B$, where N is the molecule number of atoms, for (1) hydrogenated PAHs (H/C ratio=0.5) and (2) dehydrogenated PAHs, as deduced from the histograms of Table 1 and Fig. 4 with relation (10). (3) is the experimental specific heat of graphite measured by Krumhansl and Brooks (1953). The agreement between (2) and (3) supports the model used (see text)

graphite, is also reported and is found very close to the dehydrogenated PAH curve. This agreement confirms the model proposed because a graphitic plane can be considered as an infinite dehydrogenated PAH. Our results are also close to those derived by Omont (1986) using a somewhat different procedure.

4.2. Evaluation of the constants A , B and resulting TD rates

4.2.1. TD rate for carbon

No experimental data is available concerning the TD rate of PAH molecules thermalized at high temperatures (around 2000 K). Nevertheless, it is possible to approach the canonical limit by another way; if at a given internal temperature T the size of the molecule is increased, the total energy content U will scale with the number of atoms and the energy B necessary to remove a fragment will become small compared to U , making the canonical approximation again valid. The TD rate of a larger and larger molecule [corresponding to the infinite pressure limit in chemical physics] should merge the rate for a piece of bulk material, with the same composition, at that temperature. If we assume that the parameters A and B do not depend on the size of the molecule in a given family (aromatic compounds), they can be derived from the properties of the bulk material (graphite). Such an assumption seems plausible because in a *thermalized* species, the dynamics of ejection is expected to depend only upon the local binding of atoms. In addition the sublimation from graphite corresponds to an average on different bond configurations.

The equilibrium of a solid with its vapor is achieved when the impinging flux equals the sublimation flux, if an unit sticking coefficient is assumed. Considering the vapor as a perfect gas, the sublimation rate per surface atom is

$$k_{\text{th}}(T) = \sigma P_{\text{sat}}(T) / (2\pi M k_B T)^{\frac{1}{2}}, \quad (11)$$

where σ is the surface per peripheral atom, P_{sat} the saturated vapor pressure and M the vapor molecular mass. However, at

high temperature, the C vapor above graphite is constituted not only of C atoms, but also of polymers C_2 , C_3 , ... C_n . It is necessary to take into account the sublimation rates of all these polymers:

$$k_{\text{th}}^{(n)}(T) = \sigma_n P_n(T) / (2\pi M_n kT)^{\frac{1}{2}}$$

with $\sigma_n = n\sigma_c$ $M_n = nM_c$.

The experimental determination of P_{sat} for graphite (Dwight, 1972; Herpin et al., 1965; Palmer and Shelef, 1968) gives sublimation rates well fitted by Arrhenius laws between 2000 and 4000 K which covers the domain of interest. One finds

$$k_{\text{th}}^{(n)}(T) = A_{C_n} e^{-B_{C_n}/k_B T} \quad (12a)$$

The values of A_{C_n} and B_{C_n} calculated for $\sigma_c = 2.6 \cdot 10^{-16} \text{ cm}^2 \text{ at}^{-1}$ and $M_c = 12 \text{ amu}$ are given in Table 2.

Therefore, the rate of ejection of carbon polymer C_n from a thermalized PAH molecule does have the structure of Eq. (9).

The unimolecular rate $k_n(U)$ for TD of C_n from an isolated PAH molecule is then given by (8), (1) with the numerical values of Tables 1 and 2. The total carbon loss rate will be the sum of all these processes:

$$k(U) = \sum_n n k_n(U) \quad (12b)$$

Practically, this summation can be limited to the two terms $n = 1$ and $n = 3$, C and C_3 being the dominant species in the vapor, at the temperatures of interest.

This total rate is reported in Fig. 6 for molecules with different numbers of atoms, for a vibrational energy content of 10 eV. The rate given by the thermal (or canonical) approximation is also reported for comparison. This is a *central result* of the present paper. We have determined a rate of carbon atom ejection from a hot PAH molecule that take into account the isolation of the species. The difference with the thermal approximation is substantial. For instance, if we would consider that the limit for survival in a given radiation field was a TD rate of 10^{-10} s^{-1} , the minimum size would be 26 atoms instead of 45 atoms with the thermal model.

However, the determination of the minimum size of interstellar molecules actually requires the estimate of the duration of the hot events. The Poincaré fluorescence (Léger et al., 1988) must be fully taken into account. This will be addressed in the forthcoming Paper II.

4.2.2. Remarks

(i) A crude physical interpretation is sometimes given to expressions like Eq. (9): the sublimation rate is the product of a frequency factor A by the probability that an energy greater than the binding energy B is concentrated into a dissociative mode (e.g. the bond stretch of a peripheral atom). However, the frequency A (10^{17} s^{-1} for carbon) is much higher than what would be expected in such a model: a rate of energy exchange between modes (10^{12} s^{-1}).

The discrepancy originates as follows: the factor $\exp(-B/k_B T)$ is actually the probabilities to find a harmonic oscillator in levels higher than B but a dissociative mode cannot be treated as a harmonic oscillator at high energies. Due to the free flying fragments the states are much more closely spaced. To obtain the rate of dissociation, the summation of the probabilities

Table 2. Arrhenius parameters for the sublimations of carbon atoms and polymers from graphite.

For polymer C_n , the partial pressure is:

$$P_{C_n}(T) = P_0^{(n)} e^{-B_{C_n}/kT}$$

and the thermal dissociation rate is:

$$k_{\text{th}}^{(n)}(T) = A_{C_n} e^{-B_{C_n}/kT}$$

	$B_{C_n}(\text{eV})$	$P_0^{(n)}(\text{Torr})$	$A_{C_n}(\text{s}^{-1})$
C	7.37	$9.7 \cdot 10^{10}$	$6.2 \cdot 10^{15}$
C_2	8.49	$3.9 \cdot 10^{12}$	$3.5 \cdot 10^{17}$
C_3	7.97	$1.4 \cdot 10^{13}$	$1.5 \cdot 10^{18}$

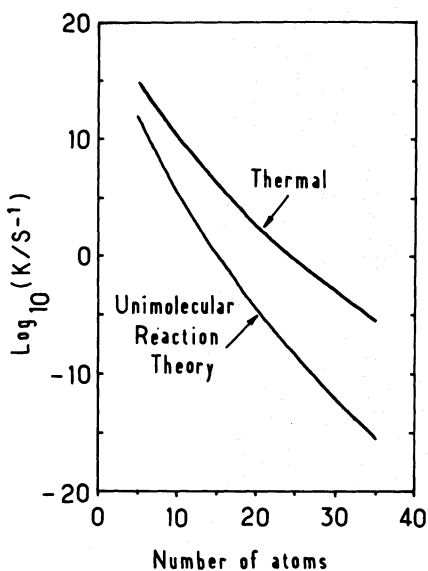


Fig. 6. Thermodissociation (TD) or sublimation rate of carbon atoms from isolated PAHs versus their number of atoms, for an internal energy $U = 10 \text{ eV}$. The two curves correspond to the thermal approximation and the unimolecular reaction theory. The former considers the molecule as connected to a thermostat, the latter takes into account the isolation of the molecule and gives a reliable result. As expected (see Fig. 3 and text), the thermal approximation overestimates the TD rate. The TD rate strongly depends on the molecule size, at a given internal energy, because the smaller the system, the higher its temperature

of occupation, $Z^{-1} \exp(-E/k_B T)$, times the rate of energy exchange (10^{12} s^{-1}) should be performed for $E > B$ taking into account the actual density of states. This has been done in the theory of the transition state (beginning of Sect. 4) and results in a much higher prefactor A .

In general, no experimental data on sublimation can be fitted with a prefactor typical of energy exchange (see Léger et al., 1985, p. 149).

(ii) It had been suggested that the energy required to extract a carbon atom from a PAH was 11.5 eV (Crawford et al., 1985). This was based on the sum of the energies of the different bonds (1 single + 1 double + resonance energy) to break in order to remove a peripheral C atom, the rest of the molecule being unchanged. But, as pointed by Benson (1965), this estimate is

incorrect when there is a rearrangement of the molecule. New bonds are formed after the ejection whose energy should be subtracted. For instance, if we assume that a single (double) bond is reconstructed between the remaining carbons, the energy would be reduced to 7.7 eV (4.4 eV). The actual energy required to remove an atom is an activation energy which is intermediate between 11.5 eV and these values. However, its determination would require the knowledge of the exact reaction scheme and a detailed quantum chemistry calculation.

Alternatively, we suggest to use the value, $B_C \sim 8$ eV, deduced from the sublimation of graphite because the extraction of carbon atoms from the periphery of a graphite plane involves bond dissociation and re-formation in a way similar to that from a dehydrogenated PAH. These energies are *definitely smaller* than the 11.5 eV formerly proposed, which has major consequences on the inferred minimum size of interstellar PAHs.

Omont (1986) has suggested a value, 8.5 eV, which is closer to ours.

4.2.3. TD rate for hydrogen

First, it must be pointed that PTD is not the only mechanism for dissociating the hydrogen atoms. Direct photo-dissociation (PD), corresponding to a transition from the binding ground state (σ) to the antibinding state (σ^*) of a C–H group (Buch, in preparation) and coulombic explosion after a double ionization (Leach, 1986) have also been proposed. Anyway, the PTD process is an additional dissociative channel which is always present and should be considered.

For hydrogen TD, a comparison with the sublimation of a solid is not directly available. On the other hand, the break of a C–H bond can be studied with the concept of bond dissociation energy (Benson, 1965). Assuming that there is no extra activation energy, one has for an aromatic CH: $B_H = 4.5$ eV (preceding reference). We are concerned with the successive extraction of the hydrogen atoms from a PAH. It is quite possible that their binding energy depends upon the hydrogen covering factor of the molecule so that the above value should be considered only as a first approximation.

The pre-exponential term A_H can be obtained by statistical physics arguments (Appendix A3). The TD rate for hydrogen has then the same expression as for carbon but with the values:

$$\begin{aligned} B_H &= 4.5 \text{ eV} \\ A_H &= 2.4 \cdot 10^{14} \text{ s}^{-1} \end{aligned} \quad (13)$$

The rate of thermo-ejection of H atoms from an aromatic species is then given by relations (8) and (1) with the numerical values of (13) and Table 1.

Because of the hierarchy in the activation energies, one expects *the H ejection to precede the C ejection*. As a consequence, the latter takes place from dehydrogenated species which qualifies the use of graphitic parameters for it. For partially dehydrogenated species, the ejection of a H atom can play the role of a fuse for further dissociation because the internal energy of the molecule is decreased by the H bond energy.

4.2.4. TD rate for other fragments

Recent experiments (Ruhl et al., in preparation) on simply ionized deuterated naphthalene have shown that the rate of ejection of C_2D_2 fragments may be comparable to that of D atoms.

If this process has the same efficiency in larger PAHs, it could bypass the effect of fuse of H atoms (Sect. 4.2.3), leading to C loss even in hydrogenated species. It would have to be taken into account in the determination of the minimum size of PAHs.

An evaluation of the dissociation energy B could be obtained from the experimental results. The preexponential factor would be found in the same way as in the case of H atoms, but here, the vibrational and rotational degrees of freedom of the fragment would appear in the free energy balance.

5. Conclusion

The importance of clusters with intermediate sizes between small molecule and grain sizes in the interstellar medium has been recently discovered. Beside their chemical reactions with the interstellar matter, these particles are submitted to spikes in their internal energy because they absorb photons of the radiation field and have a low specific heat. Thus they can lose part of their constituents.

We have derived the proper theoretical basis for this process of photo-thermo-dissociation (PTD) that fully takes into account the isolation of the species as an opposition to the thermal (or canonical) approximation. The results of the two approaches have been compared and found substantially different.

We have used a semi-empirical approach to determine the parameters of the theory of carbon ejection by fitting them to the infinite size limit of aromatic molecules which is graphite. The advantage of this approach is to be independent of any specific reaction route. We found the energies of the C, C_2 and C_3 carbon ejecta in the 8 eV range.

For hydrogen ejection we suggest to use an activation energy equal to the H binding energy (4.5 eV). We emphasize that PTD is only one of the channels for H dissociation, other ones being direct photo-dissociation (PD) and coulombic explosion after double ionization.

We have established the tools to calculate the ejection rate of hydrogen and carbon fragments from aromatic molecules at every moment of their cooling. The next step is to determine the thermal history of the molecules after the absorption of photons. Then, we will be able to calculate the integrated probability of dissociation per time unit and deduce the lifetime of species as a function of their size in different radiation fields. The recently proposed Poincaré fluorescence (Léger et al., 1988) must be included as it can very substantially shorten the duration of the hot events. This will be done in the forthcoming Paper II.

Finally, it must be noted that *PTD is a process that any free flying molecule has to face in the interstellar medium*. It is efficient provided that: (i) the molecule has some absorption in the UV domain where interstellar photons are available with an energy larger than the binding energy of its constituent atoms – this is the case for practically all molecular species –; (ii) the molecule size is sufficient for internal conversion of the electronic energy into vibrational energy to be efficient – this *does not apply to diatomic molecules* but is true above about 5 atoms for U of a few eV –; (iii) PTD is not compensated by an extremely efficient reconstruction mechanism. The PTD is a general mechanism that does not depend on the presence of specific anti-bonding electronic levels in the molecule.

Appendix A1

The empirical coefficient (a) of relation (1) has been tabulated by Whitten and Rabinovitch (1963) or fitted by the following expression (preceding reference and Forst, 1973):

$$a = 1 - \beta w, \quad (\text{A1})$$

with

$$w = \begin{cases} 10^{-1.0506(U/E_z)^{1/4}}, & \text{if } U > E_z, \\ [5(U/E_z) + 2.73(U/E_z)^{1/2} + 3.51]^{-1}, & \text{if } U < E_z \end{cases}$$

$$\beta = v_d(s-1)/s,$$

where v_d is the frequency dispersion parameter,

$$v_d = \langle v^2 \rangle / \langle v \rangle^2 \quad \langle v^2 \rangle = s^{-1} \sum_1^s v_i^2, \quad \langle v \rangle = s^{-1} \sum_1^s v_i$$

Appendix A2: Inversion of the Arrhenius law

For a set of identical molecules with a given internal energy distribution (IED), $D(U)$, (with $\int D(U) dU = 1$) the mean rate of unimolecular reactions $\langle k \rangle$ is given by the average of $k(U)$ over this distribution:

$$\langle k \rangle = \int dU D(U) k(U).$$

If these molecules are in equilibrium with a thermostat at temperature T (canonical ensemble), the IED will be of a Boltzmann type:

$$D(U) = Z^{-1} \rho(U) \exp(-U/kT).$$

$Z = \int dU \rho(U) \exp(-U/kT)$ is the partition function for one molecule.

The product $Z \langle k \rangle$, noted $Z k_{\text{th}}(T)$, is then the Laplace transform of the function $k(U) \cdot \rho(U)$. If k_{th} is known at all temperatures, the function $k(U)$ may then be obtained by an inverse Laplace transform, with $\beta = 1/kT$ as the parameter. When $k_{\text{th}}(T)$ has the exponential form of Eq. (9), the inverse Laplace transform has the simple expression of Eq. (8).

Appendix A3: Determination of the pre-exponential frequency factor for hydrogen

Under thermodynamical equilibrium at a given temperature, the chemical potential for an H atom in the gas phase or bound to a molecule should be equal. The pre-exponential factor will come out from the entropy part of this equality.

In the limit of a perfect gas, the chemical potential of an H atom in the gas phase is related to the vapor pressure P by

$$\mu_g = -k_B T \ln \left[\left(\frac{2\pi M_H}{h^2} \right)^{3/2} \frac{(k_B T)^{5/2}}{P} \right]. \quad (\text{A2})$$

The contribution of one bound H atom to the free energy of the molecule is:

$$\mu_{\text{mol}} = -B + \int_0^T C(T') dT' - T \int_0^T \frac{C(T')}{T'} dT', \quad (\text{A3})$$

with the specific heat $C(T)$ of Eq. (9) limited to the three already considered CH stretching and bending modes (hydrogen contribution to the specific heat).

In the temperature range interest, above $T_2 = 2000$ K, $C(T)$ may be crudely approximated by $3k_B$, so that

$$\mu_{\text{mol}} = -(B - b_2) + k_B T \left(3 - \frac{s_2}{k_B} - 3 \ln \frac{T}{T_2} \right), \quad (\text{A4})$$

with

$$b_2 = \int_0^{T_2} C(T) dT - 3k_B T_2$$

and

$$s_2 = \int_0^{T_2} C(T)/T dT.$$

The equality $\mu_g = \mu_{\text{mol}}$ implies a saturated vapor pressure:

$$P_{\text{sat}}(T) = \frac{(2\pi M_H)^{3/2}}{h^3} (k_B T_2)^{5/2} \left(\frac{T}{T_2} \right)^{-1/2} e^{-\left(\frac{s_2}{k} - 3\right)} e^{-\frac{B-b_2}{kT}}. \quad (\text{A5})$$

The frequency pre-exponential factor is then obtained in the same way as for C atoms, using (8) and (10):

$$A_H = \frac{2\pi M_H}{h^3} (k_B T_2)^2 \sigma e^{-\left(\frac{s_2}{k} - 3\right)} = 2.4 \cdot 10^{14} \text{ s}^{-1}, \quad (\text{A6})$$

neglecting a (T_2/T) term.

The same method can be used to determine the preexponential factor for C atoms. The specific heat in this case is that of a dehydrogenated PAH (curve 2 in Fig. 5), scaled to $C_{\text{max}} = 3k$. The result $A_C = 1.2 \cdot 10^{15} \text{ s}^{-1}$ is in rather good agreement with the experimental value given in Table 2. This confirms again that the set of modes obtained from dehydrogenated coronene is representative of a graphitic plane.

It is worth noting that the pre-exponential factor A and energy B derived from experimental vapor pressure curves of different solids are correlated. The value for A_H derived from this correlation, using $B_H = 4.5 \text{ eV}$, is $2.7 \cdot 10^{14} \text{ s}^{-1}$ which is quite coherent with the adopted value (A6).

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