

INFRARED EMISSION MECHANISM IN LARGE ISOLATED MOLECULES

L. B. D'HENDECOURT, A. LÉGER,
*Groupe de Physique des Solides de l'E.N.S.,
Université Paris VII Tour 23 - 2,
place Jussieu - 75251 Paris Cédex 05 - France*

P. BOISSEL,
*Laboratoire de Photophysique Moléculaire,
Université Paris XI Bâtiment 213,
91105 Orsay Cédex - France*

F. X. DÉSERT
*NASA Goddard Space Flight Center,
Code 685, Greenbelt, MD 20771 - USA*

ABSTRACT. The physics which governs the IR emission of a large isolated molecule (e.g. an interstellar PAH) after the absorption of an UV photon is described. We show that the simple thermal approximation is valid and we give the method to calculate emission spectra from absorption spectroscopy data.

1. INTRODUCTION

In 1984, Léger and Puget showed that there was a striking similarity between the fundamental vibration frequencies of PAH molecules and the frequencies of the unidentified infrared emission lines observed in many different interstellar objects. From the IR absorption spectrum of coronene, they calculated the emission spectrum and compared it successfully to astronomical spectra. The emission mechanism, adapted from Sellgren (1984), involved the quantum heating of an isolated molecule by a single UV photon. Truly isolated in the interstellar medium (ISM), this hot molecule then relaxes by emitting IR photons. Their model uses the rather simple thermal approach; the vibrationally excited molecule is described as a system having an internal temperature. In 1985, Allamandola, Tielens and Barker presented a different model and questioned the validity of the thermal approximation. In this paper, we focus our attention on the physics of the IR emission of molecules for which IR absorption spectra are known from laboratory measurements. We justify the use of the concept of a vibrational temperature for a molecule which has absorbed an UV photon and we derive the formulae which can be used to compute the IR emission of a cooling molecule. Physical characteristics of the emitting molecules are briefly presented.

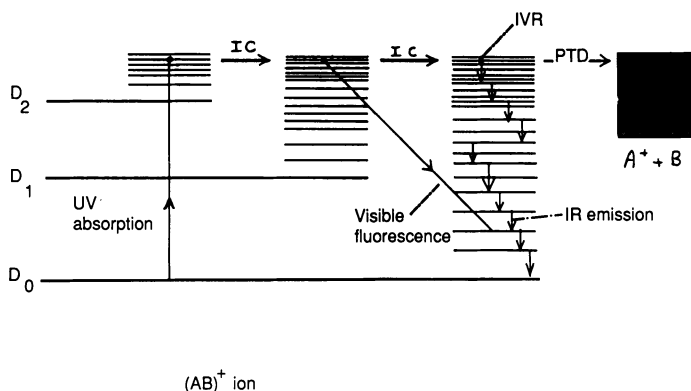


Fig. 1. Energy level diagram of a large ion. The energy levels shown involve an electronic part (D_0 , D_1 , D_2 ...) and a vibrational part. The different symbols correspond to the following processes: IC = Internal Conversion, IVR = Internal Vibrational Redistribution, PTD = Photo-Thermo-Dissociation. The transitions with energy change correspond to photon absorption or emission. As explained in the text, the Thermal Approximation can be used for IR emission but *not* for PTD events.

2. IR EMISSION MECHANISM FROM ISOLATED MOLECULES

2.1. A MOLECULAR ION AFTER THE ABSORPTION OF A UV PHOTON

We consider the case of large ions (> 4 atoms) because PAHs are expected to be ionized in the regions which are presently best observed (reflection nebulae, planetary nebulae..., see Allamandola, Tielens and Barker, 1985; Omont, 1986; d'Hendecourt and Léger, 1987; Table 1), but our derivation can easily be extended to neutral species and radicals.

The energy diagram of a molecular ion having absorbed a UV photon is shown in Fig. 1, in the one electron approximation. The absorbed photon makes a transition between the ground doublet state D_0 (one non-paired electron) to an upper state (e.g. D_2).

Then, the ion can have iso-energetic internal transitions or transitions during which photons are emitted. The former correspond to an energy exchange between the vibrational modes only (Internal Vibrational Redistribution, $t \sim 10^{-12}$ – 10^{-10} s) or involving different electronic states (Internal Conversion or Intersystem Crossing, $t = 10^{-12}$ – 10^{-8} s), and the latter to transitions between different electronic levels (Visible fluorescence, $t \sim 10^{-7}$ s) or vibrational de-excitation (IR emission, $t \sim 10^{-2}$ s). These processes have been the subject of intense activity in physical chemistry during the last two decades and are comprehensively described in the literature (Birks, 1970; Avouris, Gelbart and El Sayed, 1977; Bondibey, 1984), including aspects which are specific to highly isolated systems (Léger, Boissel and d'Hendecourt, 1988).

After UV absorption, the system is prepared in a specific state (e.g. D_2 , with little vibrational energy). Then, it evolves in its available phase space, with the

uniform probability of occupation of microscopic states (Ergodic Principle). This leads to a rapid evolution towards the ground electronic state D_0 with high vibrational energy (large density of states), apart from short excursions to the D_1 state (Inverse Internal Conversion, Léger, Boissel and d'Hendecourt, 1988). Although this hot ion is highly excited, it is in an Internal Thermodynamical Equilibrium (ITE) because the internal coupling between its states is more important (time for vibrational redistribution $t \sim 10^{-12}$ – 10^{-10} s) than the coupling with the surroundings (time for photoemission $t \sim 10^{-7}$ – 10^{-2} s). A statistical physics description is then adequate after times $t \sim 10^{-10}$ s as it has been shown extensively (Oref and Rabinovitch, 1979; Smalley, 1982).

2.2. 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 ($h\nu_i$), 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, $E_z = \sum_{i=1}^s (h\nu_i/2)$; and a is an empirical correction factor ($0 < a < 1$) whose expression is given in Appendix A. The limiting cases $a = 0$ and $a = 1$ are referred to as the classical and semi-classical approximations. The density of states is shown in Fig. 2 for a set of vibrational modes representative of an interstellar PAH (dehydrogenated coronene, see § 2.5.2.).

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, excluding the mode under consideration, 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:

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

this result comes simply from the ergodic assumption.

It must be noticed that if the number of modes, s , is large, the curve $\rho^*(U_0 - B)$ is very similar to $\rho^*(U_0)$. Owing to the logarithmic ordinate scale of Fig. 2, the logarithm of the probability ratio p_{micro} appears as the difference in ordinates between points M and N. As described below, the use of this figure will make very clear the limit of validity of the thermal approximation.

2.3. THERMAL (CANONICAL) APPROXIMATION

We call the Thermal (or Canonical) Approximation the use of the associated canonical system which has the same physical components as the isolated system, but is

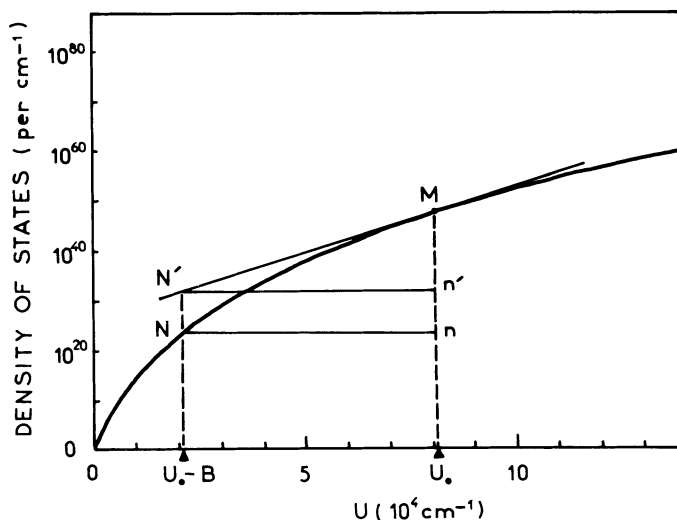


Fig. 2. Density of vibrational states for a typical PAH ion. U is the internal energy of the system given in wavenumbers.

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 the canonical system and the isolated system respectively. The average is taken over the time, because for a canonical system the temperature is fixed but the internal energy fluctuates. *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:

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

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

$$p_{\text{therm}}(B) = \exp\left(-\frac{B}{k_B T}\right) \quad (5)$$

This ratio appears simply in Fig. (2) 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 .

2.4. VALIDITY OF THE THERMAL APPROXIMATION

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

$$\ln(p_{micro}(B)) = -\frac{B}{k_B T} \left[1 + \frac{B}{2C^* T} \right] \quad (6)$$

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 to find an energy B in a given mode rather than the probability ratios $p_{micro}(B)$ and $p_{therm}(B)$ defined above. For the microcanonical system, the denominator of Eq. (2) $\rho^*(U)$ is replaced by $\rho(U)$, the total number of accessible states:

$$p_{micro}(B) = \frac{\rho^*(U-B)}{\rho(U)} \quad (7)$$

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

$$p_{therm}(B) = z_0^{-1} \exp\left(-\frac{B}{k_B T}\right) \quad (8)$$

with $z_0^{-1} = 1 - \exp(-h\nu_0/k_B T)$ in the case of an harmonic oscillator.

Figure 3 shows the ratio of the exact and 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 energy of the photon emitted. For instance, the emission of a photon at 3000 cm^{-1} from a molecule with the above parameters corresponds to $x = 3.7 \times 10^{-2}$ for $80,000 \text{ cm}^{-1}$ of internal energy and the thermal approximation gives the correct answer to within 1%. Several experiments also support the concept of thermal emission by isolated hot molecules (Gottfried, Seilmeier and Kaiser, 1984; Wild *et al.*, 1985). For the very specific cases of IR emission where x is not small (emission of the last IR photons as the molecule is near the final stages of relaxation), the microcanonical treatment 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 Photo-Thermo-Dissociation (PTD) where typical values for bond energies 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. Obviously, in the Thermal Approximation it is possible to localize an energy (B) in a mode greater than the total energy (U_0) of the molecule: that is, the Thermal Approximation gives $\exp(-B/k_B T)$ instead of the correct value which is clearly zero (see Léger, *et al.*, 1988, for a calculation of photo-thermo-dissociation rates of PAH molecules).

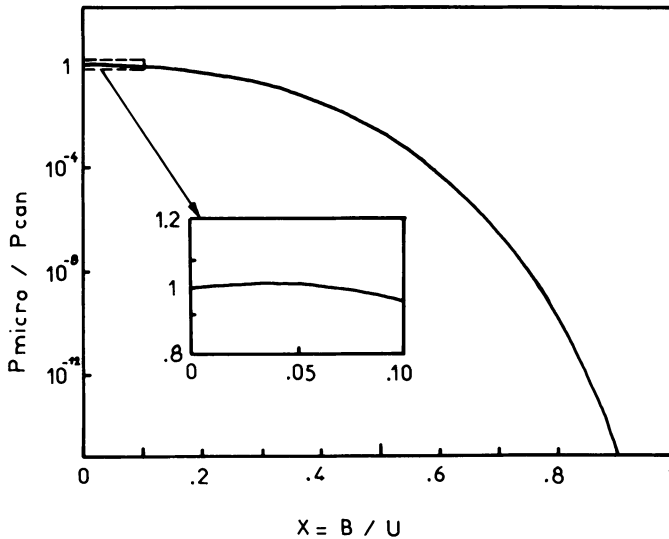


Fig. 3. Test of the validity of the Thermal Approximation. The ratio of the probabilities for having an energy B in a mode of a system with total energy U as given by the microcanonical expression and the Thermal Approximation is plotted versus B/U . The values B/U are quantized but the curve has been interpolated. The two models give similar probabilities at small B/U which validates the Thermal Approximation in this regime which is the usual case for IR emission.

2.5. IR EMISSION OF A LARGE MOLECULE AT A TEMPERATURE T

It is not the purpose of this paper to extensively describe the laboratory IR spectroscopy which we have made on various PAH molecules. These spectra and their interpretation can be found in Léger and d'Hendecourt (1987) and Léger, d'Hendecourt and Défourneau (1989a). We wish here to derive simple formulae which can be used for the computation of the IR emission of isolated molecules. These formulae are derived with the use of the Thermal Approximation, justified in the previous paragraph.

The spectral emission intensity of a physical system, at temperature T , is:

$$I_\lambda = B_\lambda(T) \epsilon_\lambda(T) \quad (9)$$

where $B_\lambda(T)$ is the black body emission at wavelength λ and ϵ the emissivity of the system.

The Second Law of Thermodynamics implies that, at the same temperature, the sample emissivity is equal to its absorptivity $A_\lambda(T)$ (Kirchoff's Law, see Reif, 1965). For an assembly of molecules, the latter quantity can be easily measured. In an *absorption experiment*, A_λ is connected to the incident flux ϕ_0 and the transmitted one ϕ_λ by:

$$A_\lambda = \frac{\phi_0 - \phi_\lambda}{\phi_0} = 1 - \exp(-N\sigma_\lambda) \quad (10)$$

where N ($\text{mol}\cdot\text{cm}^{-2}$) is the molecular column density and σ_λ ($\text{cm}^2\cdot\text{mol}^{-1}$) the cross section per molecule. In the optically thin limit ($N\sigma_\lambda \ll 1$) the same molecule assembly emits, at temperature T , an intensity:

$$I_\lambda = B_\lambda(T) N \sigma_\lambda(T) \quad (11)$$

The spectral power emitted, per molecule, is obtained by integrating over all the directions:

$$P_\lambda = 4\pi B_\lambda(T) \sigma_\lambda(T) \quad (12)$$

The total IR emission of a molecule is the sum of its instantaneous emissions at different temperatures during the cooling process.

2.5.1. IR Emission During a Thermal Spike

When a molecule absorbs a UV photon, its internal energy U is increased by $h\nu_{UV}$, and when it emits an IR or a visible photon, U decreases by the corresponding amount $h\nu_{IR}$. At each time, the vibrational temperature T of the system can be defined and is connected to the internal energy U (when the system is in its electronic ground state) by:

$$U(T) = \int_0^T C(T') dT' \quad (13)$$

where $C(T')$ is the specific heat of the molecule that we shall evaluate in the next section. During the IR emission, the ion cools as the energy is emitted, according to:

$$P(T) dt = -C(T) dt \quad (14)$$

where $P(T) = \int P_\lambda(T) d\lambda$. These expressions apply as an average, but for a given molecule, the quantization of the emission must be taken into account. The IR emission of a large interstellar molecule is then the sum of spectral emissions given by expression (12) at temperature T , during the thermal spike.

2.5.2. Specific Heat of PAHs

The specific heat of a PAH depends on: (a) N_t , its total number of atoms, (b) N_H/N_C , its relative number of hydrogen and carbon, and (c) the exact molecule considered. Taking into account points (a) and (b), the dependence on point (c) is probably minor within a category of compounds (e.g. compact PAHs) and will be neglected. The relative number of H versus C atoms is rather constant in the series: coronene (0.50), ovalene (0.44), circobiphenyl (0.53). So, we shall derive the specific heat for hydrogenated large compact PAHs from data on coronene scaled with the number of modes.

A free molecule with N_t atoms has $3N_t - 6$ vibrational modes. If the frequency ν_i of each mode is known, its vibrational specific heat is given in the harmonic approximation (Reif, 1965) by:

$$C = k \sum_{i=1}^{3N_t-6} \left(\frac{\theta_i}{T} \right)^2 \frac{\exp(\theta_i/T)}{[\exp(\theta_i/T) - 1]^2} \quad (15)$$

where $k\theta_i = h\nu_i$.

Fortunately, the frequencies of all the modes in coronene have been calculated by Cyvin (1982) and Cyvin *et al.* (1984), using a force-field model. The quality of such a semi-empirical model is indicated by the agreement with the measured active modes (IR and Raman) which are much more numerous than the free parameters of the model. The resulting mode distribution is shown in Fig. (4a) and the specific heat in Fig. (5)(curve 1).

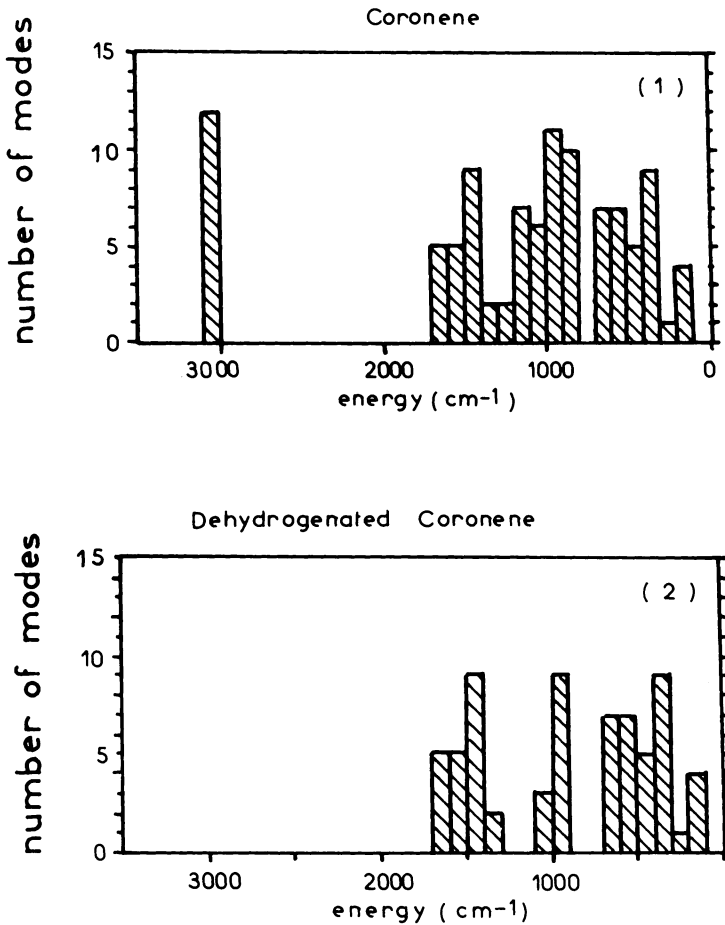


Fig. 4. Histograms of the distribution of fundamental vibrational modes of coronene (a) and dehydrogenated coronene (b).

We consider *this curve as representative for the specific heat of hydrogenated PAHs in space*. For *dehydrogenated PAHs*, the specific heat can be estimated by

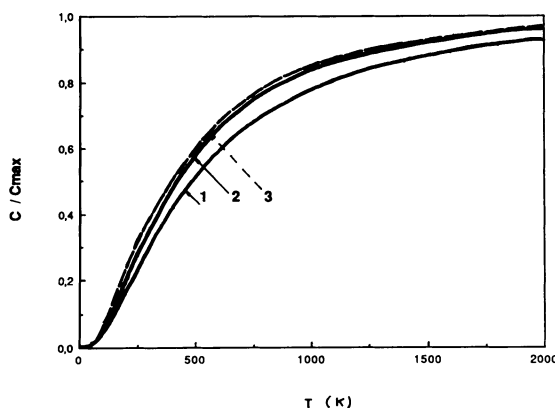


Fig. 5. Internal specific heat per molecule, $C(T)$, normalized to its maximum value, $C_{\max} = (3N - 6)k_B$ where N is the number of atoms in the molecule. Curve (1) refers to hydrogenated molecules ($H/C=0.5$) and curve (2) refers to dehydrogenated ones. Curve (3) is the experimental specific heat for graphite measured by Krumhansl and Brooks (1953). The agreement between (2) and (3) supports the model used (see text).

withdrawing, from the distribution of Fig. (4a), the modes attributed to H motions (ν_{CH} : $3.3 \mu\text{m}$, β_{CH} : $8.6 \mu\text{m}$, γ_{CH} : $11.9 \mu\text{m}$) and assuming that the remaining modes are not perturbed. The corresponding mode distribution is reported in Fig. (4b) and the specific heat in Fig. 5 (curve 2). An alternative approach is to use the specific heat of graphite, curve 3 of Fig. 5, (Krumhansl and Brooks, 1953), because a graphitic plane can be considered as an infinite dehydrogenated PAH molecule. It is encouraging that the two approaches give very similar results (the relative difference is less than 3×10^{-2} at any temperature).

2.5.3. Mean Temperature of Emitting PAHs

The emission of photons and the PAH cooling are ruled by equations (12) and (14), respectively.

For two bands, of a same atomic group (e.g. $C - H$), that occur at different wavelengths, equation (12) relates the absorptions $A_i = \sigma_i \Delta \lambda_i$, to the emissions, $P_i = P_{\lambda_i} \Delta \lambda_i$, through the Planck function. Considering the $\nu C - H$ ($3.3 \mu\text{m}$) and $\gamma C - H$ ($11.3 \mu\text{m}$) modes, one can define a mean temperature T_c for the emitting PAHs during the thermal spike as:

$$\frac{P_{11.3}}{P_{3.3}} = \frac{B_{11.3}(T_c) A_{11.3}}{B_{3.3}(T_c) A_{3.3}} \quad (16)$$

where P_i is the total power emitted in band i . Note that P_i is observed and A_i is measured in the laboratory for different species so that T_c can be determined.

2.5.4. Mean Size of Emitting Molecules

For each molecule size and absorbed UV photon energy, a peak temperature (T_p) is reached and the IR emission follows. It would be most useful to inverse the problem: deduce the nature and size distribution of molecules from observations. Unfortunately, we presently have not enough constraints to do so, and *the use of mean quantities is useful as a first step* to get orders of magnitude of the parameters, although it might be misleading.

For instance, a mean molecule size can be deduced from the color temperature T_c of § 2.5.3. as follows. Using an emission model, which calculates the cooling in each IR line, one can show that for a reasonable range of values, T_c is close to the temperature at which the molecule, cooling from T_p , has lost half of its energy:

$$U(T_c) \approx 0.5 U(T_p) \quad (17)$$

which gives, using equation (13) and for $T_c \sim 600$ K:

$$T_c \approx 0.7 T_p \quad (18)$$

So, the measurement of a color temperature implies a mean value for T_p .

Since PAH molecules have a strong absorption around 2000–2200 Å (Donn, 1968; Léger *et al.*, 1989c), we assume that the mean energy of an absorbed photon is: $\langle h\nu_{abs} \rangle = 6$ eV ($\lambda = 2100$ Å). With $T_c = 600$ K, a mean number of atoms is found:

$$\langle N \rangle \approx 60 \quad (19)$$

So, interstellar PAHs are found to be quite a large species.

2.6. CHARACTERISTICS OF THE IR EMISSION

We briefly describe here some of the results obtained by us and described elsewhere (Léger and d'Hendecourt, 1987).

2.6.1. Absorption Strengths of the Various Transitions

Quantitative absorption spectra of various large PAHs have been recorded in the laboratory. Fortunately, it has been shown that the integrated absorption strengths of the various fundamental bands do not depend much on the molecular size. Thus an *average* absorption strength expressed per unit carbon atom (for $C = C$ modes) or per unit hydrogen atom (for $C - H$ modes) can be used to interpret astronomical observations where the exact configuration of the molecules is not known *a priori*. The average values are given in Table 1.

2.6.2. General Characteristics of the IS PAHs

Besides an average size ($N \sim 60$ atoms) derived in the previous paragraph, Léger and d'Hendecourt (1987) have emphasized the fact that these IS molecules must have a compact structure (like coronene, ovalene), and that non-compact molecules are not present because they possess a strong IR signature at 7 μm which is simply

TABLE 1

Integrated Absorbency of the Main Fundamental Vibrational Transitions in Typical Compact PAH Molecules.

$\lambda_i(\mu\text{m})$	3.3	6.2	7.7	8.8	11.3
	H^{-1}	C^{-1}	C^{-1}	H^{-1}	H^{-1}
A_i^*	1.4	0.7	2.0	1.2	11

* Units are 10^{-25} cm³ per C or H atom

not observed in the astronomical spectra. Moreover, owing to the observed related strength of the 6.2 and 7.7 μm to the 3.3 and 11.3 μm features in IS objects, the IS PAHs are believed to be strongly dehydrogenated (up to 90% of the hydrogen sites are vacant).

Finally, far infrared spectra (up to 100 μm) have also been obtained: in contrast to what is observed in the mid IR range, the far IR spectra do not show band groupings and the observed bands, being due to low frequency vibrations in the whole skeleton of the molecule, are probably very dependent on the size and the shape of the molecules. Consequently, it seems rather difficult to predict spectral features in the far IR region of the spectrum unless a given (or a few) species is particularly more abundant. In any case, very high S/N data would be needed to perform useful observations to be compared with laboratory spectra. Far IR spectra of 4 different molecules can be found in Léger, d'Hendecourt and Défourneau (1989a).

3. CONCLUSION

We have presented in detail the IR emission mechanism of large isolated molecules. The justification of the Thermal Approximation to calculate the IR emission from a large PAH has been clearly given and can be summarized in two points: (1) fast internal conversion and fast internal vibrational redistribution (IVR) before the emission of an IR photon allows the system to reach a state of internal thermodynamic equilibrium, permitting a statistical description of its behaviour; (2) when the energy of a given process is small compared to the total internal energy of the system (i. e. IR photon emission), the simple Boltzmann statistics apply and a vibrational temperature can be assigned to the system. For processes in which condition (2) is not satisfied (e. g. photodissociation of a bond), the full microcanonical treatments must be applied. Note that in the model of Allamandola, Tielens and Barker (1985), condition (1) is also required. They then use the full microcanonical treatment for IR emission.

After the justification of this Thermal Approximation, we have described the IR emission from a large molecule at a temperature T , a temperature which is related to the specific heat of the molecule for which a complete description has been presented. General characteristics of interstellar PAHs, as deduced from comparison

between laboratory and astronomical spectra, have been briefly discussed: highly dehydrogenated molecules containing 60 carbon atoms are likely candidates for the IR infrared emission bands observed in many different objects. Detailed laboratory spectroscopy data can be found in Léger, d'Hendecourt and Défourneau (1989a).

Finally, for reasons of limited space, possible visible fluorescence has not been taken into account, although this important aspect is described in Léger, d'Hendecourt and Boissel (1988) and its astronomical implications is discussed by Ryter and d'Hendecourt (1989).

APPENDIX A

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

$$w = \begin{cases} 10^{-1.0506(U/E_x)^{1/4}} & \text{if } U > E_x \\ \left[5 \left(\frac{U}{E_x} \right) + 2.73 \left(\frac{U}{E_x} \right)^{1/2} + 3.51 \right]^{-1} & \text{if } U < E_x \end{cases} \quad (\text{A2})$$

and

$$\beta = \nu_d \frac{(s-1)}{s} \quad (\text{A3})$$

where ν_d is the frequency dispersion parameter,

$$\nu_d = \frac{\langle \nu^2 \rangle}{\langle \nu \rangle^2}, \quad \langle \nu^2 \rangle = s^{-1} \sum_1^s \nu_i^2, \quad \langle \nu \rangle = s^{-1} \sum_1^s \nu_i$$

REFERENCES

- Allamandola, L. J., Tielens A. G. G. M., and Barker J. R. 1985, *Ap. J. (Letters)*, **290**, L25.
 Avonis, P., Gelbart, W. and El Sayed, M. A. 1977, *Chem. Rev.*, **77**, 793.
 Birks, J. B. 1970, *Photophysics of Aromatic Molecules*, (Wiley-Interscience).
 Bondibey, V. E. 1984, *Ann. Rev. Phys. Chem.*, **35**, 591.
 Cyvin, B. N., Brunvoll J. and Cyvin S. J. 1984, *Spectrosc. Let.*, **17** (9), 559.
 Cyvin, S. J. 1982, *J. of Mol. Struct.*, **79**, 423.
 d'Hendecourt, L. and Léger, A. 1987, *Astr. Ap.*, **180**, L9, Table 1.
 Donn, B. 1968, *Ap. J. (Letters)*, **152**, L129.
 Forst, W. 1973, *Theory of Unimolecular Reactions*, (New York: Acad. Press).
 Gottfried, N. H., Seilmeier, A., and Kaiser, W. 1984, *Chem. Phys. Letters*, **111**, 326.
 Krunhansl, J. and Brooks, H. 1953, *J. Chem. Phys.*, **21**, 1663.
 Léger, A. and Puget, J. L. 1984, *Astr. Ap.*, **137**, L5.

- Léger, A., d'Hendecourt, L. 1987, in *Polycyclic Aromatic Hydrocarbons and Astrophysics*, NATO ASI Series C, V191, eds. A. Léger, L. d'Hendecourt, N. Boccara, (Dordrecht: Reidel).
- Léger, A., Boissel, P. and d'Hendecourt, L. 1988, *Phys. Rev. Letters*, **60**, 921.
- Léger, A., d'Hendecourt, L. and Défourneau, D. 1989a, accepted for publication in *Astr. Ap.*.
- Léger, A., Boissel, P., Désert, F. X. and d'Hendecourt, L. 1989, submitted to *Astr. Ap.*.
- Léger, A., Verstraete, L., Dutuit, O., d'Hendecourt, L., Schmidt, W., Lauer, J. C., Défourneau, D. 1989c, in *IAU Symposium 135, Interstellar Dust*, eds. L. J. Allamandola and A. G. G. M. Tielens, (Dordrecht: Kluwer), p. 173.
- Omont, A. 1986, *Astr. Ap.*, **164**, 159.
- Oref, I. and Rabinovitch, B. S. 1979, *Accounts of Chem. Res.*, **12**, 167.
- Reif, F. 1965, *Fundamentals of Statistical and Thermal Physics*, (McGraw Hill).
- Ryter and d'Hendecourt, L. B. 1989, *Interstellar Dust Contributed Papers*, eds. Tielens, A. G. G. M, Allamandola, L. J., NASA CP-3036.
- Smalley, R. E. 1983, *Ann. Rev. Phys. Chem.*, **34**, 129.
- Whitten, G. Z. and Rabinovitch B. S. 1963, *J. Chem. Phys.*, **38**, 2466.
- Wild, W., Seilmeier, A., Gottfried, N. H., Kaiser, W. 1985, *Chem. Phys. Letters*, **119**, 259.