

GRAINS, OR MOLECULES? THERMAL, OR NON-THERMAL?

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ABSTRACT. The effects of size and energy on infrared fluorescence (IRF) and on chemical reaction rates are investigated, using polycyclic aromatic hydrocarbons (PAHs) as examples. The range of validity of the Thermal Approximation (TA) is examined. It is found that for properties that have a near-linear dependence on the internal energy, the TA provides an adequate description of the non-thermal, time-dependent processes associated with ultraviolet photon absorption. Since IRF at high energy is nearly linear, the TA is adequate for IRF at high excitation energies, but *care* must be taken, because the TA *fails* at low energies. The TA is *never* adequate for chemical reactions under these conditions.

1. INTRODUCTION

Whether species are of molecular size, or are macroscopic grains, and whether the processes they undergo can be described as thermal, or non-thermal are closely related issues that depend on the properties being observed. The major difference between molecules and grains is the number of degrees of freedom, and the difference between thermal and non-thermal systems is a matter of the energy distribution functions. For both issues, there is actually a continuum and the extremes are only the limiting cases. Our approach here is to treat the entire range of energy distributions and species sizes in a consistent manner, insofar as possible.

Most likely, a whole range of species sizes is present in the interstellar medium (ISM). Both free molecular species and macroscopic particles in the ISM can be energized by absorption of a photon and by chemical reactions. The excitation energy can produce ionization and fluorescence, or it may find its way into the vibrational degrees of freedom and produce infrared emission, chemical reaction, reverse internal conversion, etc. Each of these processes acts to reduce the excitation energy and each has a characteristic time scale, which is usually much shorter than the time scale for collisions. Without collisions to maintain an equilibrium distribution, the overall process of excitation/de-excitation is intrinsically non-thermal and time-dependent. Thus there is no reason to expect a thermal distribution.

Although true thermal distributions may not exist in most regions of the ISM, they are very convenient for descriptions of the excited species and for model calculations. In this paper, we will review some properties of vibrationally excited species as functions of size and energy, and we will illustrate the occasional successes and frequent failures of the "Thermal Approximation" (TA) by calculations of infrared fluorescence intensity (IRF) and of chemical reaction rates.

The formal results presented here are general and are not tied to any particular excitation process, molecular species, or macroscopic structure. The properties of polycyclic aromatic hydrocarbon (PAH) species (Léger and Puget, 1984; Allamandola, Tielens, and Barker, 1985) excited by ultraviolet photon absorption (Sellgren, 1984) are used for specific illustrations, because, as a class, they may explain the ubiquitous "Unidentified Infrared Bands" (UIR Bands) associated with many astronomical objects, as discussed in several chapters of this volume. In this paper, neutral PAH molecules are used as illustrations, but their properties probably are substantially similar to the corresponding ionized species, those missing *H*-atoms, and those that are clustered in amorphous carbon aggregates (Allamandola, Tielens, and Barker, 1985, 1987*a*, 1987*b*, 1987*c*, 1988; Omont, 1986). In the case of the aggregates, the number of vibrational modes would correspond to the size of the isolated units (Duley, 1989) of the aggregates, if isolation is truly possible.

In part, the issue of thermal vs. non-thermal descriptions arose because of the different approaches taken by different groups in using the PAH Hypothesis to explain the UIR Bands and to make predictions of chemical stability. For the UIR Bands, Léger and coworkers (Léger and Puget, 1984; Puget, Léger, and Boulanger, 1985; Léger and d'Hendecourt, 1987; Léger, d'Hendecourt, and Defourneau, 1988; d'Hendecourt *et al.*, 1989) have used thermal models, while Allamandola, Tielens, and Barker (1985, 1987*a*, 1987*b*, 1987*c*, 1988; Barker, Allamandola, and Tielens, 1987) have used the non-thermal approach. In considering chemical stability, the latter workers have always used the non-thermal approach, but Léger and Puget (1984) used the thermal approach; recently, Léger and coworkers have adopted the non-thermal approach, as well (Léger, *et al.*, 1988).

In the following sections we review briefly the statistical physics of vibrationally excited species and the UV-excited IRF and the chemical reaction rates from thermal and non-thermal distributions; the concepts involved have been fully developed during the last several decades. We conclude that a combined treatment of all the processes undergone by excited species in the ISM is only possible by considering the non-thermal distribution. However, if only IRF is to be considered, it can be treated adequately with cautious use of the Thermal Approximation. Chemical reaction rates can never be treated adequately with the TA. We also conclude that there is just as much work involved to use the TA for molecular size estimates, as there is with the exact non-thermal distribution, and there is therefore little reason to use the TA.

2. SOME STATISTICAL PHYSICS

A species with N atoms has $s = 3N - 6$ vibrational modes. For energy E in excess of the zero point energy ($E_z = \sum h\nu_i/2$), there are many ways of distributing the energy among the modes, as described by the density of vibrational states $\rho(E)$.

For $E/E_x \geq 0.1$, Whitten and Rabinovitch (1963) showed that:

$$\rho_s(E) = \frac{(E + a(E)E_x)^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i} \quad (1)$$

where $a(E)$ is an empirical factor. For classical systems $a(E) = 0$, for semiclassical systems $a(E) = 1$, and for systems containing PAHs, we find $a(E) \approx 0.813 + \ln(E/E_x)$ (Allamandola, Tielens, and Barker, 1988). This expression describes the density of states based only on s , E_x , and the geometric mean frequency $\langle h\nu \rangle_g = (\prod h\nu_i)^{1/s}$, and it has been thoroughly tested (Robinson and Holbrook, 1972; Forst, 1973) by comparisons with the exact density of states calculated using, for example, the Stein-Rabinovitch (1973) algorithm.

Vibrational assignments for a number of moderately large PAHs were used with the Stein-Rabinovitch algorithm to obtain the exact densities of states. The vibrational assignments also allowed us to obtain simple expressions for E_x and $\langle h\nu \rangle_g$ (expressed in cm^{-1}) for PAHs as functions of s and hydrogen/carbon ratio:

$$\langle h\nu \rangle_g = 650 + 480(H/C) \quad (2)$$

$$E_x = s(-280 + 1.4 \langle h\nu \rangle_g - 5 \times 10^{-4} \langle h\nu \rangle_g^2) \quad (3)$$

Eq. (1), when used with these expressions, gives densities of states in acceptable agreement with the exact counts of states. These simple expressions enable us to estimate densities of states for very large species, for which vibrational assignments have not been made.

The thermal distribution function for large species with an effectively continuous density of states $\rho(E)$ is a Boltzmann distribution:

$$B(E, T)dE = \rho(E) \exp(-E/kT)dE/Q(T) \quad (4)$$

where $Q(T)$ is the partition function at temperature T :

$$Q(T) = \int_0^\infty B(E, T)dE \quad (5)$$

(Robinson and Holbrook, 1972; Forst, 1973). Note that in the thermal (canonical) distribution, all energies are represented: some species have very low energies and some have very high energies. The distribution function describes the relative number of species in the energy range from E to $E + dE$. The thermal average of any quantity $F(E)$, which may be a function of energy, is given by:

$$\langle F \rangle = \int_0^\infty F(E)B(E, T)dE \quad (6)$$

(Davidson, 1962). In particular, the average energy is $\langle E \rangle$, where $F(E) = E$. The heat capacity at constant volume is $C_v = \langle E \rangle / kT$ and can be calculated from the above expression, or directly from expressions where harmonic vibrations are assumed (Davidson, 1962).

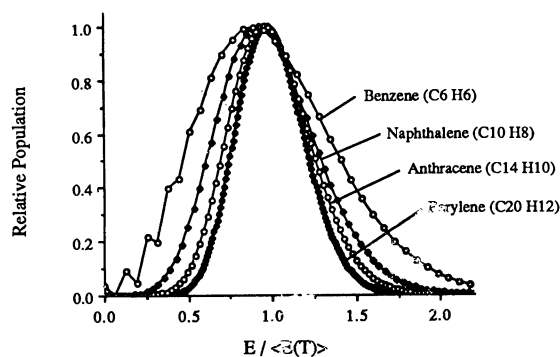


Fig. 1. Normalized thermal distributions vs. reduced energy for several aromatic hydrocarbons. $\langle E(T) \rangle$ is the average thermal energy at temperature $T = 1000$ K.

If an ensemble of isolated species with no internal energy is exposed to light of a single wavelength, all of the species that absorb the light have identical internal energies equal to the photon energy (Barker, 1983). For molecules with more than 4–5 atoms, the internal energy is rapidly redistributed among all accessible quantum states (Oref and Rabinovitch, 1979; Bondybey, 1984) and the relative weight of each such state is proportional to the density of states. The ensemble of such excited species, all with the same energy, distributed statistically among all accessible states, is called a microcanonical ensemble. This delta function in energy is quite distinct from the broad energy distributions characteristic of canonical (thermal) systems illustrated in Figure 1. Note that the thermal distributions are very broad, even for perylene ($C_{20}H_{12}$), although the relative width becomes smaller as the number of oscillators increases. Free molecules typically absorb light in bands that are relatively narrow, compared with the widths of thermal distributions. Thus, energy distributions of excited molecules sometimes may accidentally resemble thermal distributions, but the distributions usually are much better approximated by delta functions. On the other hand, macroscopic particles may absorb over broader wavelength ranges (more like blackbodies), and thus the energy distributions may more closely resemble thermal distributions. For present purposes, we will consider absorption only over narrow wavelength ranges, but a straightforward generalization can be made to extend calculations to more realistic situations. Any distribution function can be constructed from a linear combination of delta function distributions (Davidson, 1962).

3. THE THERMAL APPROXIMATION AND IR EMISSION

The TA can be summarized succinctly by the following expression:

$$F(\langle E \rangle) \approx \langle F(T) \rangle \quad (7)$$

where $\langle F(T) \rangle$ is the thermal average of $F(E)$ at temperature T and $\langle E \rangle$ is the average thermal energy at the same temperature. This approximation is more accurate when $F(E)$ is approximately a linear function of energy over the energy

range corresponding to the width of the thermal distribution. This approximation has been used extensively by Léger and coworkers (Léger and Puget, 1984; Puget, Léger, and Boulanger, 1985; Léger and d'Hendecourt, 1987; Léger, d'Hendecourt, and Defourneau, 1988; d'Hendecourt *et al.*, 1989).

Vibrationally excited harmonic oscillators with energy E emit IRF in $\Delta v = -1$ transitions from all vibrational modes, according to the fundamental expression (Herzberg, 1945):

$$I(E) = h\nu_{v,v-1} A^{v,v-1} N_v \quad (8)$$

where N_v is the concentration of oscillators containing v quanta and $A^{v,v-1}$ is the Einstein coefficient for spontaneous emission from the level v of the vibrational mode; anharmonic oscillators are well-described by the same expression. This expression can be evaluated by noting that for harmonic oscillators, $A_{v,v-1} \approx v A^{1,0}$ and by making the ergodic assumption that energy is distributed statistically among all the accessible states. These approximations are fully justified (Durana and MacDonald, 1977; Barker, 1983; Barker, 1984; Shi, Bernfeld, and Barker, 1988). According to the ergodic assumption,

$$N_v = N(E) \frac{\rho_{s-1}(E - v h\nu)}{\rho_s(E)} \quad (9)$$

where $N(E)$ is the concentration of molecules with total energy E , $\rho_s(E)$ is the total density of states, and $\rho_{s-1}(E - v h\nu)$ is the density of states for the $s - 1$ oscillators, excluding the emitting mode and the energy contained in it. Thus the IRF emission from the i^{th} vibrational mode is given by:

$$I(i, E) = \frac{N(E)}{\rho_s(E)} h\nu_i A_i^{1,0} \sum_{v_i=1}^{v_{\text{max}}} v_i \rho_{s-1}(E - v_i h\nu_i) \quad (10)$$

where the summation is over all levels that are energetically accessible; the individual terms are the contributions from each level.

The validity of Eq. (10) has been verified in experiments using laser excited gas phase azulene ($C_{10}H_8$), an unusual PAH consisting of fused five- and seven-membered rings (Barker, 1984; Shi, Bernfeld, and Barker, 1988). Very recent wavelength-resolved measurements (Cherchneff and Barker, 1989) on this emission reveal a lineshape that may indicate the contributions from the various $\Delta v = -1$ components (Barker, Allamandola, and Tielens, 1987) in the summation of Eq. (10). Note that at high energies, $I(E)$ is approximately linear, but at low energy there is a distinct threshold, since molecules with less energy than the IRF quantum cannot emit. Thus, one would expect that at high energy the TA would be more accurate than at low energy.

However, the accuracy of the TA depends not only on the function $I(E)$, but also on the relative width of the thermal distribution function, which decreases as molecular size increases. To illustrate how both of these factors interact, consider the analytic expression for the ratio $I(\langle E \rangle) / \langle I(T) \rangle$ for a collection of classical oscillators:

$$I(\langle E \rangle) / \langle I(T) \rangle = (1 - s^{-1})(1 - h\nu E^{-1})^{s-2} \exp(-sh\nu/E) \quad (11)$$

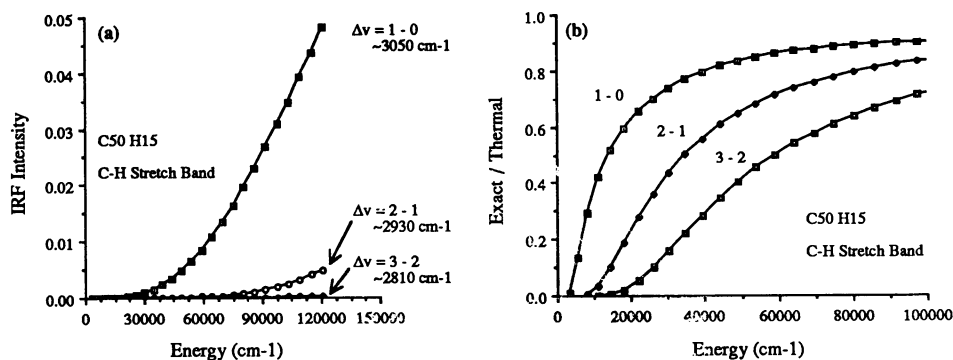


Fig. 2. (a) Relative contributions to IRF band intensity from several $\Delta v = -1$ transitions. Note that the approximate frequencies are given for each component. (b) Comparison of exact non-thermal IRF intensity to the thermal average for the same components shown in Panel (a). When the ratio equals unity, the Thermal Approximation is exact.

where $\langle E \rangle = E = skT$ and the other quantities have been defined. *Note: this expression is very inaccurate for quantitative calculations and is only used for illustrative purposes!* When this expression approaches unity the TA is accurate, but that is only when both s and E approach infinity. This is because the relative width of the thermal distribution is small for large s , and because $I(E)$ is more nearly linear for large E .

Eqns. (1) to (3) were used to estimate densities of states for the hypothetical species $C_{50}H_{15}$ and $I(E)$ was calculated for several $\Delta v = -1$ components of the emission, as shown in Figure 2(a). Once again, the curves become more linear at high energies. In Figure 2(b) are presented the corresponding ratios of $I(\langle E \rangle) / \langle I(T) \rangle$ for each of the components and the results show that the TA tends to become more accurate at high energies. Crudely speaking, we find that the TA is acceptable for IRF emission, if the internal energy is greater than about ten times the energy of the emitting level and the PAH is not too large: *Use caution!* The use of the TA is not preferred, however, since errors in intensity ratios can lead to substantial differences in estimates of molecular size. Moreover, in the ISM, excited species deactivate themselves through emission of infrared photons and their energies decay in a cascade, as calculated for chrysene ($C_{18}H_{12}$) (Allamandola, Tielens, and Barker, 1984, 1987a, 1987b, 1987c, 1988). Late in the cascade, the TA may break down badly for high frequency modes, but may still be accurate for the lower frequency modes and therefore the calculated intensity ratio will be inaccurate. Since the intensity ratios for lines near $3.3 \mu\text{m}$, $3.4 \mu\text{m}$, and $12 \mu\text{m}$ are used to estimate upper limits to the size of the emitting species (Allamandola, Tielens, and Barker, 1984, 1987a, 1987b, 1987c, 1988; Barker, Allamandola, and Tielens, 1987; Léger and Puget, 1984; Léger, d'Hendecourt, and Defourneau, 1988), use of the TA can lead to poor estimates of molecular size, unless great care is taken: we find the error in molecular size is roughly proportional to the error in the intensity ratio. Moreover, as shown below, the TA fails totally for chemical reactions, where the exact non-thermal approach *must* be used.

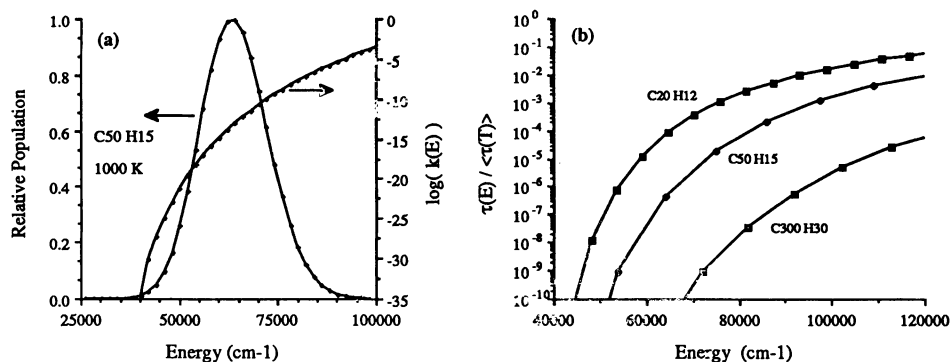


Fig. 3. Reaction rate constants and time constants for loss of H -atoms. (a) Thermal energy distribution function (1000 K) for $C_{50}H_{15}$ and reaction rate constant vs. vibrational energy. (b) Comparisons of reaction time constant for exact non-thermal distributions with those for thermal distributions. The Thermal Approximation would be exact when the ratio equals unity.

4. CHEMICAL REACTIONS

For a unimolecular reaction, the concentration of reactant C , denoted with square brackets, is described by the following:

$$\frac{d[C]}{dt} = -k(E)[C] \quad (12)$$

$$[C(t)] = [C(t=0)] \exp(-k(E)t) \quad (13)$$

The reaction time constant is $\tau(E) = 1/k(E)$, where $k(E)$ is the reaction rate constant, which is a function of the energy. Statistical theories of unimolecular reactions have been well-developed and tested over several decades (Robinson and Holbrook, 1972; Forst, 1973) and several simple versions are suitable for estimating $k(E)$'s for PAHs (Barker, 1983; Tielens, *et al.*, 1987; Allamandola, Tielens, and Barker, 1988; Léger, Boissel, Désert, and d'Hendecourt, 1988). A particularly convenient form for present purposes is $k(E)$ derived from the inverse Laplace transform of the thermal average reaction rate constant $\langle k(T) \rangle = A_{\infty} \exp(-E_{\infty}/kT)$, where A_{∞} has units of s^{-1} :

$$k(E) = A_{\infty} \frac{\rho_s(E - E_{\infty})}{\rho_s(E)} \quad (14)$$

(Forst, 1973). For convenience, the average thermal lifetime is defined as $\tau(T) = \langle k(T) \rangle^{-1}$, because $\langle k \rangle^{-1} \approx \langle k^{-1} \rangle$.

The thermal loss of H -atoms has been investigated for gas phase benzene (C_6H_6), giving $A_{\infty} = 10^{16.5} \text{ s}^{-1}$ per H -atom and $E_{\infty} = 39000 \text{ cm}^{-1}$ (Kiefer, *et al.*, 1985). These parameters were adopted in calculations comparing the thermal average chemical lifetime and that for an energy delta function. Here, $k(E)$ varies by many powers of ten over the energy width of the thermal distribution function, as illustrated in Figure 3(a), producing the expected failure of the TA illustrated in Figure

3(b). Clearly, only the exact non-thermal distribution function should be used for calculations of chemical stability in this dynamical system.

5. CONCLUSIONS

The Thermal Approximation is accurate only when the property investigated is itself approximately a linear function of internal energy over the range of the thermal energy distribution function. For infrared fluorescence intensities, $I(E)$ is sufficiently linear at high energies so that the TA gives reasonable estimates, but *caution* must be used, because the validity of the approximation depends on internal energy, IRF wavelength, and molecular size. For chemical reactions, the TA is *never* acceptable, because $k(E)$ varies very strongly with internal energy. Since IRF, chemistry, and other properties can be treated simultaneously with the exact approach (Barker, 1983), and the amount of work involved in using the exact approach for molecular size estimates is no greater than in using the TA, we recommend that the exact approach be adopted for this purpose.

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