ASTRONOMY
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Suprathermal rotation of PAHs in the ISM

I. Is the width of the UIBs affected?

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Abstract. We have shown in a previous paper that the broadening of the $\lambda\,5797$ DIB seen in emission in the Red Rectangle, can be explained by a rotational envelope indicating a high rotational temperature, and that, indeed, a molecular carrier such as a PAH, could reach an angular velocity much higher than expected from thermal equilibrium. Here, we apply our physical model of the rotation of PAHs in different conditions met in the ISM: circumstellar envelope, cirrus, dense cloud edges and reflection nebulae. We show that the prediction of a largely suprathermal rotational temperature is extended to all cases: except for the special case of the reflection nebulae, where the temperature is suprathermal but clamped to only ≈ 100K for any PAH size, we find that rotational temperatures within the range $100 - 10^5$ K could be current in all other situations as long as the PAH size is between 100 and 600 atoms. In a second step, we explore the possible consequence of a fast rotation of a PAH on the width of the Unidentified Infrared Bands, prompted by our prediction that suprathermal rotation could be current and the recent ISO results showing that the UIBs intensity ratios and band widths are similar whatever the environmental parameters are. The evaluation of the rotation-induced broadening is performed, and we show that it is, in any cases, lower than 6 cm^{-1}, i.e. much too low compared to the observed width of the UIB. We conclude that the observed universality of UIB 's width cannot be explained by a rotational structure, even if very suprathermal rotation is predicted.

Key words: ISM: molecules – molecular processes – infrared: ISM: lines and bands

1. Introduction

A recent result in the physics of the Interstellar Medium (ISM) has been obtained in the long standing problem of its Diffuse Interstellar Bands (DIB) in the visible. Remarkable observations on the Red Rectangle have shown that the widths of several of these bands were depending upon the distance to the star and could be nicely interpreted in term of rotational structure of

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molecular electronic transitions (Schmidt et al. 1991; Scarrott et al. 1992; Warren-Smith et al. 1981).

In addition to a strong indication that the carriers of these DIBs were molecular species it has prompted us to calculate the mechanism of this rotation and conclude that it was suprathermal (Rouan et al. 1997a ; hereafter RLL). It is then natural to ask the question whether such a suprathermal rotation could be found in other components of the ISM. The impact of a component of very rapidly rotating molecules could be of importance in many respects: polarization of line emission, radio emission, broadening of the line emission by the rotational structure. The purpose of this paper is twofold: a) to extend the evaluation of the rotational temperature we previously made in the case of the Red Rectangle, to other well defined situations found in the ISM (Sect. 2); b) to investigate one of the potential consequences of a suprathermal rotation of PAH, namely the possible broadening of the Unidentified Infrared Bands by a rotational structure ; this mechanism has been suggested in order to explain the surprising result of ISO that the shape of the UIBs is somewhat universal, i.e. practically independent of the conditions of irradiation of the emitting medium. In Sect. 3 we discuss this last point , while in Sect. 4 we perform the evaluation of the rotational broadening.

2. Rotational temperature of PAHs in the ISM

The $\lambda 5797$ Diffuse Interstellar Band, observed in emission at several positions in the Red Rectangle exhibits a band shape typical of molecular rotational structures of an electronic transition. A peculiarity is that the rotational temperature to explain the observed band width is much higher than the temperature evaluated for the hydrogen gas. In RLL we addressed the question of the suprathermal spinning of a free PAH molecule, investigating the physics of the rotation. Following the method of Rouan et al.(1992, hereafter RLOG), we considered different processes of angular momentum exchange with a free PAH, and we showed that only an efficient rocket effect (H-atom or H$_2$ molecule ejection) can lead to the suprathermal rotation required by observations of the Red Rectangle.

The processes that exchange angular momentum with the molecule and that we took into account are:

- collisions with the gas: elastic or inelastic when a H-atom binds to the molecule, with subsequent
- ejection of H or H_2 species, for instance as a consequence of a UV photon absorption; a peculiar and important case is an asymmetric ejection that leads to a systematic rocket effect
- absorption of UV photons
- emission of IR photons after such an absorption
- emission of radio rotational photons

The main results of Paper I and II can be summarized as follows:

- The angular momentum of an interstellar PAH is mainly built-up by the emission of IR ro-vibrational photons, when the UV flux is large; this is done through a random walk ($\Delta J = \pm 1$) with an asymmetric probability, so that the process is self-regulating, with a tight pull-back effect, and would lead, if alone, to a clamping of the rotational temperature at $T_{IR} \approx 100$K.
- The resulting distribution of J, is pseudo-thermal with $kT_J = kT_{IR}$.
- The Intramolecular Vibration-Rotation Energy Transfer (IVRET, Mc Clelland et al. 1988) is an extremely efficient mechanism that forces the large inertia axis of the molecule to be distributed around the angular momentum $\boldsymbol{J}$ with the same temperature as the vibrations (for a symmetric top molecule, $T_K = T_{vib}$). This axis is either almost isotropically distributed and suffers frequent changes just after the absorption of a UV photon ($T_{vib} >> T_J$) or aligned along $\boldsymbol{J}$ during the cold periods in between thermal spikes ($T_{vib} << T_J$).
- Interaction with the gas can be strongly dominated by the rocket effect, as long as the UV field is not too large (typically $E_{UV}/\sqrt{n_H} < 0.13\,\mathrm{eV\,cm^{-3/2}}$).
- There is , for a non-zero dipole moment μ of the molecule, an extremely fast dependence of $A_{J \to J-1}$ with the molecule size:

$$A_{J \to J-1} \quad \propto \quad N_C^{-6}\, \mu^2\, J^3;$$

this dependence dramatically limits the rotational temperature of small particles, because they cool very efficiently by radio emission.

The model we built is not specific of the Red Rectangle and can be used with any set of environmental constraints for a molecule in the ISM : from circumstellar envelopes to diluted cirrus. We examine now whether a rotational temperature as high as in the Red Rectangle, or even larger, can be predicted in other components. The four following environments have been studied to represent typical conditions met in the ISM:

- Circumstellar envelope of the Red Rectangle ; typical of high density and medium-high photon flux;
- Reflection nebulae: we used the conditions of NGC 2023, the archetype of those Photon Dominated Regions (PDR), featuring a very high level of UV irradiation and a medium gas density;

Table 1. Parameters characteristic of the four different environments we have considered as typical of the ISM.

Environment (archetype)	n_H (cm^{-3})	E_{UV} (eV cm^{-3})	T_{gas} (K)
Circumstellar envelope (Red Rectangle)	$15\,10^3$	4	35
Reflection Nebula (NGC 2023)	$15\,10^3$	50	100
Cirrus	30	0.08	100
Dense molecular cloud edge (Rho Oph)	10^3	0.8	100

- Cirrus: this is typical of the HI diluted component of the ISM, with both a low gas density and a low photon flux (standard ISRF);
- Dense clouds edges: we have chosen the conditions found at the edge of the Rho Oph cloud (Boulanger et al. 1996) ; this region is typical of a medium density and medium-low photon flux (typically $10 \times$ ISRF).

Table I summarizes the values of the gas density, radiation field and gas temperature, adopted for those four different situations we have considered.

Our model consists, for the essential, in solving the equilibrium equation of the angular momentum J, for each set of parameters. This leads to the results illustrated on Fig. 1a–d, where the quantum number J is converted to rotational temperature through the relation: $kT_{rot} = BJ^2$, where B is the rotational constant of the molecule. In RLOG, we showed that $B \approx 0.5\,10^{-3}\,(\frac{N}{78})^{-2}$ cm^{-1}. About the rocket effect, we have taken into consideration two cases: one where it is strong, i.e. with an energy of ejection of 1 eV and an asymmetry factor of 0.3 (see RLOG for the precise meaning of those quantities) and one where it is weaker, with $E_{ej} = 0.1$ eV and $\alpha_{assym} = 0.1$. Fig. 1a–d displays the results for those two cases. In all situations, we have assumed that the static dipole moment μ was 1 Debye, that the ionisation fraction of PAHs was 50 % and that all species were deshydrogenated.

One finds that, *except* for the region of high UV irradiation (*reflection nebula* exemplified by NGC2023), a suprathermal rotational temperature is the rule, even when a weak rocket effect is considered. For the largest species ($N_{carb} = 1\,000$), a temperature as high as 2-3 10^5 K could be reached in a rather dense medium such as the Rho Oph cloud or the Red Rectangle, while temperatures larger than 1 000K could be current for size implying a few hundred carbon atoms. Regarding the case of the reflection nebula, we confirm the result previously obtained that a strong UV flux is responsible of such an important exchange of angular momentum through IR photon cooling, that the temperature is maintained at a value of ≈ 100K, whatever the size of the PAH and the strength of the rocket effect are. However, these results can be affected by some uncertainties because we did not take into account in our model some gas-grain interactions such as collisions with ions and effect of plasma drag as proposed by Draine & Lazarian (1998a) and described in de-
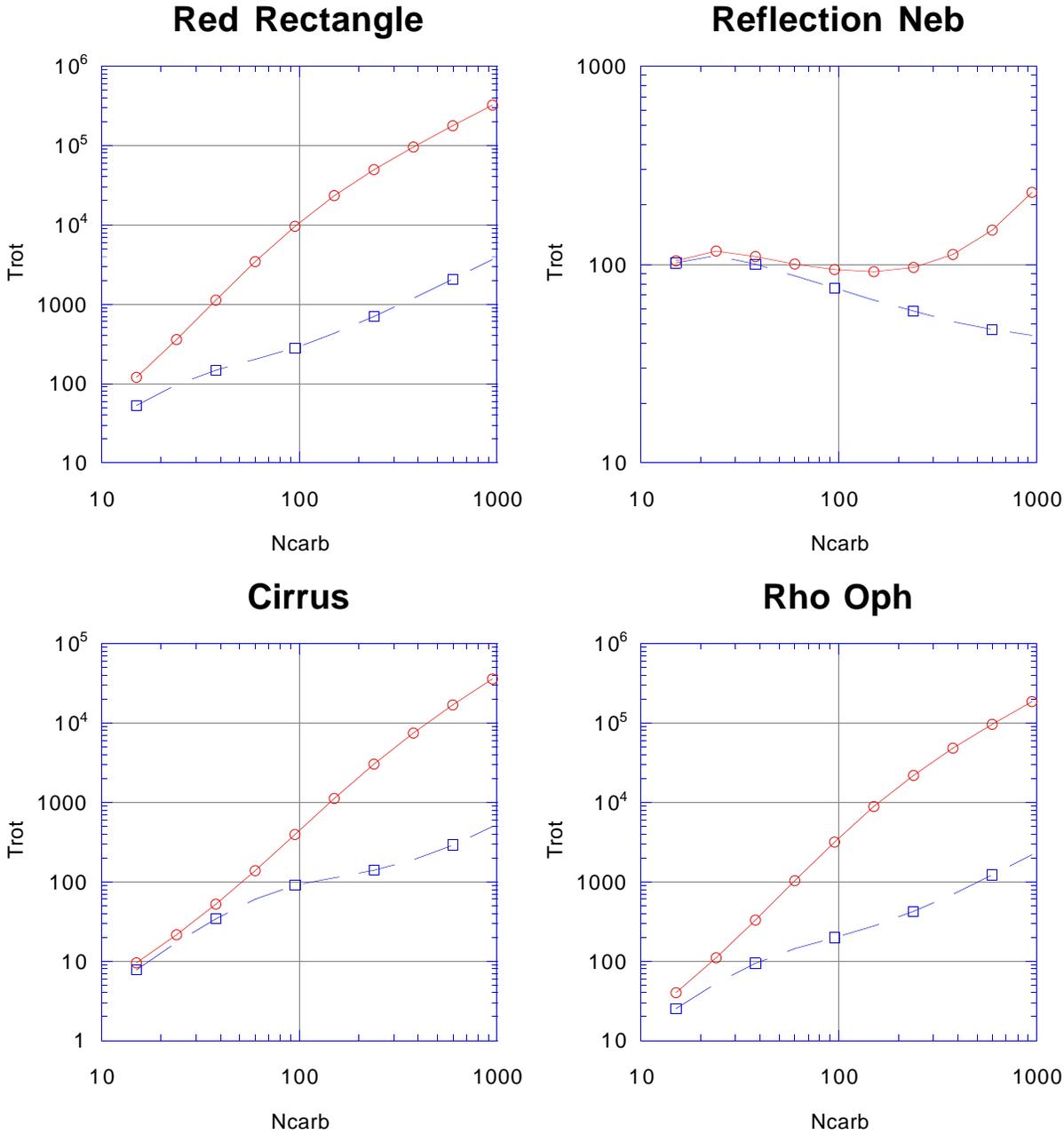
Fig. 1a–d. Rotational temperature of PAH molecules versus their number of carbon atoms, in four different environments: **a** Circumstellar envelope (10 arcsec from the central star in the Red Rectangle) ; **b** Reflection Nebula (NGC 2023); **c** Diffuse medium (IRAS cirrus); **d** edge of molecular cloud (Rho OPh).

tail in a preliminary paper (Draine & Lazarian, 1998b). These processes are not negligible in several cases and may lead to a significantly different rotational temperature compared to our model. But it is important to note that these mechanisms are not systematic effects such as the rocket effect and we expect that they will contribute essentially to damp the rocket effect, i.e. in all cases to lead to lower temperatures. For instance, in the two cases of media considered by Draine & Lazarian that can be compared to two of those we examine here (cirrus and dense molecular cloud), the rotational temperature one can derive from their result is typically 130 K for the PAH sizes we

consider. The two other cases of media where the photon flux is high are not examined by Draine & Lazarian, and a direct comparison cannot be done, but the conclusion should be the same: our temperature estimate is likely an upper limit.

The conclusion raised by those results is that, on a given line of sight through the Galaxy, there may be chance to find a large fraction of suprathermally rotating PAHs ; in such conditions, the idea that the suprathermal rotation could play a significant role in the broadening of the UIB may have a meaning: this is what we explore now.

3. A major and surprising ISO result

The PAH model of the Unidentified Infrared Bands (UIB), supported by the IRAS photometric observations, has lead to the prediction that these bands should be observed in most ISM regions, whenever they are irradiated. The prediction standed even for low levels of irradiation when the mean temperature of molecules is quite low (Boulanger et al. 1985). The UIB bands had been observed for several years in bright regions such as Reflection Nebulae and Planetary Nebulae (Gillett et al. 1973; Sellgren 1984) but recent balloon borne observations (Giard et al. 1988) and ISO ones have been necessary to study regions with low irradiation as galactic Cirrus Clouds because of the weakness of their IR emission. The former observations have given evidence of the presence of the 3.3 μm and 6.2 μm bands (Ristorcelli et al. 1994) and the latter beautiful spectra in the 4.5-16.5 μm range (Boulanger et al. 1996; Bernard et al. 1997). This result has been recently extended to the diffuse ISM of external galaxies (Rouan et al. 1997b).

A major, and surprising, result by ISO is the obvious similarity of these emission spectra in regions where the irradiation field varies by about 4 orders of magnitude (Mattila et al. 1996). This similarity deals with the position, width and relative intensities of the bands at 6.2, 7.7, 8.6, and 11.3 μm. Because of the lower sensitivity of ISO at short wavelengths, the 3.3 μm band shapes has not yet been observed in Cirrus. The main contributions to the *width of molecular vibrational band in emission* are:

– The coupling between normal modes to describe actual molecules. This coupling introduces finite life times τ and bandwidths ($\Delta E \approx \frac{\hbar}{\tau}$)
– Molecules being hot (300-1 000K) when they emit in mid IR, the transition can occur between excited levels, e.g. n=2 $\rightarrow$ 1. The anharmonicity of actual potential curves leads to photon energies somewhat different from those ending to the fundamental level (n=1 $\rightarrow$ 0). In addition these transitions occur in a hot molecule with several other vibrational modes excited. It implies a coupling with the transition mode different from what it is at low temperature. This leads to so-called hot modes with somewhat different energies.
– In the PAH hypothesis, the carriers of the UIB are not expected to be a single species, but a family of aromatic molecules. Although the bands correspond to the motion of given groups of atoms, e.g. CH bend, they occur at energies which depend on the precise species.
– Mid-IR transitions are not purely vibrational but ro-vibrational. Their rotational structure can be a significant source of spreading of the bands.

In this paper, we discuss whether the latter contribution is a minor or a major one to the observed bands, the more as there are indications of suprathermal rotation of molecules in the ISM.

4. Line broadening induced by rotational temperature

4.1. Energy's variation during a ro-vibrational transition

When excited by absorption of a UV photon, a PAH molecule can be heated to a temperature of about 1 000 K and then cools within a few seconds through emission of IR photons corresponding to ro-vibrational transitions (see the review by Puget & Léger 1989). We examine the hypothesis that the width of those band arise from the rotational structure of the transitions.

As a guide, let's consider first the case of a linear molecule which is characterized by a single rotational constant. We consider a transition between two ro-vibrational levels $E_I(v, J, B)$ and $E_F(v', J', B')$ where B is the rotational constant: it can be different between the initial and the final level, J is the angular momentum quantum number and v is the vibrational quantum number. The energy in one level can be written as:

$$E(v, J, B(v)) = (v + \frac{1}{2})h\nu_0 + B(v)J(J+1)$$

and the variation of energy during the transition is:

$$\Delta E = \Delta v\, h\nu_0 + 2BJ\Delta J + \Delta BJ^2 \tag{1}$$

where Δv and ΔJ are supposed to follow some selection rules. The first term, by far the largest one, corresponds to the central wavelength of the vibrational transition, while the last two terms describe the broadening of the band that we want to evaluate. The second term is simply due to the change of angular momentum J, while the third one is due to the variation of the rotational constant B. Such a variation is indeed expected because in a vibrationally excited state, for instance if a mode of dilatation is excited, the molecule has an average moment of inertia which is slightly different than at rest.

When considering a collection of molecules, the average effect must be computed on the statistical distribution of J. It has been shown in RLOG that the distribution of angular momentum J most generally follows a Maxwell-Boltzmann's law, since its building-up results from the competition of various random walks. Taking into account degeneracy because of the planar nature of the molecules, we assume, as in RLOG, that the statistical distribution of the number of molecules with quantum number J type follows the law:

$$N(J) = N_o J^2 exp(-BJ^2/kT_{rot})$$

4.2. Line broadening due to the PQR separation

The second term in Eq. (1) is at the origin of the so-called P,Q and R rotational branch structure. They correspond respectively to permitted variations of J of -1, 0 ,+1. The rotational constant B is inversely proportional to I, the moment of inertia of the PAH molecule, so the effect of broadening will be greater for small molecules. The P,Q and R branches can be easily computed, assuming a Boltzmann distribution of J. The broadening due to the combination of the separation of branches P and R and of the Boltzmann distribution of J can be approximated by: $\Delta(h\nu) \approx 3.3\sqrt{BkT_{rot}}$ in the linear molecule.

In order to test the validity of such an approximation for planar molecules, we have used the computations of rotational band contours by Cossart-Magos & Leach (1990) to derive the semi-empirical relation: $\Delta(h\nu) \approx 4.0\sqrt{BkT_{rot}}$ which fits well the cases of benzene and coronene. The rather close values of the coefficients of $\sqrt{BkT_{rot}}$ found in those two approximations, makes us confident that the right order of magnitude can be found with one or the other of those relations.

For instance, in the case of a molecule of about 100 carbon atoms, the rotational temperatures are respectively of $100K, 300K$ and $10^4 K$ in reflection nebula, cirrus and Red Rectangle. At most, in the case of the Red Rectangle, it correspond to a broadening of the band of: $\Delta(h\nu) \approx 5.77$ cm^{-1}.

It's clear that such an effect is negligible compared to any actual width of the UIB, for example the width of the 11.3 μm band which is about 800 cm^{-1}. However, for low energy modes of vibration, where coupling with other modes is much less efficient, it is not unlikely that this rotational envelope could be observed, for instance with the spectrometer onboard of the future FIRST satellite.

4.3. Line broadening due to the variation of the rotational constant B

The second contribution to the rotational broadening is described by the last term of Eq. (1). This is due to the difference in the rotational constant between the lower level and the excited level. In a first time, the model of a linear molecule is used to obtain the simple expression of the broadening for this case. It reads then: $\Delta(h\nu) = kT_{rot}\frac{\Delta B}{B}$

Then, using again the results of Cossart-Magos semi-empirical approximation $\Delta(h\nu) = K \; kT_{rot}\frac{\Delta B}{B}$, we adjust the coefficient K on benzene and coronene molecules and find that the broadening of the bands for planar molecules can be well approximated by the following relation:

$$\Delta(h\nu) \approx 2.5 \; kT_{rot}\frac{\Delta B}{B} \tag{2}$$

To estimate the value of $\frac{\Delta B}{B}$, we have to calculate the variation of the moment of inertia of the molecule during the transition, since:

$$\frac{\Delta B}{B} = \frac{\delta I}{I}$$

and

$$\frac{\Delta B}{B} = \frac{8\pi^2 CB}{h}\delta I$$

We consider the case of one single excited mode and a transition between this state and the fundamental one. Thus, one can describe the moment of inertia of the whole molecule in the excited state as:

$$I = \sum_i m_i < (X_i + x_i)^2 >$$

where m_i and X_i are respectively the mass and the distance at rest to the center of mass of the ith atom in the PAH molecule. The variation of I is:

$$\delta I = \sum_i m_i < x_i^2 >,$$

because

$$< x_i > = 0.$$

In the case of only one excited mode, the variation of distance of the ith atom can be written as:

$$x_i = x_i^0 \cos(w_0 t)$$

Then, the kinetic energy of the system and the variation of the moment of inertia are expressed as:

$$E_c = \frac{1}{2}\sum_i m_i < \dot{x}_i^2 > = \frac{1}{4} \; w_0^2 \sum_i m_i x_i^{0\,2}$$

$$\delta I = \frac{1}{2}\sum_i m_i x_i^{0\,2},$$

so that:

$$E_c = \frac{1}{2} \; w_0^2 \; \delta I$$

This expression is also equal to the energy of excitation of one phonon which is $\frac{1}{2}\hbar w_0$. The variation of the moment of inertia is then simply expressed as:

$$\delta I = \frac{\hbar}{w_0}.$$

This leads to a simple relation between the variation of the rotational constant B and the wavelength of the transition:

$$\frac{\Delta B}{B} = 2B\lambda$$

In the case of a molecule of 100 carbon atoms and for the band at 11.3 μm, this gives:

$$B = 3\ 10^{-4} \text{ cm}^{-1}$$

and

$$\frac{\Delta B}{B} = 6.78\ 10^{-7}$$

Then, backward in Eq. (2), taking a rotational temperature of at most $10^4 K$, we find a width $\Delta(h\nu) \approx 0.0117$ cm^{-1}.

We conclude: a) that the broadening due to ΔB is much less important than the P-R branches splitting, in contrast with the case of electronic transitions (DIB) where the reverse situation was found; b) that even for the highest rotational temperature in the ISM, this contribution is much too low to *explain the observed feature's width* of the UIB.

5. Conclusion

In a former paper (RLL), we showed that the Diffuse Interstellar Bands, if carried by PAH molecules, can be significantly broadened by a rotational structure, since the rotational temperature can be largely suprathermal, and, indeed, the DIBs seen in emission in the Red Rectangle do exhibit such a broadening. We wondered then, in the case of the UIB bands which correspond to ro-vibrational transitions – while DIBs are electronic transitions – , if a similar effect can lead to a significant broadening too. A first question is then: can a suprathermal rotation be predicted in the ISM and if yes, is it current? Using the model previously developed for the RR, which includes various physical processes of angular momentum exchange, we have estimated the rotational temperature in four different cases representative of the various conditions met in the ISM: circumstellar envelope, reflection nebulae, cirrus, dense molecular cloud edges. In *all cases* but the reflection nebula (this special case will be investigated in a forthcoming paper), we found that indeed a suprathermal rotational temperature was predicted. The larger the molecule, the more the rotation is suprathermal: for instance, temperatures up to $10^4 K$ could be found in a dense cloud for a PAH of a few hundred carbons. However, in the future, we have to add in our model interactions such as collisions with ions and plasma drag that might lower considerably these estimates because of the efficient damping effect they make. We stress then that such high rotational temperatures are then strict upper limits and do not change our following conclusion.

We have then examined the possible effect on broadening of the UIB that such a high temperature could induce. This question was prompted by the recent ISO finding that the UIB width was surprisingly large and similar, whatever the emitting medium was, as if an universal broadening mechanism was acting. The line broadening for a transition between two ro-vibrational levels consists in several contributions; we have examined, here, only those induced by a large rotational temperature: one is the split between P Q and R branches which increases as $\sqrt{T_{rot}}$ and another one is due to a possible variation of the rotational constant B between the two levels of the transition, inducing a broadening directly proportional to T_{rot}. We have, for both, evaluated their contribution to the broadening: the first effect is about 5.77 cm^{-1} for a rotational temperature of $10^4 K$ and the second one is lower than 1 cm^{-1} for a realistic rotational temperature of the ISM, when the typical width of the UIB bands are at least of hundred of cm^{-1}. The conclusion is that the universal width of the UIBs can not be explained by a rotational structure, even for a suprathermal rotational temperature whatever the size of the molecule.

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