

UIB emission without UV irradiation

A case study: M 31

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Abstract. The galaxy M 31 is interesting, in particular, because its diffuse interstellar medium emits the Unidentified Infrared Bands although it is devoid of far UV radiation. This compels us to seek an alternative to stochastic, transient, heating of dust by absorption of far UV photons. The alternative proposed here is chemiluminescence, or the excitation of the vibrations of chemical bonds of carbonaceous dust by impact of gaseous H atoms. This mechanism was studied numerically on several molecules, using standard chemical codes to simulate the molecular dynamics upon impact. It was found that this process selectively excites several IR-active modes, which fall in the astronomical IR bands of interest. After a brief transient redistribution, these vibrational modes no longer exchange energy on the long term and are expected to decay only through IR emission. The efficiency of this process was found to be ~ 0.3 . The relative intensities of the IR features do not depend on the ambient radiation field. The far UV enters only indirectly, in as much as it increases the density of ambient H atoms.

A chemical kinetic model was built on this basis for the interactions of dust, H atoms, H₂ molecules and far UV photons in the H I regions of M 31. It is in very good numerical agreement with the observations of Pagani et al. (1999).

Key words: ISM: dust, extinction – ISM: H II regions – infrared: galaxies – infrared: general – infrared: ISM: lines and bands

1. Introduction

Quite understandably, most of the earlier Unidentified Infrared Band (UIB) spectra were obtained from strongly illuminated nebulae such as H II regions and galaxies hosting active star formation regions. In these cases, the nearby young (O and B) stars radiate abundantly in the UV (110–240 nm) and even in the Far UV (FUV; 91–110 nm). The excitation of UIBs has therefore come to be ascribed to the absorption of UV photons. In the stochastic or transient heating model (see Allamandola et al. 1989), FUV photons are even preferred for the dust to be raised up to the very high “temperatures” apparently observed. Moreover, theory and laboratory data predict that the stronger the radiation flux and the more energetic the photons, the higher the probability for the dust to be ionized and, hence, for the

relative intensities of the UIBs to change drastically from their values in the case of neutral dust.

However, data accumulated over the last decade, especially on the hands of Sellgren and coll., have consistently raised objections to this model. Thus, Uchida et al. (1999) have clearly illustrated and summarized these objections in their study of ISO’s mid-IR spectra of Reflection Nebulae as a function of the hardness of the exciting radiation flux, as measured by the effective temperature, T_{eff} , of the illuminating star, and of its intensity, as measured by the distance from the source: they observed no systematic or stark spectroscopic differences with varying T_{eff} between 3600 and 19000 K, nor with varying fluxes over four orders of magnitude above that of the Galactic Diffuse Interstellar Medium (DISM).

That UV radiation is necessary for the excitation of UIBs is also contrary to the observations of M 31 by Pagani et al. (1999; thereafter P99). These authors obtained maps of the mid-IR emission in the spectral windows of the LW2 (5–8 μm) and LW3 (12–18 μm) filters on board the ISO satellite, which include a few UIBs. Using the 200 nm (UV) maps of the FOCA 1000 balloon-borne telescope, they found no obvious correlation between UV photons and mid-IR colours in most of the galaxy. By contrast, the features are extremely well correlated with the neutral gas as shown by the H I and CO maps.

In this paper, I argue that these observations (in particular, Fig. 9 of P99, reproduced here, by permission, as Fig. 1) can be accounted for quantitatively by assuming that the excitation of the UIBs results from the impact of H atoms upon carbonaceous grains, a mechanism known as infrared chemiluminescence (Papoular 1999). Upon such impacts, the chemical energy of the H radical may be deposited in the grain (exothermicity), exciting its characteristic vibrations, which ultimately decay by emitting IR bands. In this model, the intensity and hardness of the ambient UV radiation can only enter indirectly by increasing the density of H radicals in the gas and, hence, the frequency of impacts and the power emitted in the bands. No spectral changes are expected in the UIBs as a consequence.

Besides, the H impacts may induce chemical reactions, possibly even liberating particles from the condensed phase (Bortolani et al. 1994). It is precisely on these occasions that two H atoms can meet and recombine, a process which can only take place in the presence of a third body (see Duley & Williams

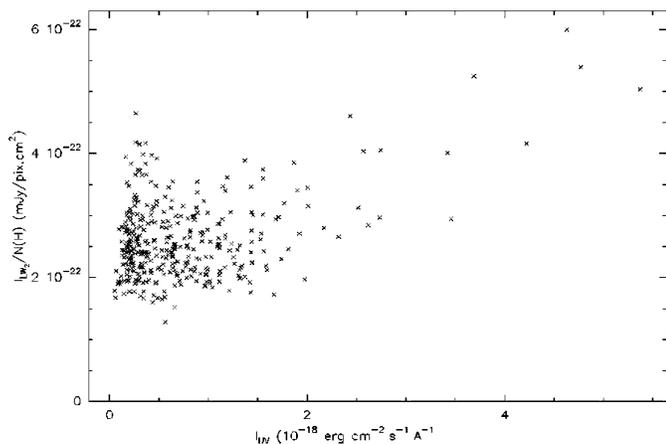


Fig. 1. The intensity in the LW2 filter (5.0–8.0 μm) normalized by the total column density of neutral gas in the SW region of M 31 as a function of the uncorrected intensity of the UV light at 200 nm. Pixel size: 45 arcsec. A weak correlation appears only above a threshold value of $\approx 2 \cdot 10^{-18} \text{ erg cm}^{-2} \text{ s}^{-1} \text{ \AA}^{-1}$. Reproduced from P99, with permission

1996); some of the features of the vibrational and rotational spectra of H_2 in space, which cannot be ascribed to UV excitation, may also be due in part to these H/grain encounters (Draine & Bertoldi 1999). UIB excitation and H_2 formation are thus intimately related processes. These processes are first discussed in some detail (Sect. 2), explaining the underlying physics and how the IR emission efficiency is obtained; this is then included in a kinetic model, from which predictions are deduced, that are shown to compare favourably with observations (Sect. 4). Details of the numerical simulation are given in the Appendix and elsewhere (Papoular 2000).

2. Elementary constituents and processes

It is now firmly established that the UIBs are associated with the vibrations of a variety of carbon and hydrocarbon bonds. It is also observed that UIB sources are always rich in atomic hydrogen, as in diffuse clouds and Photo-Dissociation Regions (PDRs). On the other hand, molecular hydrogen is always present in these sources, even if not dominant. It is therefore advisable to take these three constituents into account and consider their interactions.

2.1. Hydrogen recombination

It has long been known that H atoms can recombine into molecules only in the presence of a third body with which they can exchange energy and momentum (see Duley & Williams 1996). As discussed in Guillois et al. (1998) and Pironello (1999), recombination on grains can proceed through two main mechanisms, depending on the H coverage and the grain temperature, T_g :

- the Langmuir-Hinshelwood mechanism which, for amorphous carbon was found to be efficient only in a narrow

range of T_g around 10 K, a compromise between the necessary atom mobility and the possible desorption;

- the Eley-Rideal mechanism, in which H atoms from the gas phase react directly with chemisorbed ones; this is nearly independent of the temperature and is more suitable to the temperatures, H-bond strengths and surface roughness of the grains considered here (see Masel 1996, and Duley 1984).

Our model uses this latter mechanism, whose probability is proportional to the hydrogen coverage of the grains and to the sticking coefficient, ρ , which defines the probability against the impinging H atom being simply scattered away.

2.2. Vibrational excitation

Consider the dust grain as a system of N balls of different masses, coupled by *linear* springs in equilibrium. Think of the impinging H atom as yet another, small, ball and hang it on one of the springs. This sets the whole system in seemingly disordered motion. In fact, classical mechanics teaches us that this motion can be broken down into $3N-6$ elementary, coherent, motions characteristic of the system and called *normal modes* (Wilson et al. 1955). They involve all the balls (to different extents) but, in the limit of small ball displacements, they are independent of each other: if all the balls were simultaneously given velocities and displacements corresponding to one of the modes, this mode would persist indefinitely and none of the others would be excited.

If the springs are slightly *non-linear* (anharmonic), the movements can still be described approximately with the same normal modes as for linear springs, except that they are now “coupled” by “anharmonic coefficients”. As a result, the vibrational modes are shifted or split, and no longer separable (quasi-modes). During a very short transient (usually not longer than a few picoseconds) the initial energy distribution is *irreversibly* readjusted over the molecule by Intramolecular Vibrational Redistribution (IVR) between quasi-modes (see, for instance, Minehardt et al. 1999).

Thereafter, a quasi steady state sets in, in which some energy is *recurrently* exchanged between nearly degenerate states as is the case for coupled electric circuits (Fermi et al. 1965; Uzer 1991). These exchanges are extremely fast and are therefore averaged out over the much longer IR radiative lifetime of the vibrations. They are not to be confused with an irreversible energy decay or a long-term energy exchange between modes. For small, non-dissipative structures in the absence of interaction with a thermal bath, such as frequent collisions with other molecules at a given temperature, there is no a priori reason for a Maxwell-Boltzmann energy distribution to set in (as in the “ergodic” hypothesis of Allamandola et al. 1989), nor for energy to decay from one mode into another, and the only route for deactivation must be through IR fluorescence.

One experimental confirmation of this surmise is the work of Williams & Leone (1995): they excited gaseous naphthalene molecules with laser pulses, 10–20 ns long, at 193 or 248 nm (6.6 or 5.3 eV) and monitored their subsequent IR emission spec-

trum. The decay time of the total radiation energy in the C-H stretch band was $30 \mu\text{s}$, limited only by collisions between the molecules. Thus, if any irreversible energy decay (like IR radiation) or transfer to other vibrational modes within each molecule is at work during this lapse, it has to be much slower than $30 \mu\text{s}$. While the IR decay time indeed ranges between about 1 ms and 1 s, no non-radiative decay is known to be slower than $30 \mu\text{s}$. Besides, the authors attempted to simulate the emission spectrum according to the procedure used by Allamandola et al. (1989), based on the ergodic hypothesis: the model spectrum was found to be clearly at variance with the measurements.

As the applied perturbation and and/or anharmonicity become stronger, the energy “sharing” (“mixing”) increases in extent and the initial discrete modes are blurred into a *new* spectrum of *bands* of finite widths. These are located, roughly speaking, at the peaks of the density of the initial normal modes in the frequency spectrum, where, of course, interactions and mixing are strongest. This phenomenon is related to the appearance of *isolated narrow layers of stochasticity* in phase space (Lichtenberg & Lieberman 1992, p.56; Nesbitt & Field 1996, p.12741–12742). Here, again, energy is exchanged *recurrently* at very high rates, *this time between bands*, and the intensity fluctuations of the latter are averaged out on the long term.

In a large and complex molecule, this spectral energy distribution can only be obtained by numerical computation (see Appendix). For the type and size of molecule we are interested in, such simulations show that excitation energies of from 1 to 10 eV are sufficient to bring the system into this regime: the bands form shortly (a few picoseconds) after a sudden perturbation and their energy content does not appear to change much, on average, afterwards (at least for 240 ps, the longest computation time achieved here). I shall therefore assume again that the only route to deactivation is through IR photon emission and the IR chemiluminescence spectrum will be given by the above, non-Boltzmannian, energy distribution. *As a consequence, the IR spectrum does not depend on the intensity or hardness of the ambient radiation flux, but on the particulars of the H impact and, of course, on the nature of the target grain.* Also it will be different than the absorption spectrum of the same molecule.

It must be stressed that, in the chemiluminescent process envisioned here, by contrast to VUV excitation, energy is deposited a) locally on a C bond, b) directly to the nuclei whose vibrations we are interested in, and c) in insufficient amounts to raise the molecule even to its first excited electronic state. The relaxation, too, is therefore expected to differ notably.

Theoretical studies (1992) show that stochasticity and ergodicity increase with the number of degrees of freedom, i.e. the size of the studied system. It is therefore expected that, in larger grains, the excitation energy will “diffuse” in phase space, thus allowing a Maxwell-Boltzmann (thermal) distribution to finally set in between modes. But the corresponding temperature will be low, and the IR emission unobservable.

In this model, the immediate source of energy for the UIBs is the chemical energy of the system, i.e. the potential energy of the H radical with respect to the target grain. Such systems are to be found in the stellar winds of RGB and AGB stars, and

eventually coalesce into diffuse clouds in the ISM. The ultimate source of energy is thus the old, red stars. This is the case of faint but extended UIB sources like those observed in P99. In this work, we call efficiency, η , the ratio of IR band energy to potential energy of the chemical system. This is determined by numerical simulation below.

Another possible source of energy for the UIBs is the FUV (91 to 110 nm) of young (O and B) stars, which dissociates the molecules and ionizes the atoms of the nursing molecular cloud to form PDRs. For luminous UIB sources like the Orion Bar, M 17, etc., this is generally the main source of H atoms, whose number increases with the intensity and/or hardness of the stellar FUV. Because this relationship is roughly linear, some authors took this to be a proof that the FUV photons were the exciting agents of the UIBs, in agreement with the transient heating model (Boulanger et al. 1998). It is shown below that this need not be the case (Sect. 4).

2.3. Chemiluminescence efficiency, η

Although IR chemiluminescence was demonstrated a long time ago (Cashion & Polanyi 1958; see later bibliography in Smith 1973) and is still under study (Watanabe et al. 1996), little is known about its efficiency, particularly in the case of H atoms interacting with hydrocarbons. With this target in mind, I used standard chemical codes (see Appendix) to perform extensive numerical simulations of the dynamics of these systems and simulate vibrational excitation of various molecules upon H impact. The main relevant results are summarized here for convenience.

The codes follow the motions of all atoms together with their charges and compute the electric dipole moment of the whole particle as a function of time. A Fast Fourier Transform (FFT) can then be performed on this function to obtain the IR spectrum. Because the codes include anharmonic (non-linear) coupling forces between atoms, the normal modes are, in fact, automatically coupled, as explained in Sect. 2.1.

Vibrational excitation of the target particle by H impact is most effective when the target site is a dangling bond, C-, which ultimately captures the H atom and all its chemical energy. It was found that the potential energy of the initial system (~ 5 eV) is readily converted (partly) to kinetic energy, which is initially confined to the site of impact. After a time of order 10^{-12} s, however, this kinetic energy diffuses across the *whole* particle (non-radiative relaxation), exciting its characteristic vibrations, with the molecule in its electronic ground state.

Although a large number of aromatic molecules were studied in this way, it is desirable, for the present study, to focus on a better model for IS dust. I therefore had recourse to models of coal (Speight 1994) and kerogene (Behar & Vandenbroucke 1986) both of which materials had been shown in the laboratory to mimic the UIB spectra acceptably well (Papoular et al. 1996). These disordered natural materials, which are similar to the amorphous carbon produced in the laboratory but are more graphitic, are essentially made of C and H with traces of O, S, N... Their structure includes condensed benzenic rings, aromatic and aliphatic C-H bonds, as well as linear chains of cumulenes

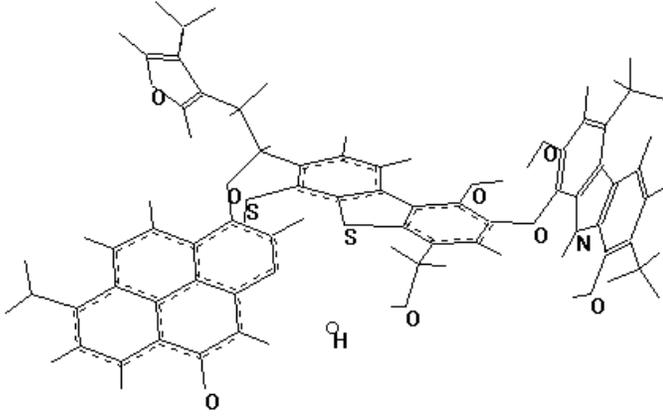


Fig. 2. A view of the model dust particle built with the Hyperchem code. Note the H radical near the middle of the figure; it is directed towards the molecule with a velocity $5 \times 10^5 \text{ cm s}^{-1}$.

(successive C=C bonds) and polyynes (alternate C-C and C≡C bonds) in various proportions. The IR spectra of such materials were shown to be in agreement with the UIB spectra of nebulae illuminated by luminous stars, such as HII regions and planetary and proto-planetary nebulae (Guillois et al. 1996).

A molecule made of 101 C,H,O,N, and S atoms, following Speight's models, was studied in particular detail (Fig. 2). Fig. 3 shows the energy spectrum of the IR-active modes which were excited upon impact of an H atom on a dangling bond; it is discussed in the Appendix. The simulation of the dynamics of this relatively small system already exhibits features within the main UIB bands and, as expected, a high feature-to-continuum ratio although there are 297 modes in all! Further tailoring of the molecular structure can be undertaken on this basis in order to fit the observed UIB spectra, but this is outside the scope of this paper. Most importantly, the relative intensities of the bluer bands are not too weak and the total IR efficiency is about 0.3.

3. The nebular model

The sources observed by P99 in LW2 are considered here to be nascent, diffuse, clouds formed by the ejecta of old stars (RGB, AGB) or supernovae, and assumed to consist of hydrogen gas and carbonaceous dust in the standard mass ratio (averaged across the Galactic ISM). Based on observations of such diffuse clouds by Savage et al. (1977), we shall take the number density ratio, H_2/H , to be 10^{-5} , considering that this ratio is found to switch abruptly from this very low value up to ~ 1 only in molecular, dense, clouds (which are not known to be strong emitters of UIBs).

For the dust, I used the Speight model described above. It is important for our present purposes to recognize the presence, on the grain surface, of three types of sites (see, for instance, Mennella et al. (1999): hydrogenated (C-H_n), normal (C-H) and dehydrogenated (dangling bond, C-). Call s_+ , s and s_- , respectively, their number per cm^3 of space; H and H_2 , the number densities of hydrogen atoms and molecules above the grain surface. In the DISM, the average projected surface area of grains

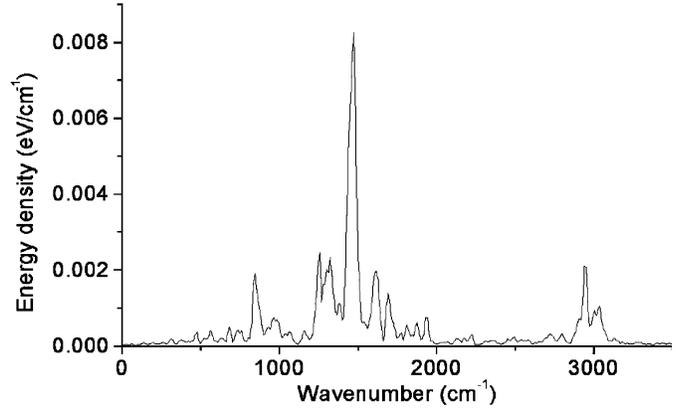
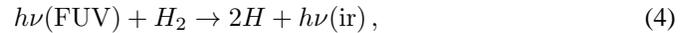


Fig. 3. Power spectrum of the electric dipole moment excited upon H impact on the "Speight" molecule which was first stripped of one of its H atoms; this leads to the formation of, and deposition of energy in, a new C-H bond (Fig. 2). As a consequence, the molecule is set in vibration. The spectrum is taken over the first 2.3 psec after impact.

is estimated to be $\Sigma = 10^{-21} \text{ cm}^2/\text{H atom}$ (Spitzer 1978). For spherical grains, the surface area available for interaction with the gas atoms will be four times larger. If there are μ ($\sim 10^{15}$) sites per cm^2 of grain surface, then, the total number of sites per cm^3 is $s_t = s_+ + s + s_- = \mu \Sigma H_t$, where $H_t = H + 2H_2$.

Consider the following set of most probable reactions



where $h\nu(\text{FUV})$ is a photon capable of dissociating H_2 molecules, which requires that it falls in the range 91–110 nm (see Duley and Williams 1996). The UV(200 nm) mapped in P99 does not satisfy this condition. Let F be the FUV flux ($\text{cm}^{-2}\text{s}^{-1}$) and $a = \sigma F$ (s^{-1}), the rate of photodissociation of the molecules, where σ is the cross-section of the process (cm^2). Following Duley and Williams, we take this rate to be χa_0 , where $a_0 = 5 \times 10^{-11} \text{ s}^{-1}$ is its value in the DISM, corresponding to $\sigma = 4 \times 10^{-18} \text{ cm}^2$, and χ is the factor by which the FUV intensity exceeds its value in the Galactic DISM. The other reaction rates are all determined by the sticking coefficient, ρ , of H atoms on the grains; we shall assume that the rate coefficients are all equal to a constant, $b = \frac{\rho v}{4\mu}$, where v is the relative velocity of the impinging H atom (cm s^{-1}). In fact, v and ρ (see Masel 1996, and Duley 1984) are functions of the gas temperature. Here, for simplicity, we shall take $\rho = 1/3$ (Masel 1996) and $v = 5 \times 10^5 \text{ cm s}^{-1}$, for a kinetic energy $\sim 0.1 \text{ eV}$. The kinetics of the problem are then described by the equations

$$\begin{aligned} \dot{s}_+ &= -bHs_+ \\ \dot{s} &= -bHs + bHs_+ + bHs_- \\ \dot{s}_- &= -bHs_- + bHs \\ \dot{H} &= -bHs_t + 2aH_2 \\ \dot{H}_2 &= bH(s_+ + s) - aH_2 \end{aligned} \quad (5)$$

4. Results

The solution of system (5) is easier in the following idealized cases.

4.1. Negligible FUV (diffuse ISM)

The variations of H are governed by the photodissociation and surface recombination rates, $2aH_2$, bHs_t . With the numerical assumptions made above, their ratio can be expressed as $r=6 \cdot 10^{-2}\chi$. Thus, in the DISM ($\chi=1$), photodissociation is negligible ($a \sim 0$), and the H atom density decays exponentially with a time constant $\frac{1}{bs_t}$, of order $2 \cdot 10^6$ y. In the same approximation, the solution of system (5) for H_2 and the dust densities is straightforward but the expressions are lengthy. They can be simplified by noting that the ratio of the characteristic decay times of the dust and of the H atoms, respectively, is of order $\frac{bs_t}{bH} \sim \mu\Sigma \ll 1$. We are therefore allowed to consider that the values of the dust densities during the cloud life are close to their limiting values at infinite time:

$$s_+ = 0, \quad s \approx s_- \approx \frac{s_t}{2}.$$

The solution for H_2 then turns out to be

$$H_2 = H_{20} + \frac{1}{2}H_0 [1 - \exp(-bs_t t)]$$

where the subscript 0 designates the initial values; this increases slowly, with the same time constant as H . Thus, for our present purposes, it is acceptable to assume that H and H_2 retain characteristic, constant, values during the time the cloud is observable in the IR, and, therefore, that H_2/H remains very small.

It is now possible to predict the observable IR radiation intensity, I_2 , in the pass band of filter LW2, in regions of very low FUV flux ($a=0$). The rate of excitation events (reaction 3) is $bHs_- \approx b\frac{Hs_t}{2}$. An energy ϵ (exothermicity) is deposited in the grain upon each such event. On average, only a fraction η_2 of this ends up in the UIBs which lie in the filter pass band, $\Delta\lambda$. Let D be the distance to the source, L its depth and S its projected area, both along the line of sight, ω the solid angle subtended at the telescope and θ the number of radians per pixel of the detector. Then,

$$I(\text{LW2}) = 1.4 \cdot 10^{20} \frac{\rho_V}{4} \Sigma H_t H \eta_2 \frac{\epsilon}{\Delta\lambda} \frac{LS}{4\pi D^2} \frac{\theta}{\omega} \quad (6)$$

where the first numerical factor converts $\text{W cm}^{-2} \mu\text{m}^{-1}$ into mJy/pixel . As a rough estimate, we take $\eta_2 = \frac{2}{3}\eta$, and $\eta=1/3$, the value found in Sect. 2. S , D and ω cancel out by definition and the pixel aperture is 45 arcsec (P99). Now, LH is equal to the column density $N(\text{H})$ of P99. Hence,

$$R \equiv \frac{I(\text{LW2})}{N(\text{H})} = 10^{-23} \eta_2 H \approx 2.2 \cdot 10^{-24} H$$

In the regions of M 31 devoid of FUV, this quantity lies in the range $1-4 \cdot 10^{-22}$ (Fig. 1). If the model is correct, this implies that, in the observed regions, H ranges between about 50 and 200 cm^{-3} . This is very nearly the range determined by Jura

(1975) in our Galaxy; thus, the approximations made above are warranted and the relevance of the model is vindicated. In this model, the limited range of values observed for R implies that the H atom density does not vary much in the regions surveyed and, hence, that the UIB intensity is simply proportional to the exposed dust surface. As to the column densities, they were found to range between 1 and $9 \cdot 10^{21} \text{ cm}^2$. For an average $H=100 \text{ cm}^{-3}$, this corresponds roughly to 3–30 pc.

4.2. Weak FUV (diffuse ISM not far from O/B stars)

Pagani et al. also observed the LW2 signal from regions where the FUV is no longer negligible. They plotted the values of R as a function of the UV flux at 200 nm (Fig. 1), taken to represent the FUV. Note, however, that, while in the DISM, $F(100 \text{ nm})/F(200 \text{ nm}) \sim 1.6$, this ratio is expected to rise in the vicinity of O and B stars, which are hotter than the average DISM stars. Thus, the values in abscissae must be considered as lower bounds to $F(\text{FUV})$. It is found that R starts to exceed systematically its low-UV average, R_0 , at $F(\text{UV}) \approx 2 \cdot 10^{-18}$; also, the excess is roughly equal to R_0 for $F(\text{UV}) = 4 \cdot 10^{-18} \text{ erg cm}^{-2} \text{ s}^{-1} \text{ \AA}^{-1} \text{ arcsec}^{-2}$. I interpret this behaviour as due to the contribution of the FUV to the production of excess H atoms by dissociating the H_2 molecules in the gas. This can be quantified by treating the small terms which then appear in system (5) as a small perturbation of the equations used in the previous subsection. Call h and h_2 the small increments induced in H and H_2 .

Taking differences of the last two equations of (5),

$$\begin{aligned} \dot{h} &= -bhst + 2aH_2 \\ \dot{h}_2 &= \frac{1}{2}bhst - aH_2 \end{aligned} \quad (7)$$

Here, because h is so small with respect to H , equilibrium is readily established and we can set $\dot{h} = \dot{h}_2$. Besides, since s_+ , s and s_- are assumed constant, conservation of matter yields $h = -2h_2$. Hence,

$$h = \frac{2aH_2}{bs_t}, \quad h_2 = -\frac{aH_2}{bs_t}$$

From (6), with the same numerical values as adopted above,

$$\frac{\Delta I_2}{I_2} = \frac{h}{H} = \frac{8\sigma H_2}{\rho_V \Sigma H_t} \frac{F(\text{FUV})}{H} = 5 \cdot 10^{-9} F(\text{FUV}) \quad (8)$$

Thus, $\Delta I_2 = I_2$ for $F(\text{FUV}) \approx 2 \cdot 10^8 \text{ cm}^{-2} \text{ s}^{-1}$, or $\chi \approx 17$, independent of the value of η . Converted to the same units as $F(\text{UV})$, with an average photon energy of 11 eV, this reads $5.6 \cdot 10^{-17}$, or 14 times the corresponding UV flux. For a black body, Planck's law sets an upper limit to this ratio: $(200/100)^4 = 16$, which is asymptotically reached in the limit of high temperatures (≥ 5000 K). This is a confirmation of the radiative contribution of nearby O/B stars to the dissociation of molecules.

Besides, the rough positive correlation between R and $F(\text{UV})$ is in keeping with the functional form of Eq. (8). Of course, for a given, spatially limited nebula, there is an upper bound to the IR emission, set by the (random) initial content of

hydrogen atoms, H_0 . This explains, at least in part, the scattering of data points in Fig. 1. The positive correlation predicted by Eq. (8) has also been observed in PDRs at the edge of molecular clouds, up to the highest values of χ (Boulanger et al. 1998). The present work shows that this does not necessarily mean that dust is directly “heated” by absorption of FUV photons. Given enough matter, it may simply be that the number of H atoms produced increases with the FUV flux. This could be modeled quantitatively from first principles, using η along the same lines as above, provided the thickness and atomic H density were known for particular PDRs.

5. Conclusion

The whole argument of this paper rests on the efficiency of the chemiluminescence process, which is deduced from numerical simulations. It may be objected that the virtual lengths of these simulations is very limited as compared with the IR decay time, about 10^{-3} to 1 s. Indeed, because of the limited computational speed of (chemically) accurate codes used here, the longest simulation of the molecular dynamics of a “large” molecule (coronene) did not exceed 13 ps. Longer runs were computed with another code (see Appendix), at the price of reduced accuracy in absolute intensities and frequency of the modes. But that was so fast that the molecular dynamics of even the large “Speight” molecule could be followed during a maximum of 240 ps: the same behaviour was observed as with the accurate code. Fortunately, even such short lengths are much longer than the time needed for all the atoms to be set in motion, and much longer than any known vibrational decay time (see McGlynn et al. 1969). If any were operative, it would have shown up during the simulations. As it were, no sign of secular decay was detected; only recurrent exchanges of energy were observed all along, and averaged out, as explained in the Appendix.

It appears, therefore, that the only remaining route to vibration deactivation is IR fluorescence (as already recognized by Allamandola et al. 1989). This is confirmed by Williams and Leone’s experiment (Sect. 2.2) and it would be valuable if other experiments of this type were designed for larger molecules and other vibrational modes. Because of the size limit set to the dust particles by energy “dilution” (Sect. 2.2), such experiments would have to use nanometric particles in the gas phase or, at least, embedded in cryogenic matrices of rare gases.

It should be clear that, in principle, the excitation process described in this paper can coexist with other processes, such as heating by absorption of photons (visible and IR only, in the case of M31) by the grains themselves. Such absorption is not likely to excite atomic vibrations directly, because only resonant photons can do so efficiently. It is more likely to heat the mobile electrons of aromatic rings, which are responsible for the strong IR continuum observed in absorption spectra. This is a very inefficient process when it comes to the emission of UIBs. However, it can contribute notably where atomic H density and VUV intensity are low but visible radiation is very strong, as in the vicinity of RGBs and AGBs. But, then, the UIB spectrum is expected to be a thermal spectrum at the equilibrium

temperature reached by the grain: a redder spectrum, with lower band-to-continuum ratio. When both chemiluminescence and photon absorption are at work, the interpretation of IR band intensity ratios is more intricate, of course.

The present model suggests that, in regions where the VUV intensity is low, the UIB intensity is proportional to the product of dust and atomic H densities. This is likely to peak at the interface between the cloud (high dust density and low H density) and the near-by ISM (low dust density and high H density). Since the interaction of atomic H and dust surface is also responsible for the recombination of H atoms, which yields excited molecular hydrogen, the quadrupolar emission of the latter near $2\ \mu\text{m}$ must be correlated with the UIBs. This is borne out by observations with high spatial resolution (see Guillois et al. (1996) and Zavagno & Ducci (1999)).

Appendix: molecular dynamics simulations

The conclusions of Sect. 2 are based upon extensive numerical simulation, using a commercially available, state-of-the-art, semi-classical code, PM3 (see Stewart 1989), included in the latest Hyperchem package from Hypercube, Inc. The computer is a PC equipped with a Pentium(r) II processor and MMX(TM) technology. The entirely classical molecular mechanics code, MM2, was also used for qualitative analysis because it is so fast; however, it is not quantitatively reliable as regards the absolute mode frequencies and intensities.

Several molecular processes of interest to astrophysics were demonstrated:

1. physisorption on a graphene (coronene)
2. chemisorption on a peripheral site of benzene, forming a methylene group, CH_2
3. recombination of an impinging H atom with an H atom of the target, resulting in the destruction of a C-H bond to form a free, excited H_2 molecule. This “abstraction” of an H atom from the target is an instance of the Eley-Rideal mechanism. The probability of this process is higher when the target site is a CH_2 group, whose bonds are weaker.
4. vibrational excitation of the target, which is the main subject of this Appendix.

In such computer experiments, a virtual particle is first built from a few tens of C and H atoms. The code then performs a small amplitude analysis to deliver the spectrum of all possible normal modes of the particle, as well as their absorbance (or *IR intensity*). Roughly, 1/10 to 1/5 of all modes have appreciable intensity.

In a chemiluminescence experiment, a free H atom is directed to the particle from a small distance (a few angstroms), with a small velocity (1 to $10 \cdot 10^5\ \text{cm s}^{-1}$). The Molecular Dynamics code then follows the movement of all atoms, together with their electric charges, so that the total instantaneous dipole moment, $\mu(t)$, can be computed by small steps (down to $10^{-16}\ \text{s}$). The latter is then analyzed by a Fast Fourier Transform (FFT) code into its power components, $|\mu_m|^2$, taken over any length of time. For a quantal harmonic oscillator (Wilson et al.

1955), the corresponding band energy, E_m , available on decay into IR photons, is proportional to $|\mu_m|^2 \nu_m^2 / I_m$ where I_m is the associated IR intensity.

Finally, the code also allows the dynamic characterization of whatever mode is excited so that it can be assigned to a definite functional group and compared, in frequency and type, with the observed UIBs. In one such experiment, a “Speight” molecule (Sect. 2.3; Fig. 2) was first stripped of one of its H atoms and the residue geometrically optimized into its ground level configuration. A free H atom was then placed near by and directed towards the dangling bond, with a velocity $5 \cdot 10^5 \text{ cm s}^{-1}$. It soon settled in the vicinity of the latter, oscillating with a large amplitude while the rest of the molecule was unaffected: this state is better described as a “local” mode, rather than by any combination of normal modes. After a transient period of order one picosecond, the available energy was spread over the molecule and all the atoms on the screen were seen to vibrate: the molecule settled in a steady-state, vibrating in distinct modes of vibrations. Fig. 3 shows the IR spectrum taken over the initial 2.3 psec (this time is limited by the unavoidable slowness of computations on large molecules; hence the unphysical width of the features in this figure). During the experiment, the *total* vibration energy of the molecule, remained constant and equal to the exothermicity, $E_c = 5.4 \text{ eV}$, while the total energy carried by the *infrared active* bands in Fig. 3 fluctuated around $\sum E_m \sim 1.7 \text{ eV}$. The ratio of these two numbers defines an IR efficiency, ~ 0.3 .

Moreover, the ratio of energies in bands around 3000 and 1300 cm^{-1} , respectively, is $\sim 1/4$. If the exothermicity had been completely thermalized, the corresponding temperature would have been $\sim 700 \text{ K}$, assuming the specific heat to be $1000 \text{ J kg}^{-1} \text{ K}^{-1}$, as for the parent materials. Then, according to Boltzmann’s law, the spectral energies would have scaled as $\frac{h\nu}{\exp(\frac{h\nu}{kT}) - 1}$ and the ratio defined above would have been $1/30$, instead of $1/4$. Clearly, thermal equilibrium did not set in, but the spectrum looks like that of a high-temperature blackbody emitter.

That part of the exothermicity which is not reemitted in the IR bands is shared between the IR-inactive modes and the weak (but extended) continuum underlying the bands.

In order to monitor the temporal behaviour of the energy in each IR band, it is convenient to use the faster code, MM+, which allows much longer simulation times (up to 240 ps). It was thus possible to quantify the quick initial propagation of the perturbation throughout the molecule. It was also found that, after this short transient, there is no long term decay of band energies: no irreversible energy exchange is expected between modes before emission of the corresponding IR photons. However, because a substantial anharmonicity is built in this chemical code, the normal modes are slightly coupled and this gives rise to fast, “chaotic”, recurrent, variations of the band energies. These “beats”, whose ubiquity has long been known in mechanics (Fermi et al. 1965; Uzer 1991), are observed in all the simulations. As a result, the energy continuously shifts to and fro between adjacent modes. Long runs accordingly yield broader bands with notable wings. This phenomenon, together

with inhomogenous broadening, is likely to contribute substantially to the observed width of the UIBs (see Papoular 1999).

As a result of the beats, the total energy in the IR spectrum also undergoes fluctuations, but their amplitude decreases with increasing length of the time over which the FFT is effected.

From experience gained during this work, it appears that the spectrum delivered by the codes for a given target molecule, does not depend notably on the details of the H impact, provided it is taken after the transient and for a reasonably long time, both times being of order 1 ps. That these conditions are met can be checked by comparing the results of successive runs on the same system.

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