Polycyclic aromatic hydrocarbons in the near-infrared spectra of 24 IRAS sources

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Abstract. We present infrared spectra of 24 IRAS sources. The observations include the IRAS Low Resolution Spectra (LRS) and ground-based three micron spectrophotometry. We selected these sources from the IRAS-LRS database because they have strong emission features at 7.7, 8.6, and 11.3 μm in their LRS spectra. In each of them, we have detected the well-known 3.3 μm emission feature which sometimes occurs together with a feature at 3.4 μm and/or an emission plateau at 3.4–3.6 μm. We analyse these observations in the context of the polycyclic aromatic hydrocarbons (PAHs) hypothesis. The rather large sample of sources observed and the homogeneity of the data presented here allow us to perform a consistent analysis. In particular we study the intensity ratio of the 11.3 μm to the 3.3 μm bands which is used to derive an average size of the emitting molecules. The emission of a cooling molecule is calculated in the various bands of PAH molecules measured in the laboratory. Discrepancies between the calculated and the observed spectra are tentatively interpreted in terms of dehydrogenation of the molecules.

Key words: infrared radiation – spectrophotometry – interstellar medium: dust, molecules, H II regions, reflection nebulae

1. Introduction

Infrared emission features at 3.3, 6.2, 7.7, 8.6, and 11.3 μm have been detected since 1973 in a variety of objects including planetary nebulae, reflection nebulae, H II regions and extragalactic objects (see review by Aitken, 1981 and Willner, 1984). Various models had been developed to understand not only the wavelength of the features but also the possible excitation mechanism and hence the respective intensities of the lines (see review by Allamandola, 1984). The situation has changed considerably only recently. In 1984, Léger and Puget have proposed a coherent model in which the excitation mechanism is provided by the absorption of individual ultraviolet photons by isolated large organic molecules

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imposed on the emission plateau (Muizón et al., 1986; Geballe et al., 1988; Jourdain de Muizón et al., 1990/Paper 2).

The conspicuous presence of the 7.7, 8.6, and 11.3 μm emission bands in many low resolution spectra (LRS) obtained with the Infrared Astronomical Satellite (IRAS) has prevailed on us to select several dozens of sources from the LRS database in order to obtain their three micron spectra and study them together with their IRAS-LRS spectra. We have obtained so far three micron spectra for 24 of these IRAS sources. Several of them were either totally new or previously poorly known infrared sources. This set of observations doubles the number of galactic sources for which both three micron and ten micron spectra characteristic of PAHs are available. The aim of this study is to obtain, for a large sample of objects, an estimate of the 11.3 μm to the 3.3 μm ratio, since the two bands originate in the same molecular subgroup, in order to evaluate its variation among different objects. The knowledge of this ratio together with that of the mean energy of the exciting UV photons can be used to derive the average size of the emitting molecules.

In Sect. 2, we summarize the observations; in Sect. 3, we present the results and discuss the possible nature of the sources. In Sect. 4, we first recall the infrared emission mechanism of a large isolated molecule having absorbed one single UV photon and we justify the concept of the use of a vibrational equilibrium temperature prior to the emission of each infrared photon. Second, this concept of vibrational temperature is applied to interpret the 11.3 to 3.3 μm intensity ratio. This allows us to calculate the average temperature of the emitting species and, with some assumptions, their average size; this latter is found to be rather large, typically 100 atoms. We have computed the cooling of a molecule after absorption of one UV photon. The relative strength of the features is thus calculated and compared to the observations. The relative strength of the observed 7.7 μm to the 11.3 μm feature can be accounted for if one assumes a thorough dehydrogenation (up to 90%) of interstellar PAHs. Assuming such a dehydrogenation, we then compute the size of the molecule now taking into account a specific heat typical of graphic material.

2. Observations

The observations presented in this paper refer to 24 galactic sources. All sources have been selected from the IRAS-LRS database, on the criterion that they definitely and unambiguously have a strong 11.3 μm feature, and a very broad feature at 7.7 μm enhanced by a shoulder on its long-wavelength slope at 8.6–8.8 μm. Only the long-wavelength edge of the 7.7 μm feature is seen in the LRS spectra due to the wavelength cut-off of the instrument. All the sources observed are listed in Table 1 together with their IRAS reference position and their associations if applicable.

We report in this paper three sets of observations: the IRAS-LRS spectra (7.7–22.5 μm), ground-based CVF 3.0–3.8 μm spectra obtained at UKIRT (for 19 sources), and ground-based 3.0–3.8 μm CVF spectra obtained at the ESO-1 m and 2.2 m telescopes (for 5 sources).

The IRAS-LRS (Wildeman et al., 1983) spectra were obtained in 1983. Two wavelength channels, 7.7–13.5 μm and 11–22.5 μm, were recorded simultaneously with respective field of view 6’x 5’ and 6’x 7.5’. Due to the LRS being a slitless spectrometer, good quality spectra, such as those selected for this study, are obtained only for sources less extended than about 30’.

The resolving power increases with wavelength and varies from about 10 to 40. The LRS spectra have been calibrated using the IRAS-survey calibration (IRAS Explanatory Supplement, 1988). We would like to point out that the sources presented here (resp. their LRS spectra) have been selected from the original LRS database, and not from the LRS catalogue. The former contains about 170,000 individual spectra of about 50,000 sources and is available in only a few places in the world including Leiden Observatory. The latter contains average spectra of about 5,000 sources and is one of the official exported IRAS products. However, due to the automatic selection criteria used to produce the LRS catalogue, some catalogue spectra suffer from spike contamination (Muizón et al., 1988). Also some interesting spectra from the LRS database are not included in the LRS catalogue. The LRS spectra presented in this paper have been obtained by averaging for each source all its good quality individual spectra from the LRS database, after rejection of spikes. It happens that 30% of these sources are not in the LRS catalogue. Additionally, the source 20376+4109 is not in the IRAS point source catalogue (IPSC), but it is in the LRS database with the reference position given in Table 1. Therefore its name is not strictly speaking an IPSC name, but we adopted it from its LRS coordinates, for homogeneity with the rest of the sample.

The 3 μm spectra of all sources at declination δ > −35° (19 sources) were obtained in 1985 September and 1986 June at the United Kingdom Infrared Telescope (UKIRT) on Mauna Kea (Hawaii). It appears from Table 1 that the position of the peak of 3.6 μm emission (L band) coincides, in most cases within a few arcseconds, with the IRAS reference position. Spectra were measured using the infrared photometer UKT6 and its Circular Variable Filter (CVF), at a resolving power of 100 (Δλ ≈ 0.035 μm). The wavelength coverage was 3.0–3.8 μm (3330–2630 cm⁻¹). The aperture diameter was 12”. For 9 of these sources, we have also obtained 3.2–3.4 μm spectra in a 26” aperture, centred at the same position as those measured in a 12” aperture. This was done to check the extension of the 3.3 μm emission. For several sources observed during the June 1986 run, we have also performed some narrow-band mapping at 3.3 μm and in the 3 μm continuum, over an area of about 1’×1’, centred on the peak of 3.3 μm emission. This allowed us to determine more accurately the extent, and the relative strength over that extent, of the 3.3 μm band emission.

The 3 μm spectra of the 5 sources at declination δ < −40° were obtained in 1985 August and 1988 March at the European Southern Observatory (ESO) 1 m and 2.2 m telescopes. The spectra were measured, using an InSb infrared photometer and a CVF wheel, at a resolving power of 70 (Δλ ≈ 0.05 μm) and the data were Hanning (triangle) smoothed, thus lowering the resolution to ≈ 50. The wavelength coverage was 3.0–3.9 μm (3330–2560 cm⁻¹). The aperture diameter was 15”.

All 3 μm CVF spectra (UKIRT and ESO) were flux calibrated by observing standard stars in the same conditions as, and close in airmass to, the objects. For each source, the coadded spectrum was divided by the spectrum of a calibration star and then multiplied by the Planck function corresponding to the flux and temperature of that star. The observing log of the 3 μm spectro-photometric observations for the 24 sources, including calibration stars parameters, are given in Table 2.

3. Results

All 3.0–3.8 μm micron and LRS (7.8–22.5 μm) spectra for the 24 sources are shown in Figs. 1–4. All sources have a more or less
### Table 1. Source positions and IRAS Point Source Catalogue data

<table>
<thead>
<tr>
<th>Source Name</th>
<th>(a) IRAS position</th>
<th>Offset from IRAS position</th>
<th>IRAS PSCAT Flux density (Jy)</th>
<th>Associations</th>
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<td>RA(1950) Dec(1950)</td>
<td>RA Dec</td>
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<td>25 μm</td>
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<td>0338+5819</td>
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<td>31 396 1055 1297</td>
<td>RAGFL 437</td>
<td></td>
</tr>
<tr>
<td>03260+3111*</td>
<td>03 26 04.7 +31 11 40</td>
<td>37 101 534 947</td>
<td>RAGFL 5096, CED 016</td>
<td></td>
</tr>
<tr>
<td>03264-0325</td>
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<td>13 38 232 380</td>
<td>CED 040</td>
<td></td>
</tr>
<tr>
<td>05303+1021</td>
<td>05 30 18.6 +10 21 39</td>
<td>13 20 109 158</td>
<td>HDE 259431, CED 061</td>
<td></td>
</tr>
<tr>
<td>05572-0742</td>
<td>05 57 16.8 -07 42 15</td>
<td>18 141 419 472</td>
<td>Parsamyan 18</td>
<td></td>
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<tr>
<td>12063-6259</td>
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<td>50 407 1819 2233</td>
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<td></td>
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<td>51 162 621 989</td>
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<td>14 127 1303 2546</td>
<td></td>
<td></td>
</tr>
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<td>34 284 2053 7101L</td>
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<td>336 595 253 442L</td>
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<td>20319+3958</td>
<td>20 31 59.7 +39 58 24</td>
<td>27 160 851 1054</td>
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<td></td>
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<td>20376+4109**</td>
<td>20 37 36.8 +41 09 20</td>
<td>- - - -</td>
<td>RAGFL 2625, DR 22</td>
<td></td>
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<tr>
<td>21282+5050</td>
<td>21 28 15.0 +50 50 42</td>
<td>51 74 33 15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22308+5819</td>
<td>22 30 52.9 +58 12 52</td>
<td>25 175 874 1038</td>
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* Not in IRAS-LRS Catalogue
** Not in IRAS Point Source Catalogue

Strong 3.3 μm emission feature, and 7.7 and 11.3 μm features; only the long wavelength slope of the 7.7 μm band is included in the LRS spectral range. Several sources also show a 3.4 μm feature, with an underlying plateau extending from 3.35 to 3.6 μm, a feature at ≈8.6 μm which appears as a shoulder on the long wavelength edge of the 7.7 μm band, and an emission plateau from 11.5 to 13.5 μm extending beyond the 11.3 μm feature. Finally, emission lines from ionized gas are present in the spectra of some of these sources, in particular, the lines of Pfβ 3.74 μm, [Siv] 10.5 μm, [Neii] 12.8 μm, [Neiii] 15.5 μm and [Siii] 18.7 μm. In Figs. 1-4, sources have been gathered as follows. Figure 1 contains sources with low continuum and very weak or no emission lines from ionized gas. They are reflection nebulae or low excitation compact H II regions, with the exception of

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Table 2. Log of 3 μm spectrophotometric observations

<table>
<thead>
<tr>
<th>Source Name</th>
<th>Observing date</th>
<th>Telescope</th>
<th>Aperture (arcsec)</th>
<th>λ—coverage (μm)</th>
<th>No. of points measured</th>
<th>Total Int. time per point (sec)</th>
<th>Calibration Star</th>
</tr>
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<td>UKIRT</td>
<td>12</td>
<td>3.0–3.8</td>
<td>56</td>
<td>24</td>
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<tr>
<td>02920+3111</td>
<td>September 1985</td>
<td>UKIRT</td>
<td>12</td>
<td>3.0–3.8</td>
<td>56</td>
<td>16</td>
<td>BS224 G5IV</td>
</tr>
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<td>UKIRT</td>
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<td>3.0–3.8</td>
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<td>16</td>
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<tr>
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<td>3.0–3.8</td>
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<td>16</td>
<td>BS224 G5IV</td>
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<td>3.0–3.8</td>
<td>35</td>
<td>120/160</td>
<td>BS150 G8IIab</td>
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21282+5050 which might be a planetary nebula (Cohen and Jones, 1987). Figure 2 contains sources with a strong continuum, and also weak or no lines from ionized gas. The continuum is most likely stellar and these sources seem to be made of a star in a low excitation nebula. Figures 3 and 4 contain sources with emission fine-structure lines from ionized gas. For all these sources, the far infrared IRAS data indicate that they are H II regions, with a possible exception for 18162–1612. All have a [Ne II] 12.8 μm line which is typical of compact H II regions and corresponds to an ionization potential of 21.5 eV. Maybe, in the case of 18162–1612, it is the feature at 12.8 μm not attributable to [Ne II]. Several of them also have a [S III] 18.7 μm line. This line corresponds to a similar ionization potential (23.3 eV) as [Ne II] but is less often detected, partly due to the poor resolution of the LRS at this wavelength. When present in the spectrum the unresolved [S III] line is much broader than the unresolved [Ne II] line due to the resolution of the LRS being systematically worse in band 2 than in band 1. Several 3 μm spectra also have the Pfβ line of hydrogen at 3.74 μm. A few of these sources were already known as compact H II regions through radio observations; these include all those having a G or RCW number (e.g. see Goss and Shaver, 1970; Wink et al., 1982). Among the others are several new IRAS sources which are most likely H II regions. Only He 2–77 (12063 – 6259) is more likely to be a planetary nebulae (Muizion et al., 1987b; Stenholm and Acker, 1987); not only does it have the lines of [Ne II] and Pfβ, but also [S IV] 10.5 μm and [Ne II] 15.5 μm, corresponding respectively to ionization potentials of 34.8 and 41.0 eV.

Fluxes for all the emission bands, when present, are given in Table 3. Only upper limits are given for the 8.6 μm band since it is often not possible to separate it accurately from the very broad and strong 7.7 μm feature. Band fluxes in the 11.3 μm feature have been measured in the LRS spectra by drawing a uniform continuum through the points at 10 μm and at 13.5 μm and extending the prominent part of the 11.3 μm feature down to this continuum line. The area thus delimited accounts for the 11.3 μm band flux as given in Table 3, with a relative uncertainty of about 15%. When there is no [Ne II] 12.8 μm line, emission above the continuum, and between ~11.5 and 13.5 μm, accounts for the plateau at 11.5–13.5 μm. When a [Ne II] 12.8 μm line is present, only an upper limit to this emission plateau can be given since it is difficult to separate it from the [Ne II] line. The band flux in the 7.7 μm feature has been measured by extending the above defined continuum up to the short wavelength cut-off of the LRS (i.e. ~7.5–7.7 μm). The area thus delimited accounts for the 7.7 μm band flux after subtraction of the estimated upper limit contribution of the 8.6 μm band. It is clear that part of the 7.7 μm band is missing at its short-wavelength end. However, we have checked on other published data (e.g. Cohen et al., 1986) that this represents generally only a small fraction of the total 7.7 μm band flux. We therefore assume that the LRS has seen most of the 7.7 μm feature; the corresponding band fluxes given in Table 3 are probably slightly underestimated (relative uncertainties are up to 25%). At 3 μm there is much less problem with the intrinsic quality of the data, or the position of the continuum, which can be drawn straightforwardly through the 3.0–3.2 and 3.6–3.8 μm ends of.
Figs. 1–4. Spectra of 6 sources are presented in each figure. Left: Three micron CVF spectra obtained at UKIRT or at ESO (see Table 2). The dashed line indicates the estimated position of the continuum. Right: IRAS-LRS spectra. The thick line is band 1 of the LRS and the thin line is band 2. Inside each figure, sources have been gathered according to their likely nature: low excitation or reflection nebulae (Fig. 1), starlike or with a strong continuum (Fig. 2), H II regions (Figs. 3 and 4); see text, Sect. 3.
Fig. 3
Fig. 4
Table 3. Flux in the IR emission features (units: $10^{-18}$ W cm$^{-2}$)

<table>
<thead>
<tr>
<th>Source Name</th>
<th>Extent of red nebula</th>
<th>3.3 μm</th>
<th>3.4 μm</th>
<th>Plateau</th>
<th>7.7 μm</th>
<th>8.6 μm</th>
<th>11.3 μm</th>
<th>Plateau</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>φ20&quot;</td>
<td>φ26&quot;</td>
<td>Totala</td>
<td>3.35–3.60 μm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>03025+5819</td>
<td>1.1</td>
<td>2.4</td>
<td>0.08</td>
<td>0.4</td>
<td>118</td>
<td>&lt;22</td>
<td>27</td>
<td>19</td>
</tr>
<tr>
<td>03269+3111</td>
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<td>5</td>
<td>0.07</td>
<td>0.7</td>
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<td>68</td>
<td>41</td>
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<tr>
<td>05444–0325</td>
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<td>10</td>
</tr>
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<td>06303+1021</td>
<td>1.0</td>
<td>3</td>
<td></td>
<td></td>
<td>19</td>
<td>&lt;5</td>
<td>6</td>
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<tr>
<td>05572–0742</td>
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<td>4</td>
<td>0.07</td>
<td>0.4</td>
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<td>23</td>
<td>10</td>
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<td>11263–6259</td>
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<td>0.20</td>
<td>0.9</td>
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<td>44</td>
<td>&lt;25</td>
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<td>12389–6147</td>
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<td>16596–4429</td>
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<td>31</td>
<td>&lt;29</td>
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<td>16555–4237</td>
<td>44&quot;</td>
<td>13.2</td>
<td>45</td>
<td>3.9</td>
<td>465</td>
<td>&lt;98</td>
<td>137</td>
<td>66</td>
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<tr>
<td>17199–3446</td>
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<td>1.8</td>
<td>2</td>
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<td>102</td>
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<tr>
<td>17439–2845</td>
<td>39&quot;</td>
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<td>3.1</td>
<td>5</td>
<td>0.05</td>
<td>0.5</td>
<td>171</td>
<td>&lt;13</td>
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<tr>
<td>18162–1612</td>
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<td>0.3</td>
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<td>6.0</td>
<td>6.0</td>
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<td>467</td>
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<td>30</td>
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<tr>
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<td>4.0</td>
<td>7</td>
<td>0.14</td>
<td>1.4</td>
<td>293</td>
<td>&lt;31</td>
<td>42</td>
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<td>19007+0847</td>
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<td>1.0</td>
<td>1.0</td>
<td>0.03</td>
<td>0.1</td>
<td>111</td>
<td>&lt;4</td>
<td>12</td>
</tr>
<tr>
<td>19213+1723</td>
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<td>2</td>
<td>0.06e</td>
<td>0.4f</td>
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<td>28</td>
</tr>
<tr>
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<td>5</td>
<td>0.07</td>
<td>0.2</td>
<td>560</td>
<td>&lt;40</td>
</tr>
<tr>
<td>20024+3330</td>
<td>40&quot; x 20&quot;</td>
<td>0.7</td>
<td>1.3</td>
<td>2</td>
<td>0.05</td>
<td>0.5</td>
<td>73</td>
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<tr>
<td>20293–3952</td>
<td>610&quot;</td>
<td>0.6</td>
<td>1.8</td>
<td>2</td>
<td>0.06</td>
<td>0.2</td>
<td>97</td>
<td>&lt;12</td>
</tr>
<tr>
<td>20319–3958</td>
<td>615&quot;</td>
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<td>10b</td>
<td>0.08</td>
<td>179</td>
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<td>21</td>
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<tr>
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<td>0.2</td>
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<tr>
<td>21282+5050</td>
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<td>3.7</td>
<td>3.7</td>
<td>3.7</td>
<td>0.24</td>
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</tr>
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<td>22308+5819</td>
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<td>2.2</td>
<td>4</td>
<td>0.06</td>
<td>0.3</td>
<td>130</td>
<td>&lt;10</td>
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</tbody>
</table>

* Estimated from on-line narrow-band measurements in large beams at 3.3 μm and in the continuum

Integrated band flux over an area 1' x 1' around the peak of the 3.3 μm emission

In a 20" beam

Each spectrum. In most cases, the 3.3 μm band flux, measured in spectra obtained in a 12" and 26" beam (UKIRT spectra) or 15" beam (ESO spectra) is accurate to ±10% (UKIRT spectra) and ±15% (ESO spectra). In order to compare the 3.3 μm band fluxes with fluxes in the other bands (those in the IRAS-LRS spectra), we need to estimate the total 3.3 μm band flux over the whole extent of the source. In order to do so, we have either mapped the area of 3.3 μm emission, both at 3.3 μm and in the 3 μm continuum, or checked the extent and relative strength over that extent of the 3.3 μm emission. The resulting “total” 3.3 μm band fluxes in Table 3 are given with uncertainties between 10 and 30%. The most accurate values are for the sources 21282+5050 and 18184–1302 which are both less extended than 12". The 3.3 μm feature looks broader in spectra obtained at ESO than in those obtained at UKIRT. This is due to the lower intrinsic spectral resolution (≈70) of the CVF used at ESO and the smoothening we applied to ESO spectra lowering the resolution to about 50.

4. Analysis

4.1. Infrared emission mechanism of a large isolated molecule

We recall here briefly the basic mechanism which governs the IR emission of a large isolated molecule, in order to justify the calculations presented in the next paragraphs. This mechanism is described in detail in Léger et al. (1989a).

Upon the absorption of a UV photon, an isolated molecule undergoes an electronic transition from its ground electronic state $S_0$ (or $D_0$, if it is ionized) to a higher electronic state (for example $S_3$). In large molecules (more than 5 atoms), non-radiative processes (i.e. iso-energetic intramolecular transitions) transfer this electronic excitation to vibrational excitation of the electronic ground state (Birks, 1970; Bondybey, 1984) on a very short timescale (≈10−12 to 10−8 s). This “hot” molecule is in an internal thermodynamical equilibrium because the internal coupling between all the vibrational modes is very strong compared to the coupling to the surroundings (emission of an infrared photon or collision with the interstellar gas). A statistical description of the system is thus adequate after times of the order of 10−16 s (Oref and Rabinovich, 1979; Smalley, 1983). In its ground electronic state, the molecule can relax only by emitting an infrared photon. Inverse internal conversion to the first excited electronic state and visible fluorescence is nevertheless possible as shown by Léger et al. (1988) and although it has been shown that this last process may be observable in the interstellar medium (red fluorescence, d’Hendecourt et al., 1986), the amount of energy emitted in the visible is small, about 10 to 20% (Ryter and d’Hendecourt, 1989); this process is thus neglected in our following calculations.

After the emission of one infrared photon, redistribution of the vibrational energy is extremely fast (IVR, Internal Vibrational Randomization; Parmenter, 1982). The vibrational energy is redistributed in ≈10−12 s while it takes about 10−1 s for an infrared photon to be emitted. Thus, between the emission of two infrared photons, a vibrational temperature can be assigned to the molecule. It can be shown that, in the case of high excitation, the population of the vibrational levels can be approximated by a Boltzman distribution, thus justifying the use of the thermal approximation which makes the infrared emission of the molecule particularly easy to calculate (Léger et al., 1989b; Léger et al., 1989a). After the emission of each infrared photon, IVR proceeds again so that each photon is emitted after thermalization at a progressively decreasing temperature. Note that the temperature
of the cooling molecule can be calculated at any given decreasing energy as long as the specific heat of the molecules is known (Léger and d’Hendecourt, 1987). The validity of this approach has been verified experimentally: in naphtalene and azulene, the production of vibrationally hot molecules and the process of IVR have been demonstrated (Gottfried et al., 1984; Wild et al., 1985). In azulene, the absorption of a UV photon of 19000 cm−1 (2.35 eV) energy leads to a transient internal temperature of about 1200 K.

Following Léger and Puget (1984) the emission intensity $I_2$ of a physical object at a temperature $T$ is:

$$I_2 = B_2(T),$$

where $B_2$ is the emissivity of the object and $B_2(T)$ is the Planck function at the emission temperature $T$. The emissivity of a given molecule is known by recording its absorptivity from its infrared spectrum. Absorption spectra of various large PAH molecules have been measured in the laboratory (Léger and d’Hendecourt, 1987). Fortunately, the measured cross-sections of the fundamental transitions in various molecules do not vary much from one molecule to another so that an average integrated absorbance $A_2$ can be used in the calculations on interstellar molecules, the precise shapes and sizes of which are not a priori known. These integrated absorbances used in our calculations, are given in Table 4. Although the assumption $B_2 = A_2$ is justified by Kirchhoff’s law (Reif, 1965), $A_2(T)$ is generally measured in the laboratory at room temperature and, to compute an emission spectrum we implicitly assume that $A_1(T_1) = A_1(T_2)$ where $T_1 > T_2$. In support of this assumption, Bernard et al. (1989) have recently measured absorption spectra of coronene between 300 and 500 K. No variation in $A_2$ was detected in this experiment.

4.2. Intensity ratio of the 11.3 to the 3.3 μm features: the size of the molecule?

As given by Eq. (1), the infrared emission spectrum is obtained from the convolution of the absorption spectrum by the Planck function at the emission temperature, a function which is strongly temperature-dependent. As a consequence, the intensity ratio of two bands is a function of the temperature. In an astronomical spectrum, the observed intensity ratio of two bands, preferentially having a large energy separation, allows us to estimate the average temperature of the emitting molecules. This only holds if the two bands pertain to the same molecular subgroup, so that the same number of oscillators are responsible for the emission of these two lines. The 11.3 μm and 3.3 μm bands belong to the = C—H group (out of plane bending and stretching respectively) and therefore satisfy our criteria. The intensity ratio of these two bands can be used to derive the average emission temperature:

$$\frac{I_{11.3 \mu m}}{I_{3.3 \mu m}} = \frac{B_{11.3 \mu m}(T)}{B_{3.3 \mu m}(T)} \times \frac{A_{11.3 \mu m}}{A_{3.3 \mu m}}.$$  

This approach is valid for unknown (i.e. interstellar) molecules if, as already stated in the previous section, the integrated absorbance of each transition does not depend much on the precise shape and size of the molecule, so that the average values $A_i$ given in Table 4 can be used in the computations. The observed intensity ratio in our sample of 24 IRAS sources and the corresponding average emission temperature of the molecules are given in Table 5. The derived temperatures are in the range 460 to 710 K, accounting for relative errors on the intensity ratios of 10 to 30%.

If one then assumes a unique molecular size as well as a unique excitation energy (energy of the incoming UV photon), it is possible to derive the average size of the emitting molecules. Upon the absorption of a UV photon, the molecule will reach a peak temperature $T_{peak}$ which is related to the energy of the incident photon and to the specific heat $C(T)$ of the molecule according to the following equation:

$$h\nu_{UV} = \int_{T_i}^{T_{peak}} C(T) dT,$$

where $T_i$ is the initial equilibrium temperature ($T_i \approx 10$ K). The specific heat depends on the total number of atoms per molecule and on the C/H ratio of the molecule. We have adopted the values given by Léger and d’Hendecourt (1987) in Fig. 16 of these authors; for saturated molecules, we use the specific heat of coronene (C/H = 2), whereas for dehydrogenated molecules (see next section) the values of graphite have to be used.

Assuming that the average temperature $\langle T \rangle$ is close to the temperature at which the molecule has released half of its energy, we obtain:

$$\langle T \rangle \approx \frac{3}{2} T_{peak}.$$  

From this relation and Eq. 3, one can deduce the average number of atoms in the emitting species, provided the excitation spectrum of the incoming photons is known. Unfortunately, for most of the IRAS sources presented here, this last information is generally not yet available. We must then rely on what is known about the UV absorption of PAH molecules. Absorption spectra in the UV of large PAHs, including coronene, show a strong absorption band around 2000 Å, i.e. 6 eV (Clar, 1964; Birks, 1970); this absorption is characteristic of conjugated bonds in carbon and is also found in graphite. However, until recently no quantitative information was available on the far UV (1800–900 Å) spectrum of PAHs. From similarities with graphite and benzene (Draine and Lee, 1984; Berkowitz, 1979; d’Hendecourt and Léger, 1987), a strong rise in the far UV is expected after the bump at 6 eV. Recently, Léger et al. (1989c) have measured the absorption spectrum of coronene between 3500 and 500 Å; they report the same behaviour as in graphite (a peak at about 2000 Å, then continuous rise in the far UV and a peak at 700 Å). From these measurements and their

---

Table 4. Integrated absorption cross sections ($A_i = \sigma_i \cdot \Delta \lambda_i$) averaged over 5 large PAHs

<table>
<thead>
<tr>
<th>$\lambda_i$ (μm)</th>
<th>3.3</th>
<th>6.2</th>
<th>7.7</th>
<th>8.6</th>
<th>11.3</th>
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<tr>
<td>Units for $A_i$</td>
<td>H$^{-1}$</td>
<td>C$^{-1}$</td>
<td>C$^{-1}$</td>
<td>H$^{-1}$</td>
<td>H$^{-1}$</td>
</tr>
<tr>
<td>$A_i$ (Compact PAHs)</td>
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<td>0.70</td>
<td>2.0</td>
<td>1.2</td>
<td>14</td>
</tr>
<tr>
<td>$f_i/10^{-6}$</td>
<td>1.45</td>
<td>0.21</td>
<td>0.38</td>
<td>0.18</td>
<td>3.4</td>
</tr>
</tbody>
</table>

1 from Léger, d’Hendecourt and Défornveau (1989). Note that the values for the 11.3μm band have been revised since Léger and d’Hendecourt (1987)

Notes to Table 4:
The wavelength positions of the bands refer to the observed astronomical bands; the exact laboratory positions do vary slightly from one molecule to another. The resulting oscillator strengths, $f_i = 1.13 \times 10^2 (A_i/\text{cm}^2)/(\lambda/\text{μm})^{-2}$ are also given. The integrated absorbance at 11.3μm quoted here has been measured in the case of isolated molecules dispersed in rare gase matrix.
Table 5. Ratio of the 11.3 µm to the 3.3 µm bands and size of the molecules

<table>
<thead>
<tr>
<th>Source Name</th>
<th>(I(11.3,\mu m))</th>
<th>(I(3.3,\mu m))</th>
<th>(&lt;T&gt;) (a)</th>
<th>(N_{TOT}) (b)</th>
<th>(N_{TOT}) (c)</th>
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</thead>
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<tr>
<td>03035+5819</td>
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<td>158</td>
<td>117</td>
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<td>94</td>
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<td>518</td>
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<td>8.5</td>
<td>523</td>
<td>108</td>
<td>140</td>
<td>105</td>
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</tbody>
</table>

1 Total number of atoms per molecule inferred from the observed \(I(11.3\,\mu m)/I(3.3\,\mu m)\) ratio assuming an incident UV photon of 6 eV (Note that if an energy of 6 eV is assumed, these numbers are reduced by a factor \(9/6 \approx 1.5\)):
   (a): based only on the colour temperature derived from the observed \(I(11.3\,\mu m)/I(3.3\,\mu m)\) intensity ratio (Equation 2)
   (b): considering the exact cooling of hydrogenated molecules in five bands
   (c): considering the exact cooling of dehydrogenated molecules in five bands

Analysis of the possible extinction curve of PAHs in the interstellar medium, the average energy absorbed by these molecules from the interstellar radiation field is about 9 eV. We adopt this value in our calculations and we discuss in the next section the possible influence of a change in this energy. The results in terms of total number of atoms in the emitting species are given in Table 5, column (a). Note that in this case we have considered hydrogenated molecules with a specific heat analogous to that of coronene \((C/H = 2)\). We obtain rather large molecules, but we emphasize that these sizes should be taken as upper limits because we have considered UV photons of mean energy 9 eV and have not taken into account the effect of a possible UV extinction.

4.3. Total cooling of a molecule

The LRS spectra also include the 7.7 and 8.6 µm emission bands. In aromatic compounds, these bands correspond respectively to a blend of C—C stretching and to C—H in plane bending modes (Bellamy, 1966; Allamandola et al., 1987). As noted by Léger and Puget (1984), the 7.7 µm band is not found in small aromatic compounds and may be specific to larger species. Integrated absorbances for these bands are known from laboratory measurements (see Table 4). We have therefore computed the total emission of a molecule in each of the five bands, from 3.3 to 11.3 µm, during the cooling from its peak temperature back to its initial temperature. Following Léger and d’Hendecourt (1987), the radiative power of a molecule is obtained by summing the power radiated in each band. It is given by:

\[ P = 4\pi \sum_{\lambda} B(\lambda, T) A^C_{\lambda} N_{C,H}, \]

where \(B(\lambda, T)\) is the Planck function, \(A^C_{\lambda}\) is the integrated cross-section per carbon (or hydrogen) atom of the \(\lambda\) th band and \(N_{C,H}\) the number of carbon (or hydrogen) atoms in the molecule. The temperature of the molecule decreases with time as:

\[ P dT = -C(T) dT. \]

The power emitted in each band is then calculated during the cooling of the molecule from \(T_{peak}\) to \(T_i\), the initial temperature taken as 10 K. The five main fundamental bands of PAHs (3.3, 6.2, 7.7, 8.6, and 11.3 µm) have been included. Far infrared spectra of various PAH molecules have been recorded in the laboratory (Léger et al., 1989a) and can be used to compute the cooling due to modes at longer wavelengths (λ > 12 µm). We have not included these latter in our calculations because they do not have a significant influence on the intensities of the bands at short wavelengths until the temperature is low \((T < 100 \, K)\), in which case the amount of emitted energy is small.

The results of this computation are presented in Table 6 for a few known PAHs. Figure 5 shows the \(I(11.3\,\mu m)/I(3.3\,\mu m)\) intensity ratio as a function of the total number of atoms in the molecule. Curve (1) is in the case of hydrogenated molecules \((C/H = 2)\), using the heat capacity of coronene; the set of curves (2) includes several cases of dehydrogenated molecules, using the heat capacity of graphite. These results are derived from a more accurate calculation than in Sect. 4.2 as given in Table 5 column...
Table 6. Cooling of a PAH molecule in the five bands

<table>
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<tr>
<th>Molecule</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
</tr>
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<tbody>
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<td>1.406</td>
<td>0.426</td>
<td>2.504</td>
<td>1905</td>
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<tr>
<td>( \text{C}<em>{20}\text{H}</em>{12} ) Coronene</td>
<td>3.139</td>
<td>1.043</td>
<td>1.821</td>
<td>0.420</td>
<td>2.555</td>
<td>1664</td>
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<td>1.156</td>
<td>2.114</td>
<td>0.436</td>
<td>2.786</td>
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</tr>
<tr>
<td>( \text{C}<em>{20}\text{H}</em>{15} ) Circodiphenyl</td>
<td>2.101</td>
<td>1.186</td>
<td>2.241</td>
<td>0.452</td>
<td>2.985</td>
<td>1263</td>
</tr>
<tr>
<td>( \text{C}<em>{24}\text{H}</em>{20} ) Discoronenone</td>
<td>1.629</td>
<td>1.177</td>
<td>2.345</td>
<td>0.478</td>
<td>3.331</td>
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<tr>
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<td>1.373</td>
<td>1.322</td>
<td>2.676</td>
<td>0.440</td>
<td>3.138</td>
<td>1055</td>
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</tbody>
</table>

Notes to Table 6:
Columns (1) to (5): Energy radiated in each band (in units of eV) during the complete cooling of the molecule, after absorption of an incident UV photon of energy 9 eV.
Column (6): Peak temperature reached by the molecule immediately after the absorption of the 9 eV UV-photon.

Fig. 5. Total number of atoms (C-atoms + H-atoms) per molecule as a function of the \( I(11.3\mu m)/I(3.3\mu m) \) intensity ratio, assuming an incident UV photon of energy 9 eV. (1) In the case of hydrogenated PAH molecules, with a chemical formula such as C/H = 2, using the heat capacity of coronenone \( \text{C}_{24}\text{H}_{12} \) as given by Léger and d’Hendecourt (1987) in their Fig. 16. (2) In the case of dehydrogenated PAH molecules, with a hydrogenation percentage of (a) 5%, (b) 10%, (c) 15%, (d) 25%. These percentages are relative to a 100% hydrogenation being equivalent to C/H = 2. Specific heat of graphite (from Léger and d’Hendecourt, 1987, Fig. 16) has been used.

(a); however, they agree with them, but, in the case of hydrogenated molecules, slightly larger sizes are obtained as listed in column (b) of Table 5.

4.4. Evidence for dehydrogenation of interstellar PAHs

From the calculations presented in the previous section, it is possible to investigate the behaviour of other spectral bands (7.7 and 8.6 \( \mu m \)). For a given \( I(11.3\mu m)/I(3.3\mu m) \) intensity ratio in a source and assuming hydrogenated molecules (C/H = 2), we first compute the peak temperature reached by the molecule and the expected intensities in the 7.7 and 8.6 \( \mu m \) bands. The results for the 24 sources of our sample are given in Table 7 [columns (1) and (2)]. Values are normalized to the 3.3 \( \mu m \) band intensity. Clearly, the observed 7.7 and 8.6 \( \mu m \) are much stronger (by about a factor 10) than the computed values. For the 7.7 \( \mu m \) band, this fact was noted by Léger and d’Hendecourt (1987). As this band corresponds to stretching vibrations of carbon atoms in the molecules, it was proposed that such a result pointed to a strong dehydrogenation (up to 95%), resulting in a corresponding reduction in the intensity of the bands pertaining to C—H relative to those pertaining to C=C vibrations. Following the same idea, this strong dehydrogenation can also be deduced from the intensity ratios in Table 7 [columns (1) and (2)]. We obtain a dehydrogenation of 75 to 95%. For a molecule containing 90 carbon atoms, only 2 to 10 hydrogen atoms should thus be allowed to account for the relative intensities of the 7.7 to the 3.3 \( \mu m \) bands.

To check this hypothesis, we have computed the emission spectrum of strongly dehydrogenated PAH molecules, using the heat capacity of graphite. We have selected the number of atoms per molecule from curves 2's in Fig. 5, according to the dehydrogenation factor determined in Table 7 for each source, and such that the \( I(11.3\mu m)/I(3.3\mu m) \) intensity ratio remains constant. We then compute the spectrum for such dehydrogenated molecules. The results are given in Table 7 [columns (3)]. The 7.7 \( \mu m \) band now agrees well with the observed one. Naturally the 8.6 \( \mu m \) band has...
<table>
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<th>C/HaHx.4</th>
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</table>

Notes to Table 7:
Columns (1), (2), (3) refer respectively to the source, the hydrogenated molecule and the dehydrogenated molecule. For each band ratio, column (1) is the ratio observed in the source, column (2) is the ratio computed for the corresponding hydrogenated molecule (C/H=2), column (3) is the ratio computed for the corresponding dehydrogenated molecule. The hydrogenated molecules have been chosen from Figure 5 and are such that the total number of atoms corresponds to the I(11.3 μm)/I(3.3 μm) ratio observed in the source. The hydrogenation percentage for each couple (source, molecule) is derived from the discrepancy between the observed (1) and computed (2) values of the I(7.7 μm)/I(3.3 μm) ratio and given in the last column of the table. This percentage is relative to a 100% hydrogenation corresponding to a C/H ratio of 2. In reality, for cation condensed PAHs, this ratio is indeed larger (C/H=3n for molecules of the form C_{6n}H_{6n}). The calculations have been made for molecules with C/H=2 because the only specific heat available was that of coronene (C_{24}H_{12}). The dehydrogenated molecules have been chosen from Figure 5 on the curve corresponding to the hydrogenation percentage derived above, and are such that the total number of atoms corresponds to the I(11.3 μm)/I(3.3 μm) ratio observed in the source. Therefore, there is a good match between observed (1) and computed (3) band ratios only for the two ratios I(7.7 μm)/I(3.3 μm) and I(11.3 μm)/I(3.3 μm). The decimal numbers of hydrogen atoms in the formulae of these dehydrogenated molecules only have a statistical meaning. The size of the molecules (columns 2 and 3) are computed for an incident UV photon of 9 eV (see caption Table 5).

5. Discussion
The results presented in Sect. 4 point to rather large molecules, of a total number of atoms between 56 and 133, which are strongly dehydrogenated. These sizes are proportional to the energy of the exciting UV photon. For an energy of 6 eV, the sizes obtained would vary between 37 and 88 atoms. The average energy of the photon absorbed by PAH molecules is the result of the convolution product of the UV excitation spectrum (i.e. the spectral type of the star) by the UV absorption spectrum of these molecules. In the case of an A 0 star (T = 10^4 K) and adopting the UV absorption spectrum of a PAH mixture measured by Leger et al. (1989c), an average energy of 6.5 eV is obtained. For a hotter star (T = 4 10^5 K), the average energy is 9.5 eV. To be precise it would be necessary to treat each source individually according to its exact UV radiation field. This information is not available for most of our sources. However, half of the sources are compact H ii regions and thus contain O or B stars. Therefore we have adopted an average energy of 9 eV for the absorbed UV photons. This represents only an approximation; it is clear that the dispersion in molecular size [Table 5, column (c)] may reflect a difference in the UV radiation field rather than a true difference in size. Note that the average energy of the absorbed UV photon would not vary too
much if local extinction is considered because, at these energies (6–13.6 eV), the extinction is largely dominated by PAHs (Léger et al., 1989c).

With the present set of data, no precise information on a possible size distribution can be obtained and only average sizes are given. Obviously larger molecules are cooler than smaller ones. If a wide range of sizes is present, the derivation of an average size is less relevant as far as the physico-chemical properties of these molecules are concerned. Clearly, an estimate of a size distribution for these molecules can be reached only if a band located at a wavelength shorter than 3.3 μm or longer than 11.3 μm can be also used. The first possibility is discussed in a subsequent paper (Paper 2). Since far-infrared spectroscopic data on PAHs do exist (Léger et al., 1989a) as well as photometric IRAS data at 25 and 60 μm, these could be used to estimate the contribution of large molecules (more than 150 atoms) to the far-infrared emission. However, the targets for this investigation must be selected with care in order to avoid confusion with heated dust (such as in planetary nebulae or galaxies). Reflection nebulae (Sellgren, 1984) and cirrus clouds (Boulanger and Perault, 1988) appear to be good candidates for such studies especially since the recent detection of the 3.3 μm band in the diffuse emission of the galactic disk by Giard et al. (1988).

The average molecular sizes obtained do agree well with those given by Léger and d'Hendecourt (1987) who derived an average number of 60 atoms in the molecules responsible for the infrared emission bands in reflection nebulae. They used at the time a photon energy of 6 eV. For an energy of 9 eV, the average number would be 90 atoms, which is consistent with our results.

Smaller values (total number of atoms between 20 and 40) have been obtained by Cohen et al. (1986) in their analysis of the \( J(11.3 \mu m)/J(3.3 \mu m) \) intensity ratio. However, they use a smaller energy for the incoming UV photon (4.8 eV), a value which does not take into account the far UV spectral properties of PAHs. Also, to calculate the infrared fluorescence yield according to the model of Allamandola et al. (1985), Cohen et al. (1986) assume that about half of the absorbed UV photon energy is released via visible fluorescence arising from electronic transitions between low-lying electronic states in the molecule. Unfortunately, the efficiency of this process in an isolated molecule is not known and might be different from the efficiency they quote (from Birks, 1970) which was given for molecules in condensed phase. If one allows all the energy to be emitted in the infrared and uses a larger energy for the incident UV photon, then the discrepancy with our results is removed and larger molecular sizes have to be considered.

The problem of electronic fluorescence has been examined by Léger et al. (1988). In large isolated molecules, inverse internal conversion from the hot ground electronic state to the first excited electronic state is possible and depends extremely strongly on the size of the molecules. This process is called “Poincaré fluorescence”. As a consequence, molecules of 36 atoms show a fluorescence yield of about 0.6 for a photon energy of 9 eV whereas for a molecule of 18 atoms, the yield is ≈ 1. In other words, if this process is valid, infrared emission from molecules smaller than 30 atoms is greatly reduced and a strong fluorescence in the visible (red) is predicted. This result has been applied by Ryter and d'Hendecourt (1989) to some reflection nebulae. In these objects, the small amount of visible light attributed to fluorescence from organic molecules (Witt and Schild, 1986) points to large molecules, i.e. 70 atoms in NGC 2023 and a lower limit of 70 atoms in M82, which is consistent with our results.

The range in the calculated average number of atoms per molecule (from 50 to 130) may reflect a genuine variation in the size of the molecules, a different size distribution, or a variation in the spectral distribution of the exciting UV radiation, as well as uncertainties in the measurements of the various bands. In sources where the UV spectrum of the exciting star is known, e.g. the Red Rectangle (HD 44179) and NGC 7027, this can be investigated further. Cohen et al. (1986) found hotter molecules in the cooler source HD 44179 than in NGC 7027. Thus, in HD 44179, the molecules might be really smaller than in NGC 7027, a fact which could be interpreted in terms of photo-thermo-dissociation of the molecules (Léger et al., 1989c); smaller molecules will be primarily destroyed in a radiation field where the average photon energy is high. The same analysis cannot be performed at the present time on our data set, by lack of information on the UV field in the sources.

The high level of dehydrogenation confirms similar results obtained by Léger and d'Hendecourt (1987) for HD 44179, NGC 2023, and M82. Dehydrogenation is also supported by the wavelength position of the band attributed to the C–H out-of-plane bending mode in astronomical spectra. The fact that a strong band is observed at 11.3 μm is highly characteristic of the presence of only hydrogen atoms at the periphery of the emitting molecules (Bellamy, 1966). For molecules such as coronene, which have only one or two hydrogen atoms, the mode occurs at 11.9 μm. For large hexagonal molecules, the C/H ratio drops (Omont, 1986; Tielens et al., 1987) and for the most symmetric family of molecules (series 1 in Tielens et al., 1987), the number of only hydrogen increases quickly with the size of the molecule. The strong dehydrogenation (say 90%), which is calculated with reference to C/H = 2 (coronene), does not imply that all the carbon at the periphery of the molecule are radicals. For example, the molecule \( C_{16}H_{24} \) in series 1 of Tielens et al. (1987) has 42 carbon atoms located at its periphery. Only 24 of these atoms are linked to a hydrogen atom in the neutral closed shell molecule. A dehydrogenation of 90% (w.r.t. C/H = 2) implies that only 19 of these C-atoms are radicals, in a molecule where the total number of C-atoms is 96.

With respect to this rather strong dehydrogenation, one might wonder if the infrared spectrum of the molecule would not be drastically modified. In fact, only carbon atoms at the periphery could be affected by dehydrogenation. Laboratory data on benzene and the formation of the benzyne radical (\( C_6H_4 \)) show that a triple bond between carbon atoms is formed (Houben-Weyl, 1981), but the infrared spectrum is barely changed. Triple \( C=C \) bonds possess only a very weak activity in the infrared (Bellamy, 1966) around 2000 cm\(^{-1}\) (5 μm), which is probably not detectable in interstellar spectra. However, more laboratory experiments on dehydrogenated molecules are highly desirable.

6. Conclusion

Additional 3 μm observations of sources observed by the IRAS-LRS instrument have enabled us to obtain an almost complete coverage of the infrared bands attributed to PAHs in these sources; only information on the band at 6.2 μm is still missing.

The \( J(11.3 \mu m)/J(3.3 \mu m) \) intensity ratio has been used to derive an average molecular temperature, which turns into an average molecular size of the emitting species. Rather large molecules (between 50 and 130 atoms) are responsible for these bands. These sizes must be considered as upper limits because the adopted energy of 9 eV for the incident UV photon may be too
high (the size derived for the molecules is directly proportional to this energy). Additionally, the molecules are strongly dehydrogenated.

It is not possible at the present time to establish whether the variation of the $I(11.3 \mu m)/I(3.3 \mu m)$ intensity ratio is due to a true variation in the average size of the molecules, or reflects the variation in the spectral properties of the UV source. With the present data, no estimate of a size distribution of the molecules is possible but this information can be obtained in the future by taking into account near ($\lambda < 3 \mu m$) or far-infrared spectra of the sources. The near-infrared spectrum will be discussed in a future paper.

The large molecular sizes obtained here are consistent with earlier estimates if the visible fluorescence of these molecules is neglected, an assumption that can be checked by obtaining visible spectra of the sources.

Interstellar PAHs are thus large, dehydrogenated as well as ionized species and represent a challenge for future laboratory experiments. Up to now, only small and middle size neutral molecules (as big as coronene, $C_{24}H_{12}$) have been studied in the laboratory. It would be extremely interesting to investigate the spectroscopic properties of large radical cations, setting the goal for new experiments.

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