Laboratory Studies on the Role of PAHs as DIB Carriers

F. Huisken[1], G. Rouillé[1], M. Steglich[1]†, Y. Carpentier[1]‡, C. Jäger[1] and Th. Henning[2]

[1]Laboratory Astrophysics Group of the Max Planck Institute for Astronomy at the Friedrich Schiller University Jena, Institute of Solid State Physics, Helmholtzweg 3, D-07743 Jena, Germany
email: `friedrich.huisken@uni-jena.de`

[2]Max Planck Institute for Astronomy, Königstuhl 17, D-69117 Heidelberg, Germany

Abstract. The electronic spectroscopy of various polycyclic aromatic hydrocarbon (PAH) molecules has been studied in the laboratory at low temperatures using both molecular beam and matrix isolation spectroscopy techniques. While molecular beam spectra can be readily compared to astronomical observations, the band positions measured in Ne and Ar matrices are extrapolated to obtain rather good estimates for the same transitions in the gas phase. Absolute absorption cross sections are determined for gas-phase and matrix spectra by comparing them with calibrated solution spectra. All laboratory results are analyzed and discussed in view of the role that PAHs can play as carriers of the diffuse interstellar bands (DIBs). Our studies suggest that regular neutral PAHs are not responsible for any of the known strong DIBs.

Keywords. DIBs, PAHs, molecular beams, matrix isolation spectroscopy, electronic absorption spectra

1. Introduction

The diffuse interstellar bands (DIBs), being first observed in the early 20th century (Heger 1922), are currently the oldest unsolved puzzle of astronomical spectroscopy. Based on observational data, it is assumed that gas phase molecules rather than dust particles are the carriers of the DIBs; but a definite identification is still lacking.

More than 25 years ago, polycyclic aromatic hydrocarbons (PAHs) were proposed as particularly attractive candidates not only for the carriers of the unidentified infrared bands (UIRs) but also for the DIBs (Léger & d'Hendecourt 1985; van der Zwet & Allamandola 1985). The existence of PAHs in various astrophysical environments has actually been inferred from the detection of infrared emission bands related to aromatic C-H and C-C vibrations. Based on these vibrational mid-infrared bands, the identification of a specific molecule is unfortunately not possible. Only information about the size and charge state distributions, as well as the ratio between aliphatic and aromatic carbon can be obtained (Draine & Li 2007). Resorting to energetic arguments, the infrared emission bands are attributed to aromatic molecules containing about 50 carbon atoms (Tielens 2008). After H_2 and CO, PAHs are probably the most abundant molecules in the interstellar medium (ISM) (Léger *et al.* 1989). It is possible that they are also responsible for various other, still unexplained spectroscopic features like the extended red emission (ERE) (Rhee *et al.* 2007), the blue luminescence (Vijh *et al.* 2005), the ultra-violet (UV)

† Present address: Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.

‡ Present address: Laboratoire de Physique des Lasers, Atomes et Molécules, CNRS Univ. Lille 1 Sciences et Technologies, UMR 8523, 59655 Villeneuve d'Ascq Cedex, France.

extinction bump at 217.5 nm (Beegle *et al.* 1997), and in particular the DIBs (Jenniskens & Désert 1994; Salama *et al.* 1999; Ruiterkamp *et al.* 2002). For recent reviews on PAHs, see, for example, the publications by Tielens (2008) and Salama (2008).

In general, the size of PAHs may range from small molecules containing a few rings to large units, which can be considered as fragments of graphene, whose peripheral carbon atoms are passivated by hydrogen. To further add to the diversity, they can be partly dehydrogenated and/or they can be charged. These species may be produced as a result of the interaction with the interstellar radiation field.

In order to prove whether observational spectra contain features, which can be attributed to PAHs, we have to compare them with laboratory spectra. To make this comparison meaningful, the laboratory measurements must be carried out under astrophysical conditions, i.e., at low temperature and in an interaction-free environment in the gas phase. The most elegant method where these requirements are ideally met is the supersonic jet technique. A rare gas is seeded with the vapor of the PAH species to be studied and expanded through a small nozzle into a high vacuum. The expansion provides an extremely rapid cooling of the molecules down to temperatures between approximately 2 and 50 K, depending on what internal degree of freedom is considered. Moreover, at a distance of a few nozzle diameters, the density has decreased so much that the PAH molecules fly freely without interacting with each other or the rare gas atoms. Due to the low density, the spectroscopic technique applied to investigate their optical properties must be extremely sensitive, a requirement, which calls for the application of laser spectroscopy. The method is referred to as molecular beam spectroscopy (MBS).

A highly sensitive direct absorption technique being well-adapted to astrophysical applications is provided by the so-called cavity ring-down spectroscopy (CRDS) (O'Keefe & Deacon 1988). The first applications of CRDS to the study of jet-cooled PAHs were reported in the late 1990s (Romanini *et al.* 1999; Ruth *et al.* 1999). In this technique, the tunable laser beam is injected into a cavity with extremely high quality (high reflectance of the mirrors) containing the supersonic jet expansion, and the decay of the transmitted laser beam is measured as a function of the laser wavelength. The resonant absorption of the PAH molecules in the jet causes a faster decay of the signal, which can be correlated with the absorption cross section at this particular wavelength. To determine absolute absorption cross sections, however, is very difficult as the density of PAH molecules in the jet is not known and as it is not homogeneously distributed along the cavity axis.

Another powerful technique to obtain spectroscopic information on molecules at cryogenic temperature, however not in the gas phase, is matrix isolation spectroscopy (MIS). It is based on the incorporation of the molecules to be studied into a solid rare gas matrix and their spectroscopic characterization with a conventional spectrometer. Although the method does not supply gas phase data, which can be directly compared with astrophysical observations, it is nevertheless extremely useful as it delivers overview spectra spanning the entire region from the UV to the near infrared (IR). These overview spectra can then be used to estimate the corresponding transitions in the gas phase and to define the spectral region where the more sophisticated supersonic jet CRDS measurements are to be carried out. Moreover, if matrix spectra in both Ne and Ar matrices are available, gas-phase band positions can be estimated with rather high accuracy by plotting the band positions as a function of the polarizability of the matrix material in which they were measured and extrapolating them to zero-polarizability. In addition, compared to the supersonic jet technique, MIS has the following advantages not yet mentioned:

- Thick layers yielding large absorptivities can be easily grown.
- Conventional light sources in conjunction with spectrometers provide sufficient resolution.

- The entire spectral region of interest can be easily covered.
- The method ensures relatively short measuring times.
- MIS consumes few amounts of sample material (important if the PAHs are only available in small quantities).
- Equilibrium between all degrees of freedom is obtained ensuring low *vibrational* temperature.
- Absolute absorption cross sections can be determined when the matrix spectra are compared with solution spectra.

In this paper, we present an overview of the efforts carried out in our laboratory to obtain low-temperature gas-phase spectra of PAHs in the UV and visible (vis). The studies included both molecular beam (MBS) and matrix (MIS) experiments. The matrix spectra were needed to determine absolute absorption cross sections for the measured gas-phase spectra. In cases where gas-phase spectra could not be measured but matrix spectra were available, the gas-phase band positions were determined by extrapolation. The respective PAH samples were either purchased or obtained through cooperations. A method for synthesizing large PAHs in the laboratory under astrophysically relevant conditions, which is based on the CO_2 laser-assisted pyrolysis of hydrocarbons, is described. All results are analyzed and discussed in view of the role that PAHs can play as carriers of the DIBs.

2. Methods

2.1. *Experimental details*

Supersonic jet cavity ring-down spectrometer. In order to study the spectroscopy of a given PAH in a supersonic jet, the molecules must be transferred to the gas phase and expanded, together with a carrier gas (typically He or Ar), into a vacuum. At room temperature, the PAHs are generally in the form of a solid powder. As far as small PAHs are concerned, their vapor pressure can be raised just by heating the powder, which is placed in a small reservoir at the exit of the pulsed supersonic jet source. When the PAHs increase in size, the temperature needed to achieve a proper vapor pressure also increases. As the high temperature may cause the decomposition of the molecules, laser vaporization can serve as an alternative (Rouillé *et al.* 2009a).

We have developed a heated source to generate supersonic jets of rare gases seeded with PAHs. It consists of a pulsed solenoid valve that controls the opening of a pinhole nozzle in the heated reservoir containing the PAH sample. Further details are given elsewhere (Staicu *et al.* 2004; Carpentier *et al.* 2013). To produce a beam of PAH cations, an electrode assembly can be attached to the nozzle exit, generating an electrical discharge in the expanding jet (Sukhorukov *et al.* 2004).

In contrast to conventional laser absorption spectroscopy, the principle of cavity ring-down spectroscopy (CRDS) is to measure the decay of a laser pulse trapped in a high-quality optical cavity containing the absorbing sample. The latter must be optically thin and can be, for example, a supersonic jet. The laser beam transmitted by the output mirror of the cavity is detected by a photmultiplier and then recorded by a digital oscilloscope, which transfers the waveform to a computer. A dedicated program fits an exponential decay to the experimental data, yielding the time constant τ.

The decay rate τ^{-1} can be expressed by

$$\tau^{-1} = c\, L_{\mathrm{c}}^{-1} \left(\sigma N L_{\mathrm{s}} - \ln R \right), \tag{2.1}$$

where c is the speed of light in vacuum, L_{c} is the length of the cavity, σ is the absorption cross section of the molecules present in the beam path, N is the number density of the

molecules in the jet, L_s is the length of the sample along the cavity axis, and R is the reflectance of the mirrors. Thus, by measuring τ^{-1} while varying the wavelength of the light beam, absorption spectra can be obtained with backgrounds that depend on R and not on the intensity of the laser beam.

Interestingly, molecular absorption cross sections can be measured by CRDS provided that the other parameters of Eq. 2.1 are known. In the case of a supersonic jet seeded with PAH molecules, it is however difficult to evaluate N with sufficient accuracy. Therefore, we will employ another method to derive absolute absorption cross sections that is based on calibrated solution spectra (see Sect. 2.2).

Further information on our CRDS setup, giving details of the laser system, the optical components, and the wavelength calibration, can be found elsewhere (Staicu *et al.* 2004; Sukhorukov *et al.* 2004; Rouillé *et al.* 2007; Carpentier *et al.* 2013).

Matrix isolation spectroscopy. Absorption spectroscopy in supersonic jets is usually applied in a very narrow wavelength range and requires rather large amounts of sample. In contrast, matrix isolation spectroscopy (MIS) allows us to explore wide ranges of wavelengths at once, while consuming only little sample. This technique consists in the preparation of a solid transparent matrix in which the molecules under study are kept isolated from each other, usually at cryogenic temperatures.

Because of the interactions taking place between the molecules and the surrounding matrix material, the bands in MIS spectra are broadened and shifted in comparison with jet-cooled gas-phase measurements. For this reason, MIS spectra should not be compared with the results of astrophysical observations. However, MIS is efficient in providing approximate band positions, which are very useful for determining the scan parameters for a measurement in supersonic jets. Moreover, gas-phase band positions can be estimated by extrapolation if MIS data for different matrix materials are available (see Sect. 2.3). Provided that this is possible, in some cases, the MIS data could be sufficient to demonstrate that a particular molecule is not responsible for a given interstellar feature.

We are routinely carrying out MIS studies using either Ne or Ar as matrix material. This choice is determined by the fact that the lighter rare gases provide an environment with the weakest interaction so that broadening and line shift effects are minimized. Our setup has already been described in detail elsewhere (Rouillé *et al.* 2008; Rouillé *et al.* 2009b; Steglich *et al.* 2010). A UV/vis-transparent CaF_2 substrate is mounted on the cold finger of a closed-cycle cryostat incorporated into a high-vacuum chamber and cooled to cryogenic temperatures (6.5 K for Ne and 12 K for Ar). The most convenient way to transfer the PAH molecules to the gas phase, from which they are deposited into the matrix, is to use an oven mounted in a separate chamber close to the CaF_2 window. However, for the deposition of large PAH molecules, laser vaporization is employed. Finally, it should be mentioned that it is also possible to study PAH ions in matrices. The simplest method to produce them is by irradiating the previously prepared neutral matrix with UV light at $\lambda = 121.6$ nm from a hydrogen discharge lamp (Steglich *et al.* 2011).

Laser pyrolysis. For the application of the spectroscopic techniques just described, the use of pure PAH samples, either commercially available or provided by cooperating partners, is most convenient. However, it is difficult to buy or synthesize larger PAHs containing more than $\sim$40 C atoms. Therefore, we resorted to a technique called CO_2 laser pyrolysis. Using a continuous (cw) CO_2 laser with a power of 60 W and ethylene as gaseous precursor, we were able to synthesize in our own laboratory a large variety of PAHs containing up to 200 C atoms (and even more). An important advantage of this particular gas-phase condensation technique is that it simulates the grain formation processes suggested to occur in various astrophysical environments. A schematic sketch
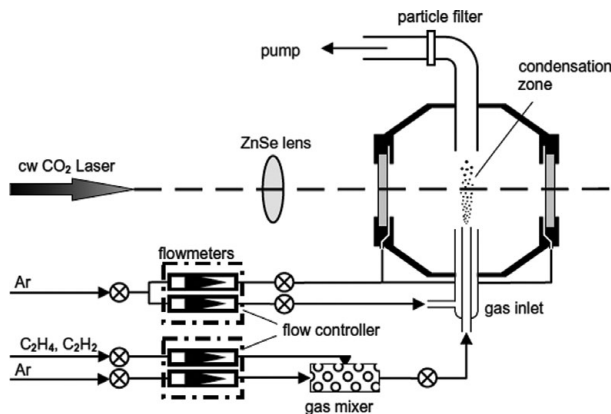
Figure 1. Sketch of the gas flow reactor in which our PAHs are synthesized by laser pyrolysis.

of the flow reactor, in which the laser pyrolysis is carried out, is shown in Figure 1. For further experimental details, the reader is referred to previous publications (Jäger *et al.* 2007; Jäger *et al.* 2009).

The molecules and soot grains created in the 1100 °C hot, flame-like condensation zone were collected in a dedicated filter. Having produced sufficient material, the soluble components (i.e., the PAHs) were extracted from the condensate with methanol and dichloromethane. To obtain information on the composition of the various extracts, they were characterized by chromatographic techniques and matrix-assisted laser desorption/ionization in combination with time-of-flight mass spectrometry (MALDI-TOF) (Jäger *et al.* 2009). An attractive feature of the high-performance liquid chromatography (HPLC) apparatus employed is the fact that it can also be used to exploit the different retention times of differently shaped (sized) PAHs and to prepare fractions with selected PAH size distributions (Steglich *et al.* 2012).

2.2. *Derivation of absorption cross sections*

The photoabsorption cross sections of PAHs in the gas phase are of particular interest for astronomers who want to derive the abundance of such molecules in space or at least quote an upper limit of their concentration relative to H if no spectral match is found (Gredel *et al.* 2011). The absorption cross section of a free-flying molecule is difficult to determine experimentally since one needs to know accurately the number density of the species interacting with the laser beam. On the other hand, for such large molecules as the PAHs, theoretical calculations do not provide a reliable alternative to experiments since the results highly depend on the level of theory.

To derive estimates of the absorption cross sections of PAHs, one can resort to the solution spectra of such molecules, which can be measured quantitatively in the laboratory. Compared to the gas phase, the spectral features of a solution spectrum are affected by a shift of the band positions and a broadening of the band profiles. Both effects result from the interaction of the solute with the surrounding solvent molecules. In a first approximation, one can neglect the solvent effect and assign to a gas-phase transition the same absorption cross section as measured in solution. Unfortunately, a single broad feature in a solution spectrum often corresponds to several bands in the jet spectrum and the jet spectra generally cover only a short wavelength range. Both circumstances make a one-to-one assignment very difficult. In this situation, the measurement of a MIS
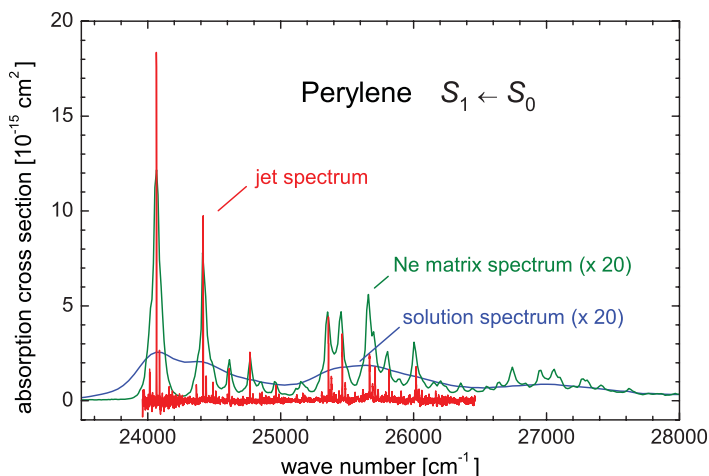
Figure 2. Calibration of the absorption cross section for the gas-phase spectrum of perylene.

spectrum in a cryogenic rare gas matrix may overcome the problem. The perturbation induced by the neighboring rare gas atoms is much smaller than in a solution at 25 °C and, therefore, the individual vibronic features are much better resolved.

Having measured the spectra of a molecule in all three media, molecular beam, cryogenic rare gas matrix (MIS), and solution, the following strategy can be applied: At first, the MIS spectrum is calibrated against the solution spectrum and then the narrow features of the jet spectrum are calibrated against the MIS data. The situation found after correcting the matrix and solution spectra for their matrix shift is depicted for the particular example of the $S_1 \leftarrow S_0$ electronic transition of perylene ($C_{20}H_{12}$) in Figure 2. Although much broader, the individual vibronic bands seen in the supersonic spectrum can still be discerned in the Ne matrix spectrum. However, the solution spectrum is so much broadened that it would be difficult to correlate the jet spectrum with the solution spectrum. Therefore, we apply the following procedure. At first, the matrix spectrum is calibrated against the solution spectrum given in absolute units by integrating both spectra from $22\,000$ to $32\,000$ cm^{-1} (i.e., the entire $S_1 \leftarrow S_0$ transition) and equaling the areas. In this way, the absorption cross section of each band of the Ne matrix spectrum is obtained. In a second step, we perform the same procedure, however, for the much smaller spectral range (from $23\,800$ to $24\,250$ cm^{-1} in the case of perylene) to calibrate the jet spectrum against the matrix spectrum. It is interesting to note that the maximum absorption cross section of the $S_1 \leftarrow S_0$ origin band in the jet spectrum is more than 20 times larger than the corresponding band in the Ne matrix. This is because the origin band is this much narrower in the jet than in the matrix. Further details of the calibration method are described in a forthcoming publication (Carpentier *et al.* 2013)

2.3. *Extrapolation of gas-phase transitions from MIS data*

We have already discussed that, due to the matrix shift, MIS data are not relevant for a close comparison with DIB spectra. Still, they can be exploited to estimate the band positions in the gas phase. These approximate positions are useful for preparing measurements in jets, and they may compensate for the lack of jet-cooled data. It can be shown (Carpentier *et al.* 2013) that, to a very good approximation, the matrix shift observed in rare gas matrices scales with the polarizability of the matrix material. Thus,
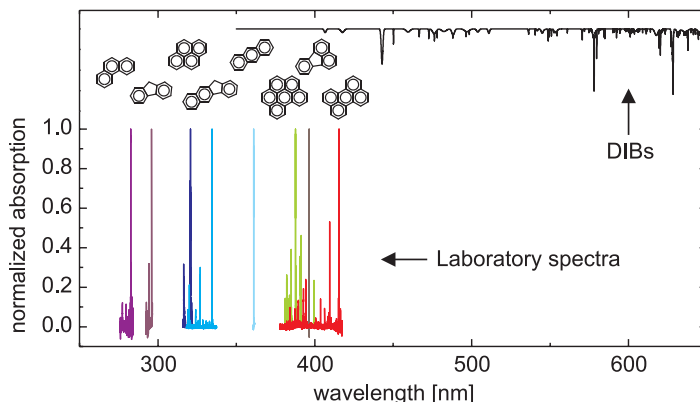
Figure 3. Absorption spectra of jet-cooled PAHs measured by cavity ring-down spectroscopy. The synthetic DIB spectrum displayed at the top for comparison is based on the data compiled by Jenniskens (http://leonid.arc.nasa.gov/DIBcatalog.html).

given that we have measured a specific vibronic band of a PAH molecule in an Ar matrix ($\tilde{\nu}_{Ar}$ in cm^{-1}) as well as in a Ne matrix ($\tilde{\nu}_{Ne}$), we can calculate the gas-phase position according to $\tilde{\nu}_{gas} = \tilde{\nu}_{Ne} + (\tilde{\nu}_{Ne} - \tilde{\nu}_{Ar})(R_\alpha - 1)^{-1}$. In this formula, $R_\alpha = \alpha_{Ar}/\alpha_{Ne} = 4.13$ is the ratio of the polarizabilities of Ar to Ne. Making use of this equation is equivalent to a determination of the gas-phase band position by extrapolating the respective positions in Ar and Ne matrices to a 'matrix' with zero polarizability.

3. Results & Discussion

3.1. *Gas-phase studies*

Applying the CRDS technique described in the experimental section, we have studied the spectroscopy of several PAHs in the gas phase at low temperature as provided in the expansion of a supersonic jet. Figure 3 presents an overview of all absorption spectra measured in our laboratory and compares them with a synthetic spectrum representing the DIBs (Jenniskens & Désert 1994). In the order of increasing wavelength, the laboratory spectra include those for phenanthrene (Huisken *et al.* 2011), fluorene (Huisken *et al.* 2011), pyrene (Rouillé *et al.* 2004), 2,3-benzofluorene (Staicu *et al.* 2008), anthracene (Staicu *et al.* 2004), benzo[*ghi*]perylene (Rouillé *et al.* 2007), fluoranthene (Huisken *et al.* 2011), and perylene (Rouillé *et al.* 2007). They cover a wavelength range from 280 to 420 nm. A comparison with the DIB spectrum shows that there are no coincidences. Moreover, it is seen that major DIBs are located at longer wavelengths. As high-quality astrophysical observations are missing for the range where the laboratory spectra were taken, new high-resolution spectra were recorded toward five different heavily reddened supergiants, using the Ultraviolet and Visual Echelle Spectrograph (UVES) at the Very Large Telescope (VLT) on Cerro Paranal in Chile (Gredel *et al.* 2011). However, also this high-quality observational data did not reveal any coincidence with the PAH spectra obtained in our laboratory.

In order to draw further conclusions from the non-observation of PAH features in the astrophysical spectra and to derive upper limits of column densities for the PAHs whose absorption bands were measured in the laboratory, absolute absorption cross sections are

needed. We applied the method, described in Sect. 2.2 for the case of perylene, to all PAH molecules whose normalized spectra are displayed in Figure 3.

It is interesting to note that, from all molecules studied, the $S_1 \leftarrow S_0$ transition of perylene with its origin band at 415.529 nm clearly dominates the long-wavelength region of the composite spectrum. On the other hand, the $S_1 \leftarrow S_0$ transitions of fluoranthene and phenanthrene are so weak that they can hardly compete with the other PAHs. On the basis of our calibration, we could establish upper limits for the column densities of some PAHs searched for by Gredel *et al.* (2011) in the wavelength range between 280 and 420 nm. They range from 0.8×10^{12} cm^{-2} for anthracene to 1×10^{14} cm^{-2} for phenanthrene. Similar upper limit values for PAHs were derived by Salama *et al.* (2011).

3.2. *MIS studies*

As the comparison between gas-phase PAH spectra and DIB surveys did not reveal any coincidence (Gredel *et al.* 2011, Salama *et al.* 2011), one is tempted to call for the spectroscopic characterization of larger PAHs, which are expected to absorb at larger wavelengths where the DIB density is also higher. However, these experiments are difficult to carry out for at least two reasons: (i) Large PAHs are difficult to bring into the gas phase and (ii) large PAHs are only available in very limited quantities. Therefore, we were not able to measure the supersonic jet absorption spectra of some interesting larger PAHs (corannulene, coronene, dibenzorubicene, and hexabenzocoronene), which were available to us. However, we could characterize these species in Ne matrices. The results are displayed in Figure 4. In order to prepare the matrices, the PAH samples were vaporized by heating them in an oven, except for coronene, which was vaporized with a laser. The arrows point to the positions of the $S_1 \leftarrow S_0$ origin bands except for corannulene where the arrow marks the $S_4 \leftarrow S_0$ transition.

As has been discussed before, the matrix spectra serve as excellent overview spectra and may even be used to determine gas-phase band positions with rather high accuracy (see Sect. 2.3). For our largest PAH molecule, hexabenzocoronene ($C_{42}H_{18}$), which is expected to be particularly stable due to its all-benzenoid nature, we have applied this extrapolation technique after having measured an Ar matrix spectrum as well. It is found that the strong doublet band ($S_\beta \leftarrow S_0$), seen in Figure 4c between 335 and 340 nm, can be located for the gas phase at 334.4 and 336.9 nm. An inspection of the astronomical observations of Gredel *et al.* (2011) in this wavelength range does not reveal any feature that could possibly be assigned to hexabenzocoronene.

3.3. *MIS studies of mixtures containing large PAHs*

For the study of larger PAHs, which should have their absorption features at longer wavelengths, we have employed laser pyrolysis of ethylene (see Sect. 2.1). The samples were processed with the HPLC apparatus to produce fractions with different size distributions: fraction S for small PAHs (retention times: 0 – 7 min; number of cycles: < 7), fraction M for medium-sized PAHs (retention times: 7 – 20 min; number of cycles: 7 – 9), and fraction L for large PAHs (retention times: 20 – 35 min; number of cycles: > 10). The given cycle numbers are approximate values (Steglich *et al.* 2012). The absorption spectra of the two fractions with larger PAHs (fractions M and L) are plotted in Figure 5. Depending on whether the samples were vaporized in an oven at ~385 °C or by laser desorption ($\lambda = 532$ nm; 0.24 mJ/cm^2), the curves are marked by "oven" or "laser vap.". The following differences should be pointed out: When the samples are evaporated in an oven the absorption curves feature more pronounced structure, in particular at smaller wavelengths. This is due to the fact that thermal heating favors the evaporation of smaller species (larger PAHs are harder to bring into the gas phase). On the other hand, if laser
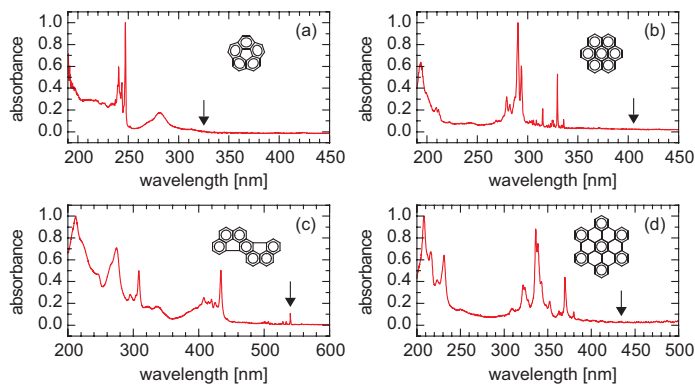
Figure 4. Normalized absorption spectra of corannulene (a), coronene (b), dibenzorubicene (c), and hexabenzocoronene (d) isolated in Ne matrices at 6 K (Carpentier *et al.* 2013).
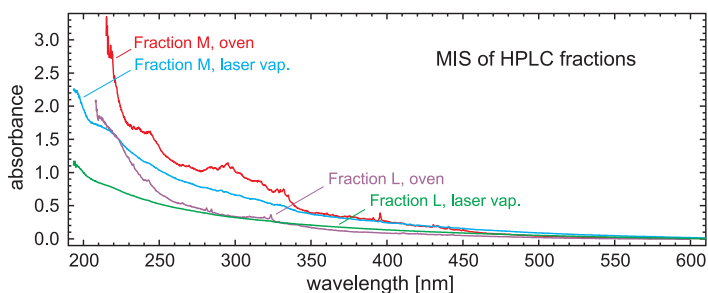

Figure 5. Absorption spectra of two fractions of medium-sized (M) and large (L) PAH molecules synthesized by high-temperature gas-phase condensation. The molecules were evaporated in an oven at ∼385 °C or by the action of a pulsed Nd:YAG laser ($\lambda = 532$ nm).

vaporization is utilized all molecules are evaporated irrespective of their size (Steglich *et al.* 2012). Interestingly, the absorption curves belonging to fraction L display much less sharp features, especially if laser vaporization is used (i.e., if the largest PAHs are incorporated). Finally, it should be noted that the matrix samples, which were deposited by laser vaporization feature less absorbance in the UV ($\lambda < 410$ nm for fraction M and $\lambda < 330$ nm for fraction L) than the samples produced by thermal heating while the opposite is true at the respectively longer wavelengths. The results can be summarized as follows (Steglich *et al.* 2012): The larger the variety of PAHs and the larger their sizes are, the smoother the absorption spectra become. Moreover, with increasing PAH size, the UV absorbance decreases at the expense of the absorbance in the visible.

4. Conclusion

We have measured the electronic absorption spectra of various selected PAH molecules in supersonic jets as well as of mixtures of larger PAHs in cryogenic matrices. The results are discussed in view of the role that PAH molecules can take as carriers of the DIBs. Despite the large amount of data, no coincidence is found. Moreover, it is shown that the large variety of PAH molecules, which is expected to be present in astronomical objects, leads to a smoothening of the absorption spectra and to an extinction of sharp and broad

features comparable to the DIBs. Therefore, it will be very difficult to observe PAH molecules in astronomical objects (if they are present in a large variety). On the basis of the present results, we are tempted to conclude that regular PAH molecules (neutral, completely passivated by hydrogen, no side groups, and no substitution of carbon by nitrogen) are not responsible for any of the stronger known DIBs.

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