

Absorption Spectroscopy of Astrophysically Relevant Molecules in Supersonic Jets

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Abstract. The jet-cooled ultraviolet absorption spectra of various polycyclic aromatic hydrocarbons (PAHs) have been measured by cavity ring-down laser absorption spectroscopy. The number of aromatic rings in the molecules studied varied from three (anthracene and phenanthrene) to six (benzo[*g,h,i*]perylene). None of the spectra comply with astronomical observations. In order to derive maximum column densities of the respective molecules in the astrophysical objects, their oscillator strengths have been determined by comparing the jet spectra with Ne matrix spectra also measured in our laboratory and with calibrated solution spectra. The paper gives an overview of the electronic spectra measured so far in our group, discusses a typical example (perylene) and some peculiarities of PAH spectra, describes the procedure how the jet spectra can be calibrated to present absolute absorption cross sections, and concludes with a perspective for finding specific PAHs in interstellar and circumstellar clouds.

Keywords: Supersonic jets, polycyclic aromatic hydrocarbons (PAHs), UV/vis spectroscopy, CRDS

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INTRODUCTION

Neutral and positively charged polycyclic aromatic hydrocarbons (PAHs) are discussed as carriers of various interstellar absorption and emission features including the unidentified infrared (UIR) bands, the diffuse interstellar bands (DIBs) in the visible and near IR region [1], the 217.5 nm extinction bump, and the blue luminescence that has been observed very recently in the Red Rectangle. It has been claimed that, after H₂ and CO, PAHs are the most abundant molecules in the interstellar medium (ISM), regulating the energy budget by photoelectric heating. Even though a great deal of work has been performed to find satisfactory agreement between observed band profiles and laboratory spectra of neutral and ionized PAHs, a firm identification of an individual PAH molecule as band carrier is still lacking.

In order to assist astronomers in the identification of the DIBs and to answer the question whether PAHs can be made responsible for some of them, it is necessary to study the electronic absorption spectra of PAHs in the laboratory under astrophysically relevant conditions. This means that they must be prepared in the gas phase at very low density and temperature. The most elegant means to achieve this is provided by the molecular beam technique in which a carrier gas (typically Ar) is seeded with the molecules of interest and then expanded at high pressure through a nozzle into a vacuum. The expansion leads to a rapid cooling and rarification of the gas so that, after they have traveled a short distance, the molecules do not interact anymore with each other. It follows that the conditions prepared in supersonic jets mimic those encountered in many astrophysical environments.

We have initiated a research program to study neutral and positively charged PAH molecules with varying size in the expansion of supersonic jets. To determine their absorption behavior associated with electronic transitions in the entire spectral range from the UV to the near IR, we apply a sensitive direct laser absorption technique called cavity ring-down spectroscopy (CRDS). The cavity is combined with a molecular beam apparatus so that the tunable laser beam interacts with the molecules in the expansion. Up to now, we have studied the spectroscopy of eight neutral PAHs [2-6] and two cations [7]. The largest neutral being studied in our group so far is benzo[*g,h,i*]perylene which is composed of six aromatic rings [5]. As the laboratory spectra do not comply with astronomical observations, one would like to derive upper limits for the concentrations of these molecules in the respective astrophysical objects. In order to do so, absolute absorption cross sections or oscillator strengths are required. Therefore, we have also measured the absorption spectra of the same PAHs in neon matrices. As these spectra can be easily compared with calibrated solution spectra it was finally possible to determine absolute absorption cross sections for the individual electronic transitions of the PAH molecules observed in the gas phase at low temperature.

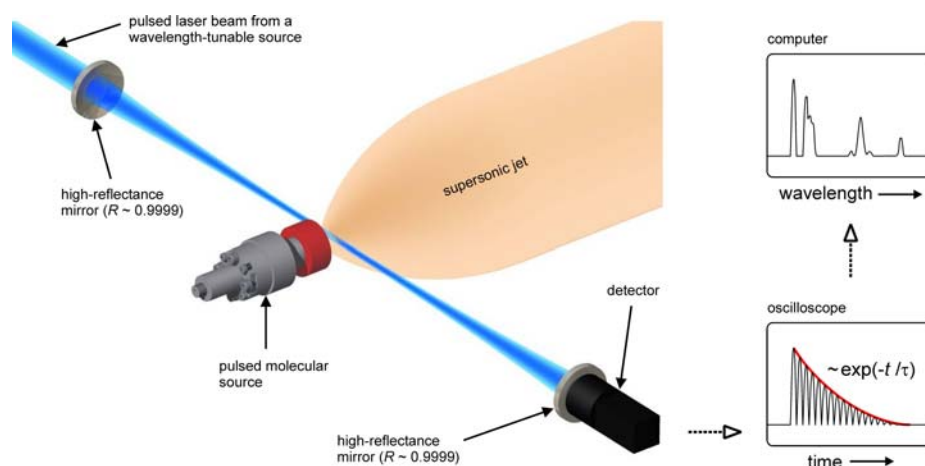


FIGURE 1. Sketch of the supersonic jet cavity ring-down spectrometer.

EXPERIMENTAL

Since details of our supersonic jet CRDS apparatus have been presented at the last RGD conference [8], only a short description is given here. The PAH powder sample is placed into the reservoir of a pulsed valve connected to a gas line providing the carrier gas (usually He or Ar). As the reservoir is equipped with a heating element, the temperature of the sample can be increased to transfer a useful quantity of PAH molecules into the gas phase and mix them with the carrier gas. Placed into a vacuum chamber, this heated pulsed valve is used as the source of PAH-seeded supersonic jets.

The main element of the spectrometer consists of a high-quality optical cavity defined by a pair of high-reflectance mirrors. Its axis crosses the expansion of the supersonic jet at right angle (see Figure 1). Photons delivered by a tunable pulsed laser are injected into the cavity where they are trapped. A photomultiplier tube allows us to detect the photons leaking out of the cavity and to observe the exponential intensity decay of the trapped laser pulses. The absorbance of the supersonic jet can be determined by measuring the time constant of the decay.

As it is essential for our purpose to obtain accurate band positions, the PAH spectra are measured simultaneously with Ne I lines that are used as references for wavelength calibration. Supplementary Ne I lines are measured outside the scanned range to enhance the accuracy of the calibration. As a convention, wave numbers are given for vacuum while wavelengths are meant for air unless otherwise stated.

Measurements in Ne matrices are carried out with a standard setup that has already been described [9]. Briefly, a transparent substrate (CaF_2) is cooled under vacuum to a cryogenic temperature, typically 6.5 K. A flow of pure Ne is directed toward the substrate to form a thin layer that will prevent the deposition of PAH molecules directly onto the substrate. After this first step, the PAH sample powder is heated in a small oven to obtain a sufficient amount of molecules in the gas phase. When the desired temperature is reached, the PAH molecules that exit the oven through an aperture are mixed with Ne atoms and deposited with them on the substrate. Since the rare gas atoms are in excess, a PAH-doped Ne matrix is formed on top of the pure Ne layer deposited previously. Absorption spectra are measured in transmission with a commercial spectrophotometer.

RESULTS AND DISCUSSION

Band Positions and Widths

Figure 2 shows the spectra of eight neutral PAHs that we have measured in supersonic jets and contrasts them with a synthetic representation of the diffuse interstellar bands [10]. Because the mechanism that produces PAHs in space may not be absolutely specific, our interest also includes species that are not PAHs in the strictest sense. For instance, the lightest molecule shown in Figure 2, fluorene (three rings, $\text{C}_{13}\text{H}_{10}$, 166 amu), contains a five-membered

carbon ring that is not aromatic. The largest PAH molecule whose spectrum is given in the figure is benzo[*g,h,i*]perylene (six rings, C₂₂H₁₂, 276 amu). In neutral PAHs, the electronic ground state is a singlet (S_0). The spectra shown in Figure 2 correspond to the excitation from the ground state to either the first (S_1) or second (S_2) singlet state of each molecule, including in many cases the excitation of various vibrational modes. We have also measured the absorption spectra of the cations of naphthalene (two rings, C₁₀H₈, 128 amu) and anthracene (three rings, C₁₄H₁₀, 178 amu) by CRDS at wavelengths longer than 650 nm [7]. In contrast to the neutrals, the ground state of the cations is a doublet (D_0) and the measured absorption bands correspond to transitions to the second excited states (D_2) of the naphthalene and anthracene cations. Most of our measurements have already been published [2-7] and we report here some new band positions. The origin bands of the $S_1 \leftarrow S_0$ transitions of fluorene, phenanthrene, fluoranthene, and perylene have been found at $33\,775.2 \pm 0.3$, $29\,323.9 \pm 0.2$, $25\,218.9 \pm 0.5$, and $24\,058.9 \pm 0.5$ cm⁻¹, respectively. The position of the origin band of the $S_2 \leftarrow S_0$ transition of phenanthrene, which we previously gave as $35\,378.2$ cm⁻¹ [4], has been corrected to $35\,370.0 \pm 1.2$ cm⁻¹. Differences with values reported by other authors may amount to more than 10 cm⁻¹. These differences cannot always be explained by the fact that the values were possibly determined for air.

While currently known DIBs are found in the visible wavelength range between 400 and 800 nm, the smallest neutral PAHs show absorption bands at wavelengths shorter than 400 nm as it can be seen in Figure 2. As PAHs grow in size, however, these bands shift toward longer wavelengths and into the visible region. In contrast, the cations of small PAHs show absorption bands in the visible range.

In our experiments, rotational temperatures from 6.5 (anthracene, 178 amu) to 40 K (benzo[*g,h,i*]perylene, 276 amu) were estimated. Under such conditions, bandwidths of 2 to 3 cm⁻¹ were determined (see Refs. 4-5 and Figure 4 in Ref. 6). These bandwidths are similar to those of numerous DIBs. Note, however, that interactions between electronic states may lead to broader bands in the transitions of PAHs, as it is the case for the $S_2 \leftarrow S_0$ transition of benzo[*g,h,i*]perylene [5,11]. Concerning PAH cations, measurements have shown bands that were much broader than DIBs. It has been proposed that broad features are a characteristic feature of PAH cations, eliminating these species from the list of possible DIB carriers. However, one must keep in mind that this does not mean that PAH cations are not present in space. Their collective presence in some regions has been inferred from the study of the infrared emission bands. Moreover, the possible detections of the naphthalene and anthracene cations (two and three rings) in molecular clouds were reported very recently [12,13].

In the search for DIB carriers, neutral, large PAHs appear as promising candidates. However, before comparing laboratory spectra with astrophysical observations, it is worth to discuss the typical characteristic features of PAH absorption spectra. It has been mentioned above that, in the UV/vis wavelength range, the spectra correspond to the excitation of electronic states and their vibrational modes. As a consequence, the spectrum of a given PAH consists of several bands. In order for this PAH to be a DIB carrier, the positions, widths, and relative intensities of *all* the

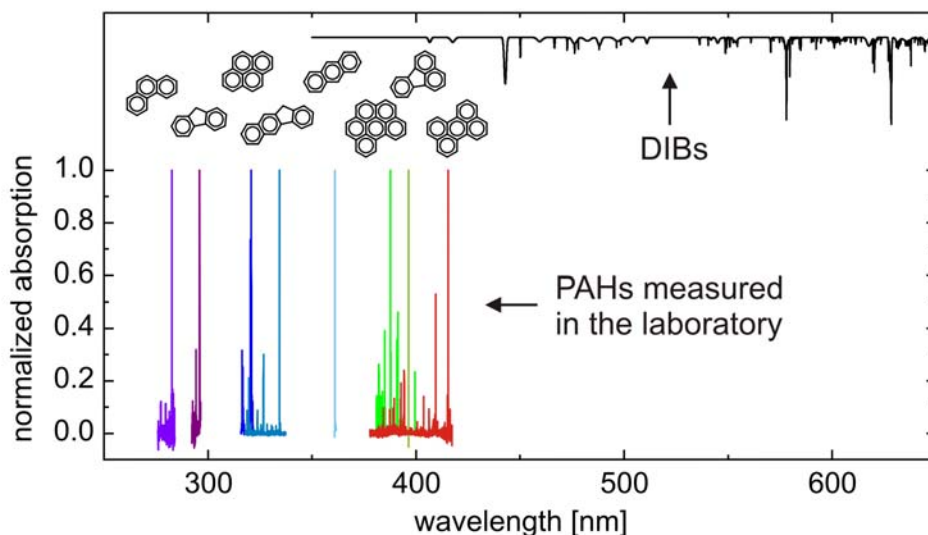


FIGURE 2. Absorption spectra of jet-cooled PAHs (in color) compared with a synthetic DIB spectrum [10]. The molecular structures, from left to right, are those of phenanthrene, fluorene, pyrene, benzo[*b*]fluorene, anthracene, benzo[*g,h,i*]perylene, fluoranthene, and perylene.

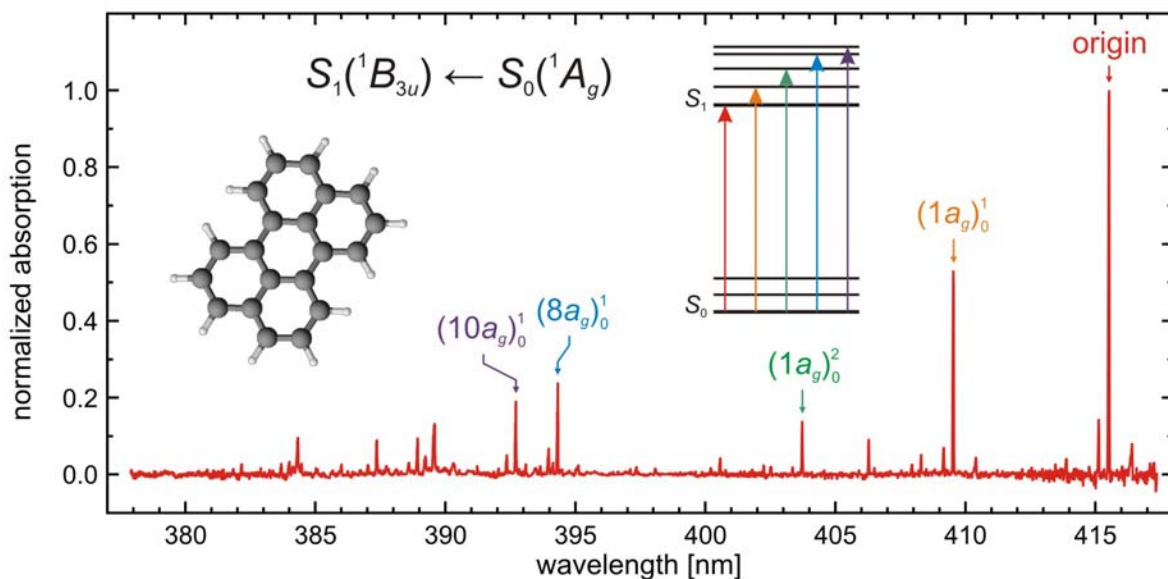


FIGURE 3. The $S_1 \leftarrow S_0$ absorption spectrum of perylene measured in a supersonic jet. Colored labels identify vibronic bands that correspond to the transitions drawn in the energy level scheme.

bands must match those of the DIBs. As an example, Figure 3 shows an expanded view of the gas phase absorption spectrum of perylene (five rings). The strongest absorption band represents the pure electronic transition (without the involvement of vibrations) from S_0 to S_1 , while the weaker bands at shorter wavelengths arise from the additional excitation of vibrational modes in S_1 made possible by the higher energy of the photons. It follows that all these features must be identified in an astrophysical spectrum before perylene can be made responsible for a specific band observed in the sky. In Figure 3, all vibrational bands belong to the same electronic transition. In some cases, the vibrational intensity pattern may be complicated due to a coupling between the vibrational levels of different electronic states. For instance, in pyrene and benzo[*g,h,i*]perylene [2,5], the vibronic interactions between the S_1 and S_2 states cause a large number of bands to appear in the region of the origin of the $S_2 \leftarrow S_0$ transition.

Derivation of Absorption Cross Sections

The wavelength position and the width of a vibronic absorption band measured in the laboratory are the most important parameters to be compared with an astrophysical observation spectrum. However, if no coincidence is found it is desirable to determine at least an upper limit for the concentration of the respective molecule in the astrophysical object considered. In order to do so, the knowledge of absolute absorption cross sections or oscillator strengths is required. Unfortunately, it is almost impossible to derive such quantity from spectroscopic measurements in supersonic jets because the species concentration is not known and the interaction path of the laser is difficult to determine. In contrast, the molar extinction coefficient, ϵ , is routinely measured for molecules dissolved with known concentration in a nonpolar organic solvent. Such data can be found in the literature (see for example Ref. 14) or obtained in a dedicated experiment. The measured extinction coefficient can then be converted into the absorption cross section, σ .

We resort to Figure 4 to describe the complete procedure for a specific example for which we chose perylene, the molecule already discussed in the previous section. The solvent spectrum (perylene in cyclohexane) measured in absolute units is given by the blue curve. Note that, in order to compensate for the redshift induced by the solvent, this spectrum had to be shifted by 1130 cm^{-1} to larger wave numbers. Superimposed on this spectrum, we have plotted the absorption spectrum of perylene trapped in a Ne matrix (green curve; shifted by 177 cm^{-1} to the blue, to account for the matrix shift). It is seen that the green curve reveals much more structure which is due to vibrational transitions. But it is also seen that, if the matrix spectrum is subjected to a suitable broadening mechanism, very good agreement between the two spectra can be expected. To proceed further, we take advantage of an approximation which is widely used in the interpretation of astrophysical data (see for example Refs. 15-17). It is based on the

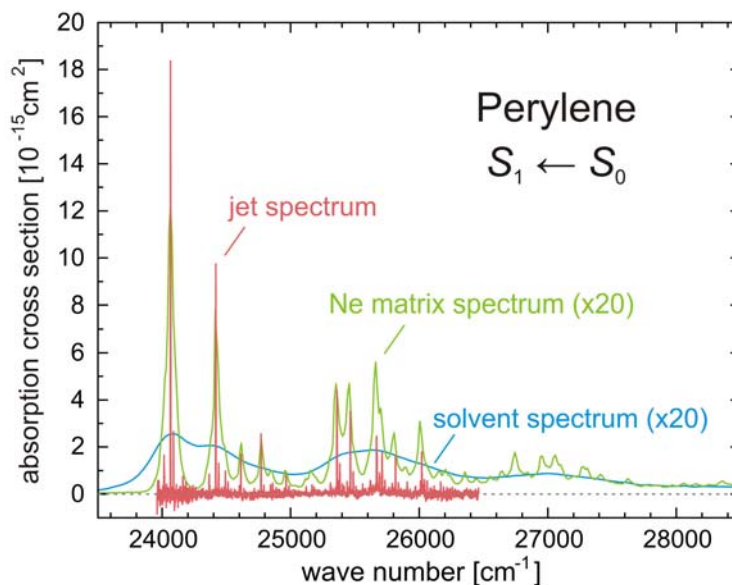


FIGURE 4. $S_1 \leftarrow S_0$ absorption spectra of perylene measured in a supersonic jet (red curve, same data as shown in Figure 3), in a 6.5 K cold neon matrix (green curve), and in cyclohexane at room temperature (blue curve). The y -axis scale refers to the jet spectrum. For a better comparison, the intensities of the Ne matrix and solution spectra have been multiplied by a factor of 20. In order to display the $S_1 \leftarrow S_0$ origin at the same wave number position, the Ne matrix and solution spectra were shifted by 177 and 1130 cm^{-1} , respectively, to larger wave numbers.

assumption that the sum over all vibrational bands of an electronic transition is constant. Doing so, i.e., integrating the solution and matrix spectra over the entire electronic $S_1 \leftarrow S_0$ transition (22000 – 32000 cm^{-1}), the Ne matrix spectrum can be calibrated. The last step involves the calibration of the supersonic jet spectrum which is displayed in Figure 4 by the red curve. For this purpose, we take the area of the first pronounced peak in the Ne matrix spectrum and equal it to the integral over all narrow features of the jet spectrum contained in the same wave number range. Note that the procedure results in an origin band of the $S_1 \leftarrow S_0$ transition, the intensity of which is 30 times stronger in the gas phase ($18 \times 10^{-15} \text{ cm}^2$) than in the Ne matrix ($6 \times 10^{-16} \text{ cm}^2$). Further note that the Ne matrix spectrum was indispensable to determine absolute absorption cross sections for the low-temperature gas phase spectrum from the solution spectrum. In this way, the Ne matrix spectrum can be considered as a mediator between gas phase and solution spectrum. Once the gas phase absorption peaks are properly calibrated, the astronomical spectrum can be analyzed to derive upper limits for the column densities of the given molecule in the molecular cloud under observation (see for example Ref. 16).

SUMMARY AND OUTLOOK

With the aim to contribute to the elucidation of the molecular carriers of the diffuse interstellar bands (DIBs), we have studied the gas phase absorption behavior of several polycyclic aromatic hydrocarbons (PAHs) associated with their electronic transitions in the UV/vis range. Low temperature and interaction-free environment were realized by the supersonic jet technique. As sensitive absorption technique, we employed cavity ring-down laser absorption spectroscopy (CRDS). In addition to neutral PAHs, we also studied two positively charged PAHs (cations). Comparing band positions and band widths with astrophysical observations, we must state that the spectra of none of the studied molecules can be made responsible for an interstellar feature. While the bands of the smaller neutral PAHs are too far in the UV, the absorption bands of the cations are too broad. The latter finding excludes PAH cations from being potential carrier candidates. As far as neutral PAHs are concerned, we come to the conclusion that it will be necessary to study larger molecules.

As PAH molecules have been identified in interstellar clouds upon their infrared fingerprints, it follows that they are present but that their concentration is too low to be detected by UV/vis spectroscopy. Resorting to solution and neon matrix isolation spectra, we have been able to calibrate molecular beam spectra so as to derive absolute absorp-

tion cross sections. With this knowledge, it is possible to estimate upper limits for the column densities (concentrations) of a particular PAH molecule in a specific astrophysical object [18].

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