

### 3.1 Bericht Teilprojekt 11

#### 3.1.1 Thema / Title

*Spektroskopie von astrophysikalisch relevanten Molekülen in der Gasphase und in ultrakalten Helium-Tröpfchen*

*Spectroscopy of astrophysically relevant molecules in the gas phase and in ultracold helium droplets*

#### 3.1.2 Berichtszeitraum / Reported period

15.11.2003 – 31.12.2006

#### 3.1.3 Projektleiter / Principal investigator

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### 3.2 Zusammenfassung / Abstract

#### 3.2.1 Wortlaut des Antrags / Abstract of the proposal

Die innerhalb dieses Projekts durchgeführten Laborexperimente sollen einen Beitrag zur Identifizierung der Diffusen Interstellaren Banden (DIBs) leisten. Insbesondere soll untersucht werden, inwieweit Polyzyklische Aromatische Kohlenwasserstoffe (PAHs) und andere kohlenstoffhaltige Moleküle oder Cluster als mögliche Träger in Frage kommen. Die Experimente werden parallel und aufeinander abgestimmt an zwei verschiedenen Molekularstrahlapparaturen durchgeführt. In einer mehrstufigen Hochvakuumapparatur werden neutrale und kationische PAHs sowie Kohlenstoff-Cluster und Nanoteilchen in ultrakalte Helium-Nanotröpfchen eingebettet und mit Hilfe der sehr empfindlichen laserinduzierten Fluoreszenz sowie der massenspezifischen Depletion-Methode im Bereich zwischen 400 und 900 nm spektroskopiert. Im Gegensatz zur konventionellen Matrixspektroskopie weisen die Spektren wegen der viel geringeren Wechselwirkung nur sehr geringe Linienverschiebungen auf, so dass ein besserer Vergleich mit astrophysikalischen Beobachtungen möglich wird. In einer zweiten Apparatur sollen die gleichen bzw. ähnliche Spezies mit einer ebenfalls sehr empfindlichen Methode, der Cavity Ring-Down Spektroskopie (CRDS), im Expansionsbereich eines Molekularstrahls untersucht werden. Diese Methode, die insbesondere zum Studium kleiner geladener PAHs geeignet ist, bietet den Vorteil einer echten Gasphasenspektroskopie an freien isolierten Spezies.

The laboratory experiments carried out within this project aim at contributing to the identification of the diffuse interstellar bands (DIBs). In particular, we will explore to what extent polycyclic aromatic hydrocarbons (PAHs) and other carbon-containing molecules or clusters can be made responsible for this observation. The experiments will be carried out in parallel in two different molecular beam machines. In the first high-vacuum apparatus, which consists of several stages, neutral and cationic PAH molecules as well as carbon clusters and nanoparticles will be incorporated into ultracold helium nanodroplets, and their spectroscopy will be studied in the spectral region between 400 and 900 nm using mass-specific depletion techniques and laser-induced fluorescence. In contrast to conventional cryogenic matrix spectroscopy, the spectra are characterized by smaller shifts, due to the significantly reduced interaction with the host. This allows for a better comparison with astrophysical observations. In another apparatus, the same or similar species will be investigated in the expansion region of a nozzle beam, employing a very sensitive method, namely cavity ring-down spectroscopy (CRDS). This method, which is particularly suited for the study of small charged PAHs, offers the advantage of genuine gas phase spectroscopy of isolated free species.

#### 3.2.2 Zusammenfassung des Berichts / Abstract of the report

In the course of the present project, we have performed various studies on a number of PAHs either in the gas phase or in liquid helium droplets. At first, the PAH *cations* of naphthalene and anthracene were studied in the expansion of a supersonic jet employing cavity ring-down spectroscopy (CRDS). The absorption bands are rather broad which is partly due to the insufficient cooling of the vibrational degrees of freedom. The larger

PAH, 2,3-benzofluorene, was studied as *neutral* species in the gas phase, *i.e.* in the expansion of a supersonic jet, and in liquid helium droplets using molecular beam depletion spectroscopy (MBDS). It turned out that, for this molecule, the matrix shift is rather small ( $<5\text{ cm}^{-1}$ ) whereas for an argon matrix the shift is  $250\text{ cm}^{-1}$ . Another molecule that we have studied is benzo[ghi]perylene which is composed of 6 rings. We concentrated on the weak  $S_1 \leftarrow S_0$  transition and located the origin at  $25\,027\text{ cm}^{-1}$ . For both neutral molecules studied (2,3-benzofluorene and benzo[ghi]perylene) no coincidence with strong DIBs was found. Finally, we have produced our own PAHs by  $\text{CO}_2$  laser pyrolysis of hydrocarbons and by separating the molecules from the soot. High pressure liquid chromatography and mass spectrometry reveal that the extract contains various PAHs with masses up to 600 amu. First spectroscopic experiments applied to the extract (employing both CRDS in the gas phase and MBDS in liquid helium droplets) confirmed the presence of phenanthrene and anthracene as prominent constituents.

### 3.3 Ausgangsfragen, neuester Stand der Forschung / Initial goals, current status of the field

The Diffuse Interstellar Bands (DIBs), first discovered in 1922, represent the oldest unsolved problem in astronomical spectroscopy. Surveys with sensitive CCD detectors have shown that they consist of more than 250 absorption lines in a spectral region reaching from the blue to the IR (400 – 800 nm) (Jenniskens & Désert 1994, Herbig 1995, Galazutdinov *et al.* 2000, Tuairisg *et al.* 2000). The individual bands vary in intensity and width. In general, they are too broad to be identified as atomic lines. On the other hand, if recorded with very high resolution, some bands reveal finer details that resemble the rotational fine structure of gas phase molecules. In fact, it is now well accepted that the carriers of the DIBs must be gas phase molecules.

Compatibility with astrophysical constraints (photostability, producibility under astrophysical conditions, and abundance criteria of the elements) led to the suggestion of only a few families of molecules (Snow 1995). These are carbon chains ( $C_n$ ), unsaturated hydrocarbon chains ( $C_nH_m$ ), fullerenes, and polycyclic aromatic hydrocarbons (PAHs).

#### 3.3.1 Initial Goals

In order to contribute to the clarification of the diffuse interstellar bands, we proposed to carry out electronic spectroscopy of PAH cations in supersonic jets using cavity ring-down spectroscopy (CRDS). The first species to be studied should be naphthalene<sup>+</sup> ( $\text{Np}^+$ ) and anthracene<sup>+</sup> ( $\text{An}^+$ ). At a later stage, we wanted to investigate larger cations. Besides PAH cations, it was also planned to study the absorption behavior of neutral PAHs whose absorption bands are located at shorter wavelengths than those of their cationic counterparts. Here it was the goal to go to increasingly larger species which are more difficult to prepare in the vapor phase.

At the same time and in another molecular beam apparatus, it was planned to study the same PAH molecules (neutral and cationic) in liquid helium droplets by mass spectrometer-assisted molecular beam depletion spectroscopy (MBDS). This technique has various advantages, among which the low temperature achieved for *all* degrees of freedom and the low sample concentration required are most noteworthy. On the other hand, the spectra will be affected by a small matrix effect (band shift and broadening); but, in conjunction with the gas phase spectra, very valuable information on internally *cold* molecules can be anticipated.

While the described studies are carried out with PAH samples which can be purchased from chemical suppliers or which are synthesized by cooperating organic chemists, it was also proposed to prepare our own carbonaceous samples employing  $\text{CO}_2$  laser pyrolysis of carbon-containing gaseous precursors. These experiments should be carried out in collaboration with Dr. Ion Voicu from the National Institute for Lasers, Plasma and Radiation Physics in Bukarest/Romania who is an expert in fullerene production using this method. In contrast to purchased PAHs which are synthesized by standard wet chemical methods, it is expected that laser pyrolysis will give rise to the production of PAH species which are difficult to obtain by other means. It is hoped that the high temperature achieved during synthesis will favor the production of the most stable species which are able to survive under harsh astrophysical conditions. The molecules prepared by this technique should be studied by both CRDS in the gas phase and MBDS in helium droplets.

#### 3.3.2 Current status of the field

In recent years, after the start of the present project, the absorption spectra of a few PAHs have been investigated under conditions relevant for astrophysics. They include neutral species such as perylene (Tan & Salama 2005a) and benzo[ghi]perylene (Tan & Salama 2005b), the cations of pyrene and acenaphthene (Biennier *et al.* 2003; Biennier *et al.* 2004), and those of 1-pyrenecarboxyaldehyde and 1-methylpyrene (Tan & Salama 2006). The main result of these studies is that the bandwidths are much larger in the electronic spectra of cations ( $20 - 30\text{ cm}^{-1}$ ) than in the spectra of neutral molecules. The large bandwidth is attributed to the short lifetime of the cations. Since the width of most DIBs is about  $2 - 5\text{ cm}^{-1}$ , which is comparable to the bandwidths

observed in the spectra of neutral PAHs, cations, as they have been characterized so far, do not seem to be good candidates for DIB carriers (Tan & Salama 2005a).

Carbon chains and derivatives have been candidates for carriers of DIBs since a long time. Such species have been extensively studied in supersonic expansions by the group of Maier in Basel. An important outcome of these investigations is that such chains and their simple derivatives cannot be associated with strong DIBs if they contain less than ten carbon atoms (Maier *et al.* 2004). Carbon rings form a new class of molecules that has come under investigation in context with DIBs. The study of band profiles in the electronic spectrum of the C<sub>18</sub> ring suggests that “platelike nonpolar molecules” with sizes from C<sub>20</sub> to C<sub>100</sub> could possibly explain the structures observed in some DIBs (Maier *et al.* 2006).

The dissociation mechanism of PAHs following the absorption of photons has become a research topic since it is expected to occur in the interstellar medium. The dissociation of the fluorene cation under conditions similar to those encountered in the ISM has been studied by Van-Oanh *et al.* (2006a, 2006b).

Recently, it has been proposed by scientists of NASA Ames that N-substituted PAHs, so-called polycyclic aromatic nitrogen heterocycles (PANHs), could be present in molecular clouds since nitrogen is rather abundant and reactive. Therefore, such species should also be considered as possible candidates responsible for some of the DIBs. Both, experimental (Bernstein *et al.* 2005; Mattioda *et al.* 2005) and theoretical work has already been carried out to follow this idea. Recent calculations on N-substituted circumcoronene cations show that the C-C stretching frequency shifts to higher energies when the N-atom moves from a peripheral position to the center of the molecule (Mattioda 2006).

### **3.4 Angewandte Methoden / Experimental methods**

#### **3.4.1 CRDS in supersonic jets**

Cavity ring-down spectroscopy is a very sensitive absorption technique which was developed in the 80ies of the last century (O’Keefe & Deacon 1988). It is based on the measurement of the decay or ring-down of the laser intensity coupled into a resonator of extremely high quality. The sensitivity is high enough to carry out direct absorption experiments in the low density environment of a molecular beam or supersonic jet. Preferably, the molecular beam is provided in a pulsed mode. The nozzle, into which ~0.1 cm<sup>3</sup> of PAH powder is placed, can be heated up to 500 °C. Thus, we achieve sufficiently high vapor pressures for many PAHs with less than 6 aromatic rings. In order to obtain efficient rotational cooling in the expansion (~10 K), argon is used as carrier gas. By combining the pulsed nozzle with an electric discharge, it is possible to generate a plasma in which radicals and ions are produced (Motylewski & Linnartz 1999). For the study of neutral molecules, the discharge device was removed, in order to achieve a better cooling.

#### **3.4.2 MBDS of helium droplets containing PAH molecules**

Matrix isolation spectroscopy (MIS) has been very popular to study the spectroscopy of PAHs and other species of astrophysical interest at low temperature (Ruiterkamp *et al.* 2002). Conventional matrix materials (N<sub>2</sub>, Ar, and Ne), however, suffer from the fact that the spectral bands are shifted (easily by ~100 cm<sup>-1</sup>) and broadened, due to the interaction with the matrix material. An innovative and elegant means to employ helium, the least interactive rare gas, as matrix material has been pioneered by the laboratories of Scoles (Higgins *et al.* 2001) and Toennies (Toennies & Vilesov 2004). Helium is expanded at high pressure (~20 bar) through a small (~5 μm) nozzle cooled to temperatures below 20 K. Under such conditions, the helium atoms condense and form clusters and even nanodroplets containing up to several thousand helium atoms. If the beam of helium droplets is directed through a pick-up cell containing PAH molecules at sufficiently high pressure (>10<sup>-6</sup> mbar), the molecules are incorporated upon collisions into the interior of the helium droplets and carried by them to the ionizer of a quadrupole mass spectrometer. Here they are detected on the mass of the incorporated PAH since all helium atoms are evaporated following the ionization process. Spectroscopy can be performed by exciting the PAH molecules in the droplets with a tunable laser beam. The absorption can be monitored by the following laser-induced fluorescence (LIF) or the induced evaporation of helium droplets using molecular beam depletion spectroscopy (MBDS).

#### **3.4.3 PAH synthesis by laser pyrolysis of gaseous precursors**

In a cooperation with Dr. Ion Voicu, National Institute for Lasers, Plasma and Radiation Physics, Bukarest, we have employed cw CO<sub>2</sub> laser pyrolysis of hydrocarbons (C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>) with laser powers around 650 W to produce our own PAH samples. Efficient PAH formation was achieved by adding a small amount of benzene which acts as nucleation center. It turned out that the soot produced by this method contained up to 30

weight % of PAHs. The soot was used in its original form and heated to release the PAH molecules into the vapor phase and to carry out laser spectroscopy using both CRDS and MBDS. Helium droplet incorporation was found to be ideally suited to perform mass spectrometry and to obtain information on the PAH molecules present in the soot. In addition and in cooperation with Dr. Harald Mutschke (TP 8), the soluble part of the carbonaceous powder (which is mainly composed of PAHs) was separated from its insoluble counterpart by soxhlet extraction in toluene. Various techniques were used to obtain additional information on the composition of the extract. These included UV/visible and IR absorption spectroscopy and gas chromatography combined with mass spectrometry and, finally, high pressure liquid chromatography (HPLC).

### 3.5 Ergebnisse und ihre Bedeutung / Results and their importance

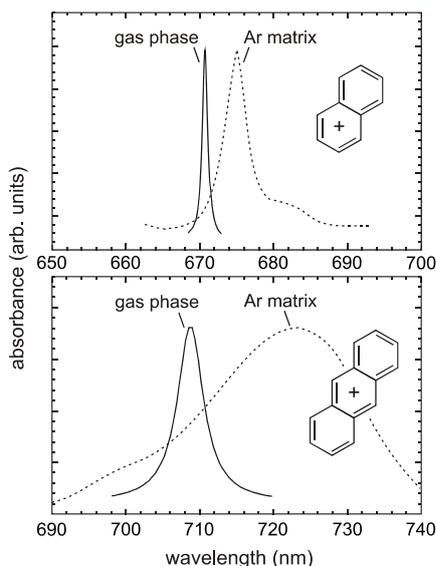
#### 3.5.1 Electronic absorption spectroscopy of PAH cations

After having studied a few neutral PAH molecules such as pyrene (Rouillé *et al.* 2004; Staicu *et al.* 2004a) and anthracene (Staicu *et al.* 2004a, 2004b), we have devoted our interest to the spectral characterization of small PAH cations (positively charged ions) because, under the severe radiation conditions of the interstellar space, ionized PAH molecules should be more abundant than their neutral counterparts. Successful experiments could be carried out for the naphthalene and anthracene cations,  $\text{Np}^+$  and  $\text{An}^+$ , respectively (Sukhorukov *et al.* 2004). While naphthalene and its cation consists of two benzene rings, anthracene is composed of three rings in a linear configuration. Both are important PAH candidates which are expected to be present in the interstellar space.

The absorption spectra of  $\text{Np}^+$  and  $\text{An}^+$  corresponding to the electronic transition between the ground state,  $D_0$ , of the cations and their  $D_2$  states consist of single-peaked bands in the red and near infrared spectral range. Figure 1 shows the gas phase spectra of the two species as obtained in the present study using cavity ring-down spectroscopy (solid curves). They are compared with the spectra obtained earlier by other investigators using matrix isolation spectroscopy (dashed curves; Salama & Allamandola 1991 and Szczepanski *et al.* 1993). In the latter technique, the molecules are trapped (isolated) at low temperature in a matrix of frozen argon. Due to the interaction of the PAH molecules with the host matrix, their absorption spectra are significantly broadened and shifted to the red as is clearly demonstrated in the figure. The comparison further shows that, due to the pronounced shift and broadening, matrix isolation spectra cannot be used to explain astrophysical observations. Instead, gas phase spectra obtained at low temperature and pressure are mandatory.

It should be mentioned that the absorption band of  $\text{Np}^+$  has already been studied before in supersonic jets by Romanini *et al.* (1999) and Biennier *et al.* (2003). Our spectrum agrees very nicely with this earlier result. In contrast, the  $\text{An}^+$  spectrum has been observed for the first time in our laboratory.

Regarding the comparison with astrophysical observations, it is interesting to note that, in a dedicated search, Krelowski *et al.* (2001) found two features which were reasonably close to the earlier laboratory observations for  $\text{Np}^+$ . It follows that our  $\text{Np}^+$  band is also very close. In contrast, our new  $\text{An}^+$  band has no analogue in the broad DIB survey of Jenniskens & Désert (1994). It could be that this survey is not representative of PAH-rich regions. Therefore, a dedicated search in the spectral region around 709 nm, where we locate the  $\text{An}^+$  absorption band, would be highly desirable.



**Fig. 1:** Comparison of gas phase absorption spectra of  $\text{Np}^+$  (top) and  $\text{An}^+$  (bottom), measured by CRDS and represented by their Lorentzian fits (solid curves) with argon matrix spectra (dashed curves) (Salama & Allamandola 1991; Szczepanski *et al.* 1993).

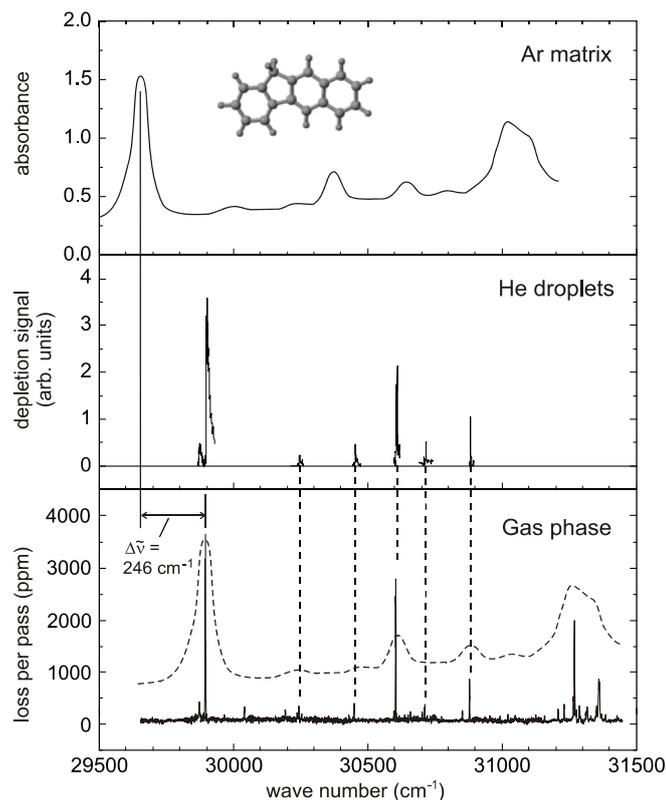
In order to obtain information on the vibrational temperature of the PAH cations which were produced in our discharge, we investigated in detail the vibrational bands of neutral anthracene (Staicu *et al.* 2004b). Comparing the results obtained without and with discharge device mounted on the pulsed nozzle, we found that the expansion was seriously disturbed by the apertures of the discharge device. This resulted in rather high rotational ( $<40$  K) and vibrational ( $\sim 500$  K) temperatures as could be seen by the broadening of the vibrational bands and the appearance of hot bands, respectively. The discharge itself had only a minor influence on the vibrational temperature. From this observation, we can conclude that the cation bands displayed in Fig. 1 are at least partly broadened as a result of the insufficient cooling of the vibrational degrees of freedom.

An ideal means to obtain vibrationally ultracold cations is provided by the helium droplet technique. After having studied the spectroscopy of a few neutral PAH molecules embedded in helium droplets (pyrene: Rouillé *et al.* 2004; anthracene: Krasnokutski *et al.* 2005), we tried several methods to incorporate PAH cations into helium droplets, but without success. The only method which was finally successful was to incorporate neutral PAH molecules and to ionize the helium cluster subsequently. The positive charge originally localized in the helium droplet diffuses quickly to the molecule giving rise to the formation of a PAH cation. However, due to the charge transfer, approximately  $2 \times 10^4$  helium atoms are evaporated. Therefore, it is necessary to start with very large helium droplets. On the other hand, the number of helium atoms evaporated as a result of the photo-excitation of the PAH cation is at most  $2.5 \times 10^3$ . This explains that, up to now, spectroscopic experiments on cations in helium droplets were not successful.

### 3.5.2 2,3-Benzofluorene

Another PAH molecule that we have studied in both gas phase and helium droplets is 2,3-benzofluorene ( $\text{C}_{17}\text{H}_{12}$ ) (Staicu *et al.* 2006). Its molecular structure is composed of 1+2 benzene rings with a five-fold ring in between giving rise to a bent structure with only one symmetry element except of the identity, a plane of symmetry. Neither gas phase nor helium droplet spectra were available for this molecule. However, we could resort to argon matrix isolation studies (Banisaukas *et al.* 2004; Geigle & Hohlneicher 1999) which helped us to easily locate the origin of the  $S_1 \leftarrow S_0$  transition.

Figure 2 presents the spectra that we have recorded in the wavelength range between 317 and 338 nm. The gas phase spectrum measured by cavity ring-down spectroscopy in the expansion of a supersonic jet using argon as carrier gas and a nozzle temperature of  $200^\circ\text{C}$  is displayed in the bottom panel. The most intense band at  $29\,894.3\text{ cm}^{-1}$  corresponds to the origin of the  $S_1 \leftarrow S_0$  transition. The other bands at higher energies belong to vibronic transitions not yet assigned. Some of



**Fig. 2:**  $S_1 \leftarrow S_0$  absorption spectra of 2,3-benzofluorene measured in the gas phase (supersonic jet) by cavity ring-down spectroscopy (bottom panel) and in helium droplets by molecular beam depletion spectroscopy (middle panel) in comparison with the Ar matrix study of Banisaukas *et al.* (2004).

the vibronic bands including the origin band have also been measured in helium droplets employing molecular beam depletion spectroscopy with the mass spectrometer tuned to the mass of benzofluorene ( $m = 216$  amu). The results are plotted in the frame above the gas phase spectrum. It is important to note that the helium droplet spectrum has not been shifted in frequency. In contrast to some other PAH molecules studied before, it appears that the frequency shifts (compared to the gas phase) are very small (blue shifts between 4.5 and 5.0  $\text{cm}^{-1}$ ). The uppermost panel shows the argon matrix spectrum measured by Banisaukas *et al.* (2004). For a better comparison, the same spectrum, but shifted by 246  $\text{cm}^{-1}$  to higher wave numbers, is also plotted as dashed curve directly above the gas phase spectrum. This comparison nicely reveals that all the broad vibronic features of the matrix spectrum have their much narrower counterparts in the gas phase spectrum. The width of the origin band is with 71  $\text{cm}^{-1}$  more than 40 times larger than in the gas phase (1.6  $\text{cm}^{-1}$ ). In contrast, the vibronic bands observed in helium droplets come very close to those found in the gas phase. More details of the spectroscopy of 2,3-benzofluorene will be published soon (Staicu *et al.*, in preparation). As in the case of the neutral PAHs studied earlier, we found no coincidence with astronomical observations.

### 3.5.3 The $S_1 \leftarrow S_0$ transition of benzo[ghi]perylene

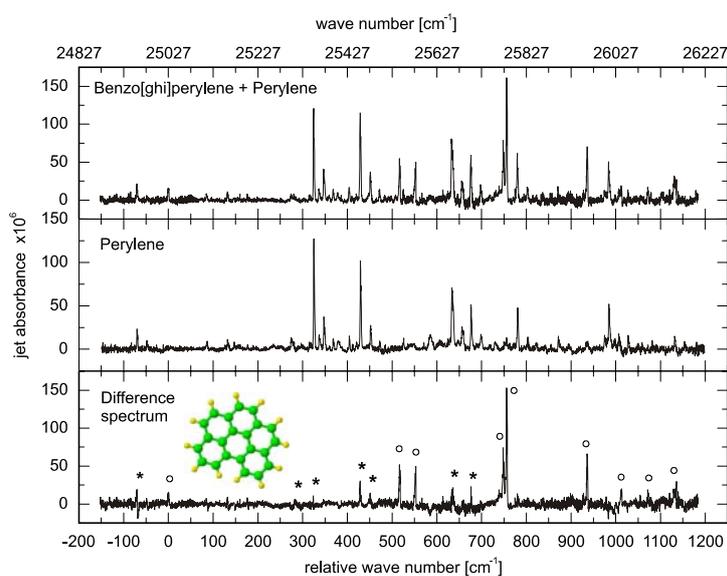
It is only recently that spectroscopists became interested in benzo[ghi]perylene (BghiP;  $\text{C}_{22}\text{H}_{12}$ ) under conditions relevant for astrophysics. The first study of this molecule cooled in a gas expansion was devoted to the investigation of the strong  $S_2 \leftarrow S_0$  transition near 369 nm (Tan & Salama 2005b). At that time, preliminary studies of the much weaker  $S_1 \leftarrow S_0$  transition by CRDS in a supersonic expansion were initiated by our group. Moreover, an absorption spectrum covering the region which includes both transitions had been recorded by argon matrix spectroscopy at 12 K. The goal was to determine whether the  $S_1 \leftarrow S_0$  transition, and especially the origin band of the system, could be detected. We estimated that we would be working close to the limit of the sensitivity of our CRDS set-up.

In the meantime, the absorption spectrum of jet-cooled BghiP has been successfully recorded and investigated (Rouillé *et al.*, submitted for publication). According to HPLC measurements carried out in our

group, it was found that the commercial samples contained traces of perylene (on the order of 1%). As a consequence, the upper trace in Fig. 3 shows bands of the  $S_1 \leftarrow S_0$  transition of benzo[ghi]perylene and perylene as well. The center trace shows a control spectrum of perylene, and the lower trace represents the difference between the two spectra, emphasizing the bands related to BghiP (marked by circles).

The analysis of these spectra concerning band positions and rotational contours has yielded the position of the origin band of the  $S_1 \leftarrow S_0$  transition of BghiP at 399.567 nm ( $25\,027.1 \pm 0.2$   $\text{cm}^{-1}$  in vacuum). In addition, the fundamental frequencies of a dozen vibrational modes for the  $S_1$  states of BghiP could be specified. It was important to determine the position of the origin band, in order to test the accuracy of theoretical predictions established by the means of TD-DFT-based calculations (Tan & Salama 2005b). Our conclusion is that such calculations do not perform well, especially compared to calculations based on semi-empirical models.

Incidentally, the analysis of the spectra has also yielded the position and assignment of about twenty new bands in the  $S_1 \leftarrow S_0$  transition of perylene, and of a dozen bands associated with complexes of perylene with argon.



**Fig. 3:** CRDS spectra of benzo[ghi]perylene containing 1% of perylene (top) and pure perylene (middle), as well as the difference spectrum (bottom). The peaks designated with circles are assigned to benzo[ghi]perylene while those labelled with an asterisk are reminiscent of perylene.

Evaluating the upper trace of Fig. 3 and comparing two bands of BghiP and perylene exhibiting the same absorbance, we obtained the result that the absorption cross section related to the perylene band is about hundred times larger than the one corresponding to the BghiP band. This ratio is indicative of the very weak oscillator strength of the  $S_1 \leftarrow S_0$  transition in benzo[ghi]perylene.

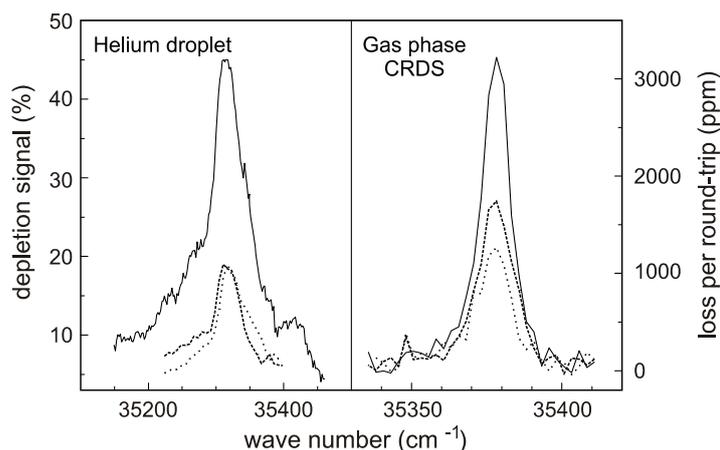
Finally, the comparison of the jet-cooled gas-phase spectrum with the spectrum measured in an argon matrix reveals a larger redshift for the  $S_2 \leftarrow S_0$  transition than for the  $S_1 \leftarrow S_0$  transition. The essential cause of redshifted electronic transition energies for PAHs in rare gas matrices is the increase of the dispersion interaction energy. In a basic model, this value depends linearly on the mean static dipole polarizability of the embedded molecule. The larger redshift of  $S_2 \leftarrow S_0$  is therefore attributed to a higher polarizability of BghiP in its  $S_2$  state than in its  $S_1$  state.

As far as the problem of diffuse interstellar bands is concerned, the comparison of the benzo[ghi]perylene spectrum with astronomical data bases does not lead to any identification. This can be due to the fact that the first strong transition,  $S_2 \leftarrow S_0$ , near 369 nm, is out of the ranges covered by current DIB surveys. Yet, an interesting point is that the band contour analysis has yielded a band width of  $2.7$   $\text{cm}^{-1}$  associated with a rotational temperature close to 40 K. This supports the assumption that neutral PAHs are better candidates for DIB carriers than their cations which exhibit band widths on the order of  $20 - 30$   $\text{cm}^{-1}$  (Tan & Salama 2005a). But in order to present electronic transitions at wavelengths longer than 400 nm, neutral PAHs have to be heavier than benzo[ghi]perylene.

### 3.5.4 PAHs produced by laser pyrolysis

Besides commercially available PAHs, we have also studied the carbonaceous powder that was synthesized by CO<sub>2</sub> laser pyrolysis of a 2:1 mixture of ethylene and benzene vapor. The resulting soot was expected to contain a large amount of PAH molecules as could also be verified by FTIR spectroscopy of the extract obtained by dissolving the soot in toluene. Moreover, UV spectra taken from the toluene extract in hexane suggested that the 3-ring PAHs phenanthrene and anthracene should be a major component (Jäger *et al.* 2006; Jäger *et al.*, in preparation). In order to corroborate this finding, we have investigated the soot as well as the extract using both spectroscopic techniques discussed before, *i.e.*, cavity ring-down and helium droplet spectroscopy. The present investigation has been focused on the detection of phenanthrene (C<sub>14</sub>H<sub>10</sub>) as major component of the samples (Staicu *et al.* 2006; Jäger *et al.* 2006).

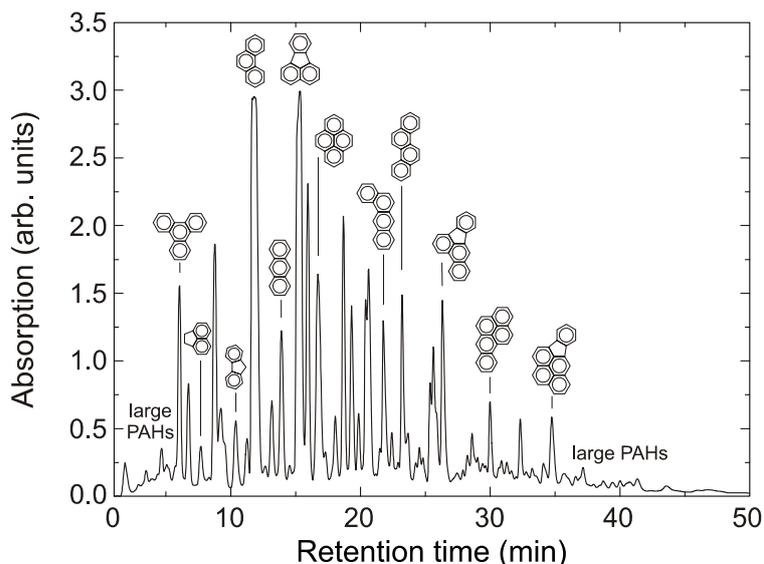
To calibrate the spectrometers, we have at first characterized the pure chemical substance by measuring the S<sub>2</sub> ← S<sub>0</sub> origin band at 35 378.2 cm<sup>-1</sup> (282.7 nm) and 35 316 cm<sup>-1</sup> (283.2 nm) in the gas phase and in helium droplets, respectively. The results of the complete study of phenanthrene evaporated from the soot and extract are presented in Fig. 3. The right panel shows the gas phase spectra obtained by cavity ring-down spectroscopy while, in the left panel, the results for helium droplets are displayed as obtained by depletion spectroscopy with the mass spectrometer tuned to the mass of phenanthrene ( $m = 178$  amu). In both panels the solid curves refer to the pure substance while the dashed and dotted lines correspond to the soot and extract, respectively. The spectra clearly reveal that phenanthrene is a constituent of all samples. The smaller amplitudes of the respective peaks in the CRDS spectra (compared to the peak of the pure substance) merely reflect the fact that the phenanthrene densities are lower when the soot/extract samples are heated to 130 °C. In



**Fig. 4:** Phenanthrene absorption spectra measured by cavity ring-down spectroscopy in supersonic jets (right panel) or by depletion spectroscopy in helium droplets (left panel). The solid curves refer to the pure substances of phenanthrene while the dashed and dotted lines correspond to phenanthrene spectra obtained from laser pyrolysis soot or the extract thereof. The soot and extract were heated to 100 °C in the helium droplet experiment and to 130 °C in the CRDS study while the pure substances were kept at -7 °C or 100 °C in the respective experiments.

contrast, their smaller amplitudes in the helium droplet spectra (19 % depletion compared to 45 % for the pure substance) indicate that only 42 % of the total count rate at mass  $m = 178$  amu originate from phenanthrene. The remaining 58 % are due to other molecules with the same mass (for example anthracene) or fragments of larger PAHs to this mass. Aside from the matrix shift of -62 cm<sup>-1</sup>, the helium droplet spectra reveal substantial broadening. This is however difficult to quantify since the helium droplet spectra were measured at higher laser energy so that power broadening is effective.

In order to obtain quantitative information on the PAHs produced by laser pyrolysis and to separate the species from each other, high pressure liquid chromatography (HPLC) seems to be most appropriate. After having extracted the soluble molecular components from the soot by soxhlet extraction in toluene, the sample was redissolved in benzonitrile and analyzed in our HPLC apparatus (Jäger *et al.*, in preparation). Figure 5 displays the chromatogram together with the assignments of most of the important peaks.



**Fig. 5:** High pressure liquid chromatogram of the extract of the carbonaceous powder produced by CO<sub>2</sub> laser pyrolysis of a C<sub>2</sub>H<sub>4</sub>/C<sub>6</sub>H<sub>6</sub> mixture. Most of the peaks can be assigned to PAHs.

### 3.6 Zusammenfassung und Ausblick / Summary and future

Within the present project, we have studied electronic absorption spectroscopy of a few neutral and cationic PAHs in the gas phase at low temperature as provided by a supersonic jet. The method employed was cavity ring-down spectroscopy. In addition, some selected neutral PAHs were also investigated in superfluid helium droplets where the internal degrees of freedom are in equilibrium at 370 mK. For the cations of naphthalene and anthracene, we observed rather broad absorption bands around 671 and 709 nm, respectively. For the neutral species 2,3-benzofluorene and benzo[ghi]perylene, the vibrationless transitions to the lowest electronically excited state ( $S_1$ ) were determined for the first time to be at 335 nm (29894 cm<sup>-1</sup>) and at 400 nm (25027 cm<sup>-1</sup>), respectively.

Up to now, none of the PAHs (neutral or cationic) studied by other groups or in our laboratory, showed any coincidence with astronomical observations. The cation bands are notoriously too broad. Part of the large bandwidth can be associated with the fact that the cations are not as cold as they are expected to be in astronomical environments. Therefore, experiments with vibrationally relaxed PAH cations (for example in ion traps) are urgently needed. Attempts to incorporate PAH cations into helium droplets were successful; but spectroscopic studies are still missing due to the difficulty to monitor the absorption of photons. Experiments in this direction should be pursued. In contrast, the absorption of neutral PAHs in helium droplets can be conveniently studied by monitoring the resulting evaporation of helium atoms. We studied the PAHs pyrene, anthracene, phenanthrene, and 2,3-benzofluorene. Although the measured bands are somewhat shifted and broadened due to the matrix effect, the data are very valuable especially if they can be compared to gas phase data. Note that the molecular vibrations are definitely cooled.

The experiments carried out so far dealt with PAH molecules that were synthesized by standard wet-chemical procedures. Such synthesis conditions are certainly not representative for astrochemical production routes. Therefore, we propose to use other production techniques which are more relevant for astrophysics. Laser pyrolysis of hydrocarbons could be a good example. Using this technique, we have produced carbonaceous powders with a high concentration of PAHs. The synthesis was performed by our partners in Romania. We were able to extract PAHs with molecular weights up to 600 amu. The first successful spectroscopic characterization was obtained for phenanthrene and anthracene, species which can also be purchased from chemical suppliers. In the future, it will be interesting to study the heavier species as well. However, it will be necessary to have a means of efficient separation and to be able to collect enough material from the desired species. This should be most conveniently achieved with the high-pressure liquid chromatography (HPLC) apparatus that we have recently acquired.

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