PAHs and the Universe
C. Joblin and A.G.G.M. Tielens (eds)
EAS Publications Series, **46** *(2011) 355-371*
www.eas.org

ELECTRONIC SPECTROSCOPY OF PAHS

T. Pino[1], Y. Carpentier[1], G. Féraud[1], H. Friha[1], D.L. Kokkin[2], T.P. Troy[2], N. Chalyavi[2], Ph. Bréchignac[1] and T.W. Schmidt[2]

Abstract. Polycyclic aromatic hydrocarbons are a class of molecules of broad interest that has long been explored by various spectroscopic techniques. The electronic spectroscopy of these species is of particular interest since it provides a framework for the understanding of the electronic structure of large polyatomic molecules. Such studies also allow the systematic investigation of electronic relaxation mechanisms in large molecules. In this review, we focus on the gas-phase experimental work on such systems and present the latest progress. We also underline the challenges that remain to be tackled. A focus on the understanding of the electronic relaxation pathways at work in gas-phase PAHs will also be presented, as well as their possible manifestation in space.

1 Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are found in many diverse environments on earth and in space, either from natural or industrial sources. Because of their implication in various physico-chemical phenomena, many studies have been devoted to them. This peculiar class of molecules has also received attention from fundamental studies towards a better understanding of molecular structure and dynamics. A comprehensive review of their electronic structure can be found in Clar's series of books (Clar 1964a; Clar 1964b), where the basic PAH science may also be found. A few examples illustrate the importance of PAH science and their profound impact on molecular science. The study of their quantum yield of fluorescence during the sixties and early seventies (Hunt *et al.* 1962; Siebrand 1967) led to major developments in the understanding of intramolecular dynamics and radiationless transitions in particular (Englman & Jortner 1970). At the beginning of the eighties, with the advances of molecular beam techniques, the first

---

[1] Institut des Sciences Moléculaires d'Orsay, Univ Paris Sud, CNRS, France
[2] School of Chemistry, The University of Sydney, NSW 2006, Australia

DOI: 10.1051/eas/1146037

systematic studies of their gas-phase electronic spectra were performed. Two major breakthroughs in molecular science were thus achieved: the first high-resolution spectrum of a large polyatomic molecule, fluorene, was measured in 1984 (Meerts *et al.* 1984) and the first study of intramolecular vibrational energy redistribution (IVR) in such molecules was measured for anthracene using a picosecond laser (Felker & Zewail 1985; Felker & Zewail 1985b). Such studies mark the birth of time-resolved intramolecular dynamics in large polyatomic systems.

PAHs are thought to carry at least some of the diffuse interstellar bands (DIBs) (Léger & d'Hendecourt 1985), some of the Red Rectangle emission bands (Sarre 2006; Sharp *et al.* 2006), the aromatic infrared bands (AIBs) (Léger & Puget 1984; Allamandola *et al.* 1985) and may have a significant contribution to the "bump" at 217 nm (Joblin *et al.* 1992; Li & Draine 2001). All these spectral features imply electronic absorption and/or intramolecular dynamics such as electronic relaxation and IVR. However, although PAH science may be thought as mature, the experimental data that are of real pertinence for the identification of interstellar or circumstellar PAHs are rather scarce. In fact, the questions posed by the existence of these compounds in space are all real challenges for laboratory astrophysicists and thus the "PAH hypothesis" has triggered many fundamental studies. However, concerning the electronic spectroscopy of PAHs, only few cations have been spectroscopically investigated in the gas phase (see Salama 2007 for a review), even fewer neutral radicals and no anions. Deep-UV spectra around the bump region at 217 nm are available only for few gas-phase neutral species (Joblin *et al.* 1992; Suto *et al.* 1992). This may seem somehow disappointing, but recent progresses on PAH science may be seen as a prelude for many advances in a relatively near future.

In this review, a focus on the recent progress on the electronic spectroscopy of PAHs will be presented. This review mainly concerns works published after the review of Salama (Salama 2007) and is hopefully pedagogical enough to provide the astrophysicist with the background to evaluate the work that has been achieved and that remains to be done in order to make progress on testing the PAH hypothesis in the laboratory, and enable firm identification of some species. The first section will present the experimental methods that are used or developed, followed by a short tour on the main results in the second section. Conclusions and perspectives will be thus given in a third section.

2 Experimental approaches

2.1 The constraints for laboratory astrophysics studies of the PAHs

The PAH hypothesis relies on the molecular rather than solid behavior of the carrier of the AIBs (Puget & Léger 1989). It involves the transient heating mechanism, which may be explained within the framework of molecular physics as follows: after absorption of a starlight photon through an electronic transition, electronic relaxation takes place dominantly by nonradiative processes and subsequent IVR scrambles the resulting vibrational energy over all accessible vibrational states of the electronic ground state. Thus infrared fluorescence proceeds on the ground electronic state. These AIBs imply very large molecules – up to a few hundreds of carbon atoms – completely isolated *in vacuo* on timescales ranging from a few tens of femtoseconds up to a few seconds.

In order to study the astronomical PAHs in the laboratory, generally gas-phase isolation is a strong requirement, in particular when spectroscopy or intramolecular processes are concerned. Thus, depending on the specific timescales of the mechanism being investigated, several methods for isolation are necessary, but also several experimental methods for interrogation of the molecules as well. Most studies use laser technology that permits the study of ultrafast dynamics with femtosecond lasers or high-resolution spectroscopy with continuous lasers. Therefore, laboratory astrophysics devoted to PAHs necessitates the use of state-of-the-art methods taken from molecular and/or cluster sciences that combine gas phase molecules either in a molecular beam or ion trap with different laser sources and detection methods. In addition, it is best to work on cold or even ultracold PAHs in order to avoid spectral congestion.

2.2 Gas-phase PAHs?

PAHs are not naturally available in the gas phase, except when the experiment uses a gas-phase reactor directly coupled to diagnostics. As such, they have to be vaporised before being studied. Many approaches have needed to be developed since a simple heated oven becomes less efficient at sample vaporization beyond the size of coronene. The most successful method for large molecular systems is laser desorption (Haufler *et al.* 1991). Many different protocols may be adapted to each case, using different wavelength, pulse duration and source geometries.

Neutral PAHs are of prime interest, but cations and radicals are also to be studied. In this case additional ingredients have to be added to produce such species. Laser ionisation (Pino *et al.* 1999), laser photolysis and electric discharge (Romanini *et al.* 1999) are favorite tools for this purpose but these additional steps render the experiment much more complex and only few species have been effectively studied.

Before spectroscopic investigation, it is better to cool the PAH. However heating, desorption, ionization, and discharge are all in favor of producing hot PAHs rather than cold ones. As such, these methods are usually coupled to supersonic expansions in order to cool down the target molecule (Haufler *et al.* 1991). When adding all these techniques, one may realize that not all has been effectively experienced yet! Producing a large PAH cold in the gas phase is, in fact, the most limiting problem for experimental investigation, either because the PAH itself is difficult to produce in large enough quantities or because the necessary densities in the gas phase for a given technique cannot be achieved. However, with the advances on new production methods and with the very useful guidance of quantum

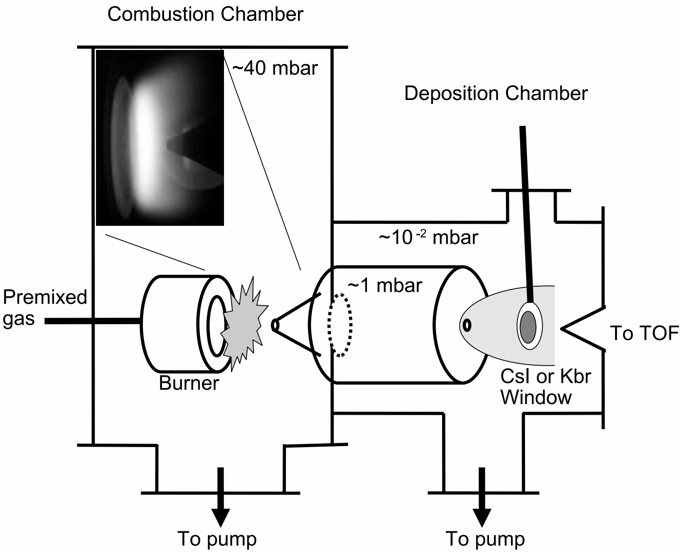

Fig. 1. A schematic view of the experimental set-up that was built at Orsay. The combustion chamber contains the flat burner, cooled by circulating water. The flame is horizontal and the flow (pre-mixed) is maintained at a constant pressure within the chamber, at about a few tens of mbar. The burner is movable along the horizontal axis. The quartz sampling cone (shown) allows species produced at a given distance from the burner to enter the copper thermalisation chamber. This chamber is placed inside the deposition chamber, which is maintained at a pressure of about 10^{-2} mbar under the operating conditions. A window is then placed into the jet that is formed at the end of the thermalisation chamber, where the gas passes through the nozzle. Possible extraction through a skimmer forms a molecular beam at the entrance of a Time-Of-Flight mass spectrometer.

chemical calculations, much progress has been recently reported (Kokkin *et al.* 2008) which may strongly influence our knowledge of PAHs larger than coronene in the near future.

The source of PAHs itself is also of importance. Recent advances in chemical synthesis have led to the production of PAHs up to the $C_{222}H_{42}$ (Simpson *et al.* 2002). In fact, as long as a target PAH is chosen, chemical synthesis is favoured. However gas-phase reactors offer the opportunity to directly produce many of them in the gas phase. Flame and laser pyrolysis are among the most promising of such sources. At Orsay, we have incorporated a low pressure, flat and premixed flame that can be coupled to a time-of-flight mass spectrometer (Fig. 1). Under favorable conditions, a large distribution of PAHs may be produced (Fig. 2). It is remarkable that this PAH distribution is very similar to that obtained in different burning conditions (Apicella *et al.* 2007) and using laser pyrolysis or laser ablation (Jäger *et al.* 2007; Jäger *et al.* 2009).

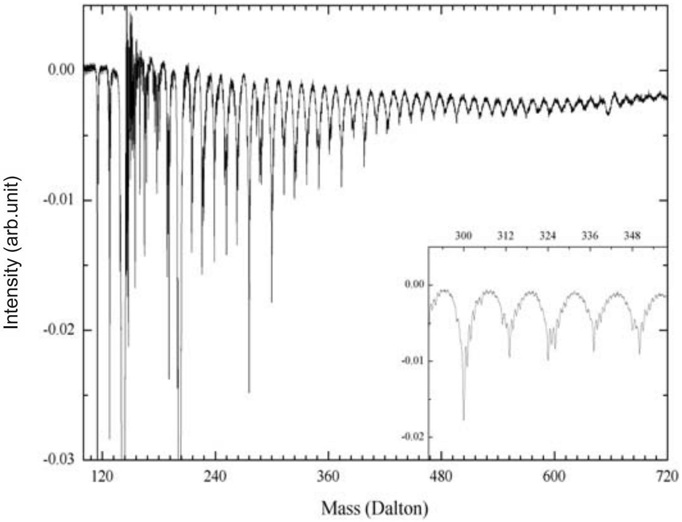

Fig. 2. Mass spectrum measured with the experimental set-up Nanograins at Orsay. The sampled flame was a low pressure (about 80 mbar) of premixed ethylene and oxygen with a C/O ratio of 1.6. Laser ionization was used and the mass spectrum is dominated by PAHs up to a few tens of carbon atoms.

2.3 The experimental techniques

2.3.1 Laser induced fluorescence

Laser Induced Fluorescence (LIF) is the first technique that made the measurement of electronic transitions of PAHs in the gas phase accessible. The first was measured in the group of Smalley and published in 1981 (Beck *et al.* 1981a; Beck *et al.* 1981b). It concerned the naphthalene molecule in its neutral form and presented excitation and dispersed fluorescence spectra. The method is as follows: resonant absorption of a tunable laser through an electronic transition between the electronic ground state and an excited one is measured by collecting the electronic fluorescence from the excited molecule. The fluorescence excitation spectrum is measured by scanning the laser wavelength and monitoring the total fluorescence as a function of the wavelength. It is closely related to the absorption spectrum, only intensity ratios may differ due to differences of the quantum yield of fluorescence of the molecular states. Dispersed fluorescence spectra consist of monitoring the frequency resolved spectra of the fluorescence at a given resonant excitation wavelength. The coupling of both techniques provides information on both ground and excited electronic states, Franck-Condon factors, changes in geometry, dynamics in the excited states and so on. Following advances in CCD technology led by astronomy, two-dimensional fluorescence has been developed.

This consists in measuring excitation and disperse spectra simultaneoulsy (Reilly *et al.* 2006). The strength is a fully allowed characterisation of both states, even from a complex distribution of molecules arising from a gas-phase reactor. Time-resolved fluorescence spectra can also be measured which provides information on the excited state dynamics, such as the contribution of both radiative and nonradiative decay.

2.3.2 Resonant 2-colour 2-photon ionisation spectroscopy

Instead of detecting photons, ions (or electrons) can be measured in combination with a mass spectrometer. In this case, after excitation to a given electronic excited state of the PAH, a second laser (or when possible the same laser) is used to photoionize the molecule, which is the basis of resonant 2-colour 2-photon ionisation spectroscopy – R2C2PI (Duncan *et al.* 1981). The ion or electron current thus traces the resonant absorption during the first tunable step. This method is basically as sensitive as LIF but provides additional information when ions are detected – the mass of the species. This is of importance when dealing with a distribution of PAHs, or unidentified species from a discharge (Reilly *et al.* 2008), for example. If the first laser is tuned to a resonant transition, scanning the second provides the photoionization efficiency curve which reveals the ionization potential (*e.g.* Troy *et al.* 2009). When electrons are detected, the photoelectron spectrum may be used as a projection of the excited state wavefunction onto the cationic molecular states and provides information on the dynamics or the coupling between states in the neutral molecule (Stolow *et al.* 2004). These experiments are generally performed in the time-resolved domain. A similar approach may be performed on anions: The photodetachment rather than the photoionisation is measured, and appearance of the neutral and depletion of the anion must be measured if the detection does not involve the photodetached electrons (Tschurle & Boesl 2006).

2.3.3 Resonant multiphoton dissociation

In the case of the cations, the second ionization potential to access the doubly charged species is generally very high and cannot be easily reached for a R2C2PI technique using benchtop equipment. In addition, aromatic cations are almost all non-fluorescent, *i.e.* the quantum yield of fluorescence is close to zero and electronic relaxation processes are dominated by nonradiative phenomena. Regarding such a situation, mass spectrometry appears as the privileged tool. The signature of the resonant absorption has to be traced through a measurable charge-to-mass ratio change, and involve a change in mass rather than a change in charge via fragmentation of the cation. Actually PAHs are rather stable towards photodissociation. Thus, efficient measurement requires time for measuring slow processes and/or large pulse energies to accelerate the process. To overcome these limitations, two techniques have been developed: either the cations fragment after absorption of multiple photons (Useli-Bacchitta *et al.* 2010) or the departure of a loosely bound tagging atom (a rare gas atom for example) after absorption of a single photon may be used to trace the absorption spectrum (Bréchignac & Pino 1999; Pino *et al.* 1999). In the latter case the effect of the presence of the weakly bound rare gas atom has to be carefully investigated in order to properly extract the spectrum of the bare cation. However it has been shown to be the most productive method (Salama 2007) up to now, but the latest developments seem promising to explore and provide novel results on cations (Useli-Bacchitta *et al.* 2010).

2.3.4 Cavity ringdown spectroscopy

Cavity ring down spectroscopy (CRDS) is the only direct absorption method that can be used for any species (O'keefe & Deacon 1988). However, although the sensitivity can be even better than the previously cited methods, the technique suffers from the absence of any two dimensional information which is needed for the identification of the absorbing species if the spectrum is not self-sufficient (via the complete rotational line's assignment for example). It implies that as long as the spectrum can not be unequivocally assigned, no additional measurements guide the attribution. But, it remains a valuable tool when the other methods are applied, as a cross-check of the absorption spectrum. The principle is a follows: A laser pulse is trapped in an optical cavity and the ringdown time is maximum and defined by the reflectivity of the mirrors, when the laser wavelength is resonant with a transition of the gaseous medium the ringdown time decreases due to cavity loss. Its evolution as a function of laser wavelength traces the absorption spectrum.

2.3.5 Other methods

Other experimental methods do exist and most may be considered as evolutions and improvements upon those cited above. Either the detection or laser scheme changes, offering possibilities for peculiar aspects. Present efforts mainly concern ion or electron imaging for dynamical purposes (Stolow & Underwood 2008), with the development of detectors with time and spatial resolution, as well as optical cavities used under various configurations (Bernhardt *et al.* 2010).

3 Recent progress

3.1 Toward Larger PAHs in the gas phase

Until very recently, the largest molecule conclusively identified in an extraterrestrial environment were the carbon chains $HC_{11}N$, found in the circumstellar shell of

IRC+10216 by rotational spectroscopy.[1] However, photophysical models of PAHs in interstellar environments conclude that they must contain at least 30 carbon atoms to be sustainable against the weathering photon flux. Prior to 2007, the largest PAH studied as an isolated, free-flying molecule in the vacuum was ovalene, $C_{32}H_{14}$ (Amirav *et al.* 1981). Recently the terrylene $C_{30}H_{16}$, which exhibits a strong transition in the visible range of wavelength, was also studied by LIF in the gas phase (Deperasinska *et al.* 2007). Even these giants are not unambiguously large enough to satisfy the criteria set out by interstellar PAH models.

Troy's all-benzenoid hypothesis motivated the study of those PAHs which can be drawn as isolated benzene rings joined by "single" bonds. A R2C2PI and LIF spectroscopic study of the smallest of these, triphenylene ($C_{18}H_{12}$), was reported by the Sydney laboratory in 2007 (Kokkin *et al.* 2007). By early 2008, an $S_1 \leftarrow S_0$ excitation spectrum of the hexa-*peri*-hexabenzocoronene ($C_{42}H_{18}$: HBC) was obtained (Kokkin *et al.* 2008). This R2C2PI spectrum was recorded following laser desorption of a pressed pellet of HBC in a supersonic expansion of argon. The skimmed beam was interrogated by a pair of laser beams some 30 cm downstream in the extraction region of a TOF-MS. This difficult experiment stands as the record for a PAH studied by gas-phase spectroscopy. Subsequent condensed phase spectra of HBC confirm that these α-bands near 425 nm are extremely weak compared to bands lying in the near ultraviolet (Rouillé *et al.* 2009). It remains for these higher $S_n \leftarrow S_0$ transitions to be recorded in truly isolated molecules. The absence of these signatures in the spectrum of the interstellar gas should provide interesting constraints for interstellar PAH chemistry.

Larger PAHs than HBC have been synthesized. The pioneering organic chemistry of Müllen has produced the monster $C_{222}H_{42}$ - a hexagonal sheet of graphene consisting of 37 separate benzenoid rings whose peripheral carbon are passivated by H (Simpson *et al.* 2002). Before attempting to obtain the R2C2PI spectrum of such a beast, other all-benzenoid PAHs await, such as $C_{78}H_{26}$ and $C_{96}H_{30}$.

3.2 From the visible to the 217 nm bump region absorption of the PAHs

Electronic spectra of PAHs have been generally studied in the vicinity of the first electronic states (Beck *et al.* 1981a). Most of the gas-phase spectra of neutral PAHs were measured in the early 80's by LIF. In the case of the cations, because of the DIBs hypothesis, the electronic absorption spectra were monitored in the visible range (Salama 2007). Of course, matrix isolation spectroscopy provided important measurements, even up to the deep UV. Unfortunately, few were studied in the gas phase around the bump region, most spectra being published in 1992 using synchrotron light sources (Joblin *et al.* 1992; Suto *et al.* 1992). Since that time, nearly no new spectra were published and moreover no cold ones. However

---

[1] Recently, Sellgren *et al.* (2010) reported the detection of the IR emission bands of C_{60} in reflection nebulae (see Sellgren *et al.*, elsewhere in this volume) and Cami *et al.* (2010) reported the detection of C_{60} and C_{70} in a young planetary nebula.

it seems more and more clear that this component of the ISM should contribute significantly to the bump at 217 nm (Malloci *et al.* 2007).

Recently, using a gas-phase reactor for the production of large PAHs, new insights on their electronic spectra have been obtained. At Orsay, a R2PI experiment coupled to a low-pressure flame has been set up. Electronic spectra of the small aromatics have been recorded from 207 nm up to 330 nm. Nearly 20 spectra have been recorded, assigned to benzene and PAH derivatives with mono- and di-substitution by methyl, vinyl and ethynyl groups (Carpentier *et al.* 2010). Some correspond to known data from vapor phase measurements and others are new. This study focused on species up to pyrene derivatives since the combustion conditions could not produce sufficient and stable enough amounts of larger PAHs for electronic spectra to be recorded. In this experiment, the temperature of the measured PAHs was about 300 K. In the near future, we plan to cool down the extracted PAHs from the flame using a supersonic expansion and extend the study to larger sizes.

Important progress has been performed recently using PAHs produced by laser pyrolysis (Steglich *et al.* 2010). The visible to UV spectra of the molecules dispersed directly on a subtrate in the form of thin film and in rare gas matrices were measured. A size dependence could be inferred. Even more the effect of conditions were shown to be very important for the observed band profiles. The matrix isolation spectroscopy data contained considerably more substructures than the thin film. It is clear that gas-phase spectroscopy is a requirement in order to assigned properly the carrier of the bump, even for such a broad and featureless absorption.

3.3 Ultra-high resolution spectroscopy of PAHs

During the last decade, recent advances have allowed ultra-high resolution spectra of some PAHs to be recorded. The developments were performed in the group of M. Baba in Kyoto (Japan). Although the spectra were somehow all known, the unprecedented spectral resolution opened the possibility of a complete analysis, from spectral linewidths to rotational constants and detailed geometries. Azulene, naphthalene, pyrene and perylene, as well as benzene, have all been measured (Baba *et al.* 2009; Yoshida *et al.* 2009; Baba *et al.* 2009b; Semba *et al.* 2009; Kowaka *et al.* 2010). In addition, application of a magnetic field in the laser-molecules interaction zone was performed in order to probe the Zeeman effect. The outcome is a precise measure of the mixing between the first electronic S_1 state with the triplet manifold. All results have revealed that in fact it is very small and that the nonradiative decay is dominated by the internal conversion and not the intersystem crossing.

3.4 The PAHs derivatives: Ions and radicals

As only closed shell PAHs may be purchased from chemical suppliers, these species dominate the spectroscopic PAH literature. However, there exist many PAHs

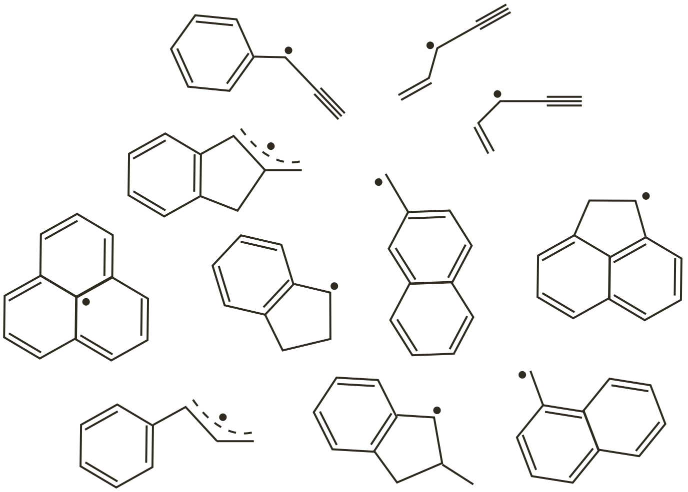

Fig. 3. The collection of aromatic and resonance-stabilized radicals for which excitation spectra have been obtained by the Sydney group. The origin bands lie between 450 nm and 600 nm. While none exhibit a perfect match to any diffuse interstellar band, the naphthylmethyl radicals exhibit spectra in the Red Rectangle emission region (see text).

which are either open-shell or cationic, or both. All of these species have electronic spectra in the visible region, making them especially interesting as DIB candidates. Indeed, many photophysical models predict that a large proportion of interstellar PAHs should be ionized.

3.4.1 Open-shell cations

Most gas-phase spectra of cationic PAHs have been obtained about ten years ago, and have been reviewed in Salama 2007. At Orsay, a new approach is under development with the goal to simplify the photoionisation scheme for the production of the cations. Instead of a R2C2PI process, photoionisation is performed within the supersonic expansion in order to produce cold cationic clusters with a single laser. Test experiments are under progress on naphthalene and its methyl derivatives. In the IRAP (ex-CESR) at Toulouse, thanks to the use of a cold ion trap, investigations of the electronic spectroscopy of cations and their fragments are now possible and should provide challenging data on such species by resonant multiphoton dissociation of the trapped ions, as it was done on the coronene cation (Useli-Bacchitta *et al.* 2010).

3.4.2 PAH radicals

In the past years there have been many new spectra of polycyclic radicals reported, but almost none of radical derivatives. The significance of resonance stability in aromatic radicals was realized with the observation of the phenylpropargyl radical as the brightest feature, after C_2, C_3 and CH, in the laser-induced fluorescence spectroscopy of an electrical discharge containing benzene (Reilly *et al.* 2008). Phenylpropargyl is not a true PAH, but could be a precursor to PAH formation in flames and other environments (see Cherchneff 2011 in this volume), given the putative importance of propargyl itself in benzene and subsequently soot formation. The radical can be considered as a benzyl and propargyl radical sharing a carbon, conferring it with a stability, as compared with methyl radical, similar to the sum of those of benzyl and propargyl. Phenylpropargyl, C_9H_7, which presents an origin transition at 476 nm, is an isomer of the indenyl radical, never reported in the gas phase. An attempt to produce indenyl from indene yielded indanyl radical, C_9H_9 (Troy *et al.* 2009). Indene adds a hydrogen atom barrierlessly, affording the radical presenting a dominant origin at 472 nm, with a true benzylic chromophore. This barrierless addition is of potential interest to interstellar chemistry, where low reaction temperatures predominate. A benzylic chromophore is also presented by 1,2,3-trihydronaphthalene, the spectrum of which was recorded by the Zwier group at Purdue (Sebree *et al.* 2010). This species has its origin near 468 nm, being very similar to indanyl radical in many respects. The Purdue group has also reported the spectra of 1-, and 2-hydronaphthalene, the spectra of which are dominated by origins at 528 and 516 nm respectively. Both possess extended conjugation as compared to the benzylic chromophores. The 1-hydronaphthalene is perhaps the more interesting, it being an allylic and a benzylic radical sharing the “radical” carbon. The unligated version, Ph-CHCHCH_2, which is the cinnamyl radical, was observed by the Sydney group very recently (Troy *et al.* 2010). A polycyclic cinnamyl radical, was produced in Sydney by H-loss from the methyl group of 2-methylindene. This radical absorbs principally at 516 nm, in the neighbourhood of the monohydronaphthalenes.

These bicyclic radicals all possess either a benzylic (460–480 nm) or a cinnamylic chromophore (510–530 nm). By extending the naphthalene backbone to one extra carbon we obtain the naphthylmethyl chromophore, with absorptions around 580 nm. The Sydney laboratory has obtained excitation and emission spectra of both CH_2-Np radicals, $C_{11}H_9$, and the acenaphthyl radical, a tricyclic $C_{12}H_9$ species. The plethora of possible radicals with this chromophore may have a relationship to the emission bands of the red rectangle nebula, which exhibits prominent unassigned emission features in the 580 nm region (Sarre 2006; Sharp *et al.* 2006).

The most symmetric tricyclic PAH radical is the phenalenyl radical, $C_{13}H_9$. Its gas-phase spectrum was recently obtained in the Sydney laboratory, it closely resembles that obtained previously under matrix isolation. The spectrum is not origin dominated as are those of the other aromatic radicals mentioned above. Rather, the origin is small with the spectrum being dominated by e' vibration modes presumably gaining intensity through Herzberg-Teller interactions: the positions are perturbed through Jahn-Teller interactions. A full analysis of this spectrum shall be presented in the near future.

All of these open-shell PAH radicals present an opportunity to produce a different class of PAH cation, closed-shell cations. The closed shell cations possess much higher HOMO-LUMO gaps than similarly sized open-shell cations. As such, their spectra in the visible region should be much sharper than the open-shell cations, and there is the possibility that they emit fluorescence. It will be possible to measure the spectra of such cations in the near future.

3.5 Nonradiative transitions in PAHs: Present status

Nonradiative transitions are at the core of the PAH hypothesis. The main concepts should be recalled here. The molecular states are first described within the adiabatic Born-Oppenheimer approximation that separates the electronic and nuclei momenta. This is done at a level beyond the harmonic approximation to account for Fermi resonance at low vibrational energies and wholesale intramolecular vibrational energy redistribution higher up the well. The energy levels are obtained and the overall mechanism may be discussed in term of time-dependent dynamics between bright and dark states. It is noteworthy that such a description belongs to the Bixon and Jortner approach (Bixon & Jortner 1968), while others prefer manipulations of the eigenstates as long as it is possible, which is particularly adapted when ultra-high resolution spectroscopy in the frequency resolved domain provides the complete set of information (Quack 1990). In the case of PAHs, the dominant description is that from Bixon and Jortner. Electronic relaxation can then take place. When it occurs between two states of same multiplicity, the process referred to as internal conversion (IC) and part of (or all) the electronic energy is converted into vibrational energy. Between states of different multiplicity, intersystem crossing (ISC) occurs which relies on spin-orbit coupling. This is generally much slower (by about a million times) for hydrocarbons and the upper (fastest) limit should be found in the nanosecond timescale. Several configurations may be found, depending on the shape of the potential energy surface: The change of geometries and the existence of surface crossings shape the radiationless processes. In the latter case, conical intersections (CI) are thought to play an important role in intramolecular dynamics as it appears more and more than they are more systematic than peculiarities (Yarkony 2001). When relaxation takes place within a particular state, only vibrational energy is concerned and the process is called intramolecular vibrational energy redistribution (IVR). In all cases, the strength of the coupling and the density of states (vibrational and/or electronic) control the nonradiative processes, there being various regimes (weak and strong coupling limit, intermediate case and statistical limit). Very good reviews can be found in the literature for a complete analysis of this topics (Avouris *et al.* 1977; Freed 1978; Medvedev & Osherov 1995).

The PAH family of molecules has long served the exploration of these processes. In particular the energy gap law (EGL) was inferred from measurement of fluorescence lifetime of PAHs in solution and proved to involve ISC (Siebrand 1967). The EGL states that in the statistical limit an exponential dependence of the nonradiative rates versus the energy gap between the prepared state and the electronic states immediately below is to be found (Englman & Jortner 1970). A summary of nearly all available data is presented in Figure 4. Benzene derivatives, azulene derivatives, neutral and cationic PAHs are reported. Actually, although the EGL was obtained from the ISC rate in neutral PAHs, it is not clear whether in IC such a dependence may be deduced here. The particular role of the CI seems to be very important in the case of ultrafast (below 0.1 ps) electronic relaxation, and recent calculations have shown that these intersections are systematically present in cations (Tokmachev *et al.* 2010). Additionally, in benzene where a CI has long been known to promote IC and quench the electronic fluorescence at a certain excess vibrational energy into the S_1 state (about $4000\,\mathrm{cm}^{-1}$), new insights are becoming available and point to fast ISC as well (Parker *et al.* 2009). In the case of neutral PAHs, the dominant relaxation pathway of the S_1 state was long thought to be ISC, *i.e.* similar to the solution phase. However recent ultra-high resolution measurements of the Zeeman effect point to a weak ISC and a dominant IC (Kasahara *et al.* 2006; Kato *et al.* 2007). In fact the actual strong ground on which electronic relaxation of PAHs were understood is rapidly changing and we expect a new view on this aspect in a near future.

Still, IC is clearly at work in open shell cations and this is completely consistent with the PAH hypothesis. The existence of fast relaxation channels in highly excited states of neutral PAHs remains to be explored, only one study seems to be available Suto *et al.* (1992). The strength of the coupling in radicals or superhydrogenated PAHs is still unknown.

4 Conclusions and outlook

Between our laboratories and others, there has been real progress in obtaining new spectra and sources of PAHs, their radicals and cations since 2007. In Orsay, a new experiment has been built to produce beams of large PAHs from a combustion source, and work progresses on efficiently producing open-shell PAH cations within a molecular beam. The Sydney laboratory has obtained a collection of open-shell PAH radical spectra from electrical discharges, with the view to produce a larger diversity of species. Looking forward, we aim to obtain close-shell PAH cation spectra in the coming years.

The astrophysical PAH hypothesis relies on the concepts of molecular nonradiative processes occuring in the gas phase. Using high-resolution spectroscopy, Baba's group continues to uncover the links between gas phase spectroscopy and the classical ISC studies of PAHs in solution. However, there remains a mismatch in the conditions available to laboratory spectroscopists and astronomers – that of timescale. Unless confined to an ion-trap (where low ion numbers pose their own problems), it is difficult to confine a PAH to the one point in space for longer than a few microsecond – a molecule beam moves at about a millimeter per microsecond. However, the full mechanism underlying the PAH hypothesis takes place on timescales up to seconds. To fully explore the dynamical behaviour of PAHs and

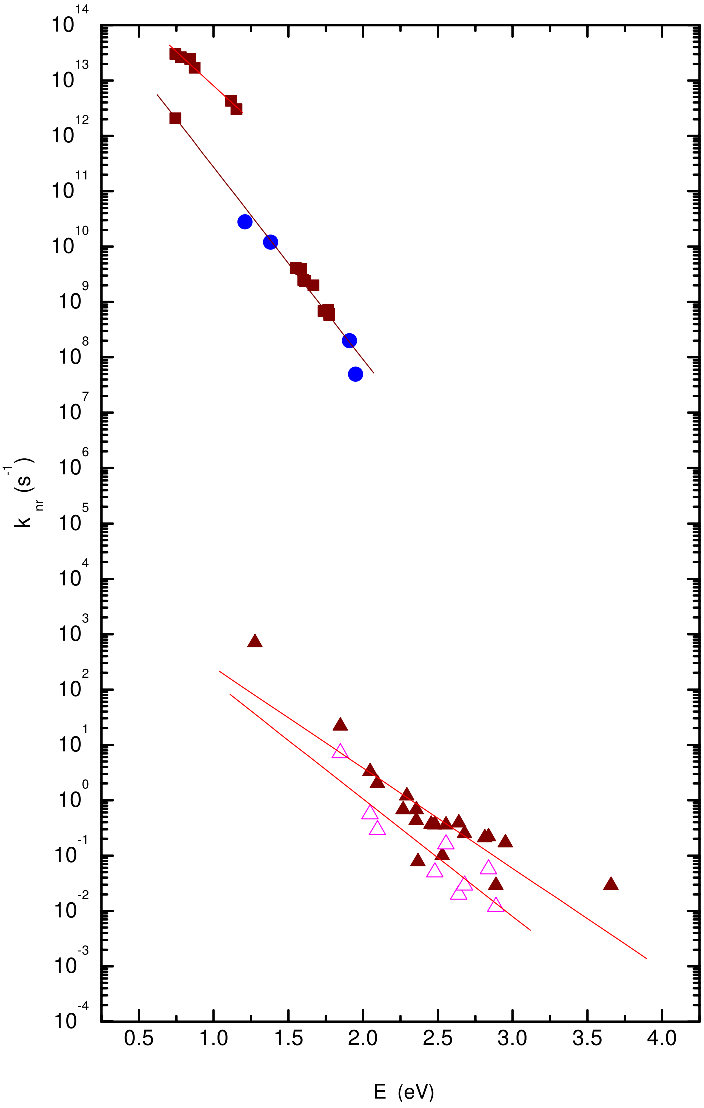

Fig. 4. Nonradiative electronic relaxation rate of the PAHs. Triangles are for the ISC (intersystem crossing) measured in solution for neutral species in their hydrogenated (full) and perdeuterated (open) form (Siebrand 1967), squares are those for IC (internal conversion) measured neutral (azulene derivatives from Murata *et al.* 1972 and phenanthrene from Ohta & Baba 1986) and cationic PAHs (for a detailed list of the references, see Salama 2007). Circles are for the neutral fullerenes. The lines are mainly there to guide the eyes to signify the relative efficiency of the Energy Gap Law and underline the deuterium effect when present. In the case of the azulene derivatives, it was shown to be very weak (Griesser & Wild 1980) unlike for the ISC in the neutral PAHs.

their cations under the full range of timescales available to astronomers, we must perform experiments on larger scales, or slow down our molecular beams. Towards the latter, there have been developments in Stark and Zeeman deceleration for smaller molecules in recent years, but in favour of the former, let us go to space with our molecules. It would certainly be a very interesting experiment to place an artificial small comet into space and observe this with all the spectroscopic tools available to the astronomical community. Such an experiment would produce a wealth of data, of interest to astrochemists, astrophysicists and molecular physicists. Space is still the greatest laboratory of all, where so much more is possible than on Earth.

References

Allamandola, L.J., Tielens, A.G.G.M., & Barker, J.R., 1985, ApJ, 290, L25

Amirav, A., Even, U., & Jortner, J., 1981, J. Phys. Chem., 85, 309

Apicella, B., Carpentieri, A., Alfe, M., *et al.*, 2007, Proc. of the Comb. Inst., 31, 547

Avouris, P., Elbart, W.M., & ElSayed, M.A., 1977, Chem. Rev., 77, 793

Baba, M., Saitoh, M., Taguma, K., *et al.*, 2009, JCP, 130, 134315

Baba, M., Saitoh, M., Kowaka, Y., *et al.*, 2009, J. Chem. Phys., 131, 224318

Beck, S.M., Powers, D.E., Hopkins, J.B., & Smalley, R.E., 1981, J. Chem. Phys., 73, 2019

Beck, S.M., Hopkins, J.B., Powers, D.E., & Smalley, R.E., 1981, J. Chem. Phys., 74, 43

Bernhardt, B., Ozawa, A., Jacquet, P., *et al.*, 2010, Nat. Photon., 4, 55

Bixon, M., & Jortner, J., 1968, J. Chem. Phys., 48, 715

Bréchignac, P., & Pino, T., 1999, A&A, 343, L49

Cami, J., Bernard-Salas, J., Peeters E., & Malek, S.E., 2010, Science, 329, 1180

Carpentier, Y., *et al.*, in preparation

Cherchneff, I., present volume

Clar, E., "Polycyclic Hydrocarbons vol. I" (Academic Press and Springer Verlag 1964)

Clar, E., "Polycyclic Hydrocarbons vol. II" (Academic Press and Springer Verlag 1964)

Deperasinska, I., Zehnacker, A., Lahmani, F., Borowicz, P., & Sepio, J., 2007, J. Phys. Chem. A, 111, 4252

Duncan, M.A., Dietz, T.G., & Smalley R.E., 1981, J. Chem. Phys., 75, 2118

Englman, R., & Jortner, J., 1970, Mol. Phys., 18, 145

Felker, P.M., & Zewail, A.H., 1985, J. Chem. Phys., 82, 2975

Felker, P.M., & Zewail, A.H., 1985, J. Chem. Phys., 82, 2961

Freed, K.F., 1978, Acc. Chem. Res., 11, 74

Glinski, R.J., Michaels, P.D., Anderson, C.M., *et al.*, 2009, Ap&SS, 323, 337

Griesser, H.J., & Wild, P.U., 1980, Chem. Phys., 52, 117

Haufler, R.E., Wang, L.S., Chibante, L.P.F., *et al.*, 1991, Chem. Phys. Lett., 179, 449

Hunt, G.R., McCoy, E.F., & Ross, I.G., 1962, Aust. J. Chem., 15, 591

Jäger, C., Huisken, F., Mutschke, H., *et al.*, 2007, Carbon, 45, 2981

Jäger, C., Huisken, F., Mutschke, H., Llamas Jansa, I., & Henning, Th., 2009, ApJ, 696, 706

Joblin, Ch., Léger, A., & Martin, P., 1992, A&A, 393, L79

Kasahara, S., Baba, M., & Kato, H., 2006, Bull. Chem. Soc. Jpn., 79, 75

Kato, H., Baba, M., & Kasahara, S., 2007, Bull. Chem. Soc. Jpn., 80, 456

Kokkin, D.L., Reilly, N.J., Troy, T.P., Nauta, K., & Schmidt, T.W., 2007, JCP, 126, 084304

Kokkin, D.L., Troy, T.P., Nakajima, M., *et al.*, 2008, ApJ, 681, L49

Kowaka, Y., Suganuma, Y., Ashizawa, N., *et al.*, 2010, J. Mol. Spec., 260, 72

Léger, A., & Puget, J.L., 1984, A&A, 137, L5

Léger, A., & d'Hendecourt, L., 1985, A&A, 146, 81

Li, A., & Draine, B.T., 2001, ApJ, 554, 778

Malloci, G., Mulas, G., & Joblin C., 2007, A&A, 426, 105

Medvedev, E.S., & Osherov, V.I., 1995, "Radiationless Transitions in Polyatomic Molecules" (Springer Series in Chemical Physics), 57

Meerts, W.L., Majeski, W.A., & Van Herpen, W.M., 1984, Can. J. Phys., 62, 1293

Murata, S., Toda, T., Kokubun, H., & Iwanaga C., 1972, Ber. Bunsen-Gesellschaft Phys. Chem., 76, 1176

Ohta, N., & Baba, H., 1986, Mol. Phys., 59 921

O'keefe, A., & Deacon, D.A.G., 1988, Rev. Sci. Inst., 59, 2544

Parker, D.S.N., Minns, R.S., Penfold, T.J., Worth, G.A., & Fielding, H.H., 2009, Chem. Phys. Let., 469, 43

Pino, T., Boudin, N., & Bréchignac, P., 1999, J. Chem. Phys., 111, 7337

Puget, J.L., & Léger, A., 1989, ARA&A, 27, 161

Quack, M., 1990, Ann. Rev. Phys. Chem., 41, 839

Reilly, N.J., Schmidt, T.W., & Kable, S.H., 2006, J. Phys. Chem. A, 110, 12355

Reilly, N.J., D.L., Kokkin, Nakajima, M., *et al.*, 2008, J. Amer. Chem. Soc., 130, 3137

Romanini, D., Biennier, L., & Salama, F., 1999, Chem. Phys. Lett., 303, 165

Rouillé, G., Steglich, M., Huisken, F., Henning, Th., & Mullen, K., 2009, J. Chem. Phys., 131, 204311

Salama, F., 2007, "Molecules in Space and Laboratory", ed. J.L. Lemaire and F. Combes, Paris

Sarre, P.J., 2006, J. Mol. Spectrosc., 238, 1

Sebree, J.A., Kislov, V.V., Mebel, A.M., & Zwier, T.S., 2010, J. Phys. Chem. A, 114, 6255

Sellgren, K., Werner, M.W., Ingalls, J.G., *et al.*, 2010, ApJ, 722, L54

Semba, Y., Yoshida, K., Kasahara, S., *et al.*, 2009, J. Chem. Phys., 131, 024303

Sharp, R.G., Reilly, N.J., Kable, S.H., & Schmidt, T.W., 2006, ApJ, 639, 194

Siebrand, W., 1967, J. Chem. Phys., 46, 440

Simpson, C.D., Diedrich Brand, J., Berresheim, A.J., *et al.*, 2002, Chem. Eur. J., 8, 1424

Steglich, M., Jäger, C., Rouillé, G., *et al.*, 2010, ApJ, 712, L16

Stolow, A., Bragg, A.E., & Neumark, D.M., 2004, Chem. Rev., 104, 1719

Stolow, A., & Underwood, J.G., 2008, Adv. Chem. Phys., 139, 497

Suto, M., Wang, X.Y., Shan, J., & Lee, L.C., 1992, J. Quant. Spec. Rad. Trans., 48, 79

Tokmachev, A.M., Boggio-Pasqua, M., Mendive-Tapia, D., Bearpark, M.J., & Robb, M.A., 2010, J. Chem. Phys., 132, 044306

Troy, T.P., O'Connor, G., Chalyavi, N., Nauta, K., & Schmidt, T.W., in preparation

Troy, T.P., Nakajima, M., Chalyavi, N., *et al.*, 2009, J. Phys. Chem. A, 113, 10279

Tschurle, M., & Boesl, U., 2006, Int. J. Mass Spec., 249, 364

Useli-Bacchitta, F., Bonnamy, A., Mulas, G., *et al.*, 2010, Chem. Phys., 371, 16

Yarkony, D.R., 2001, J. Phys. Chem. A, 105, 6277

Yoshida, K., Semba, Y., Kasahara, S., Yamanaka, T., & Baba, M., 2009, J. Chem. Phys., 130, 194304