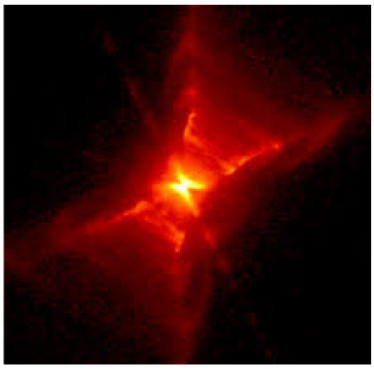
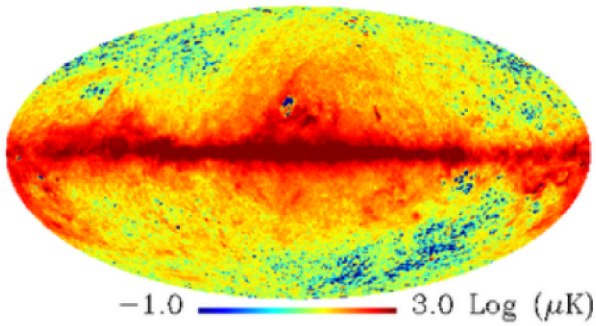
AstroPAH

A Newsletter on Astronomical PAHs

Issue 25 | February 2016

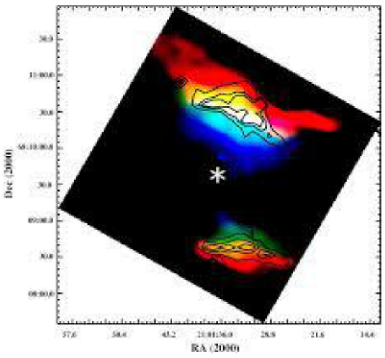




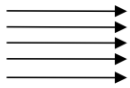
[A] Vibrational emission (contributing to AIBs)

[B] Rotational emission
AME

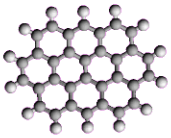
emission



[C] Fluorescence and
Phosphorescence
(contributing to BL and ERE)

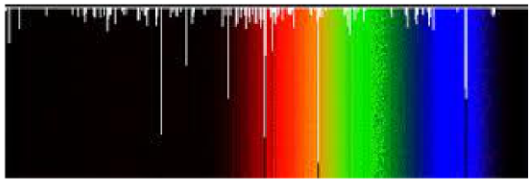


Radiation field

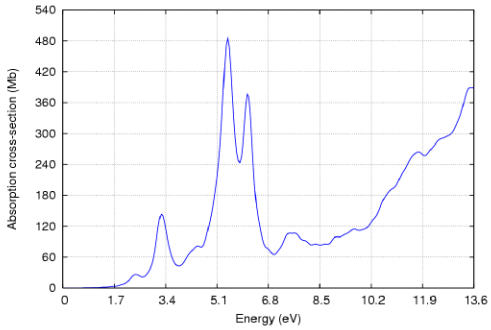


absorption

[D] Discrete absorptions in
the visible (contributing to DIBs)



[E] Broad bands in the UV
(contributing to UV extinction
bump and non-linear rise)



Modelling PAH Spectra

Editorial

Dear Colleagues,

Welcome to the first AstroPAH newsletter of 2016! The year started well with the scientific world being shaken by gravitational waves!

In this issue of AstroPAH, we are pleased to present an In Focus on modelling PAH spectral features, where Giacomo Mulas, Giuliano Malloci, and Christine Joblin describe what modelling has to offer to bridge the gap between laboratory, theoretical and observational studies. This topic is highlighted also in our Picture of the Month.

This month, the papers in the Abstract section report the simulation of pyrene spectra in water matrices, recent experimental results on the desorption of benzene from water ice surfaces, studies on the formation of pentalene, PAHs and nitrogen-substituted PAHs following various chemical paths, and experimental and theoretical study of the photoionization and photodissociation of toluene by soft X-rays in circumstellar environments.

The Announcements section advertises one postdoctoral and two faculty positions in amazing places like Hawaii and Chile.

If you enjoy social networks, connect to other scientists interested on carbonaceous molecules in space through Facebook. More information also in the Announcements section.

The Editorial Team

Next issue: 15 March 2016.
Submission deadline: 4 March 2016.

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PAH Picture of the Month

A schematic view on the role PAH molecules have to explain different astronomical phenomena. From top to bottom: the Aromatic Infrared Band dominating the IR emission of the Red Rectangle; the Anomalous Microwave Emission (AME) as seen by Planck at 22.8 GHz; the Extended Red Emission (ERE, contours) compared to the PAH (green, blue) and very small grain (red) emission in NGC 7023; the Diffuse Interstellar Bands. See the In Focus for more details
Credits: Montage by A. Candian (Leiden Observatory, Netherlands) **Credits for individual figures:**[A] The Red Rectangle Nebula - Raghvendra Sahai (NASA/JPL, USA). [B] AME foreground map - S. von Hausegger & H. Liu, arXiv:1507.05171. [C] ERE map - Berné et al. (2008), A&A 479, L41. [D] Diffuse Interstellar Bands - P. Jenniskens & F.-X. Desert. [E] Photoabsorption cross-section of a typical PAH - Cecchi-Pestellini et al. (2008), A&A 486, L25

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Background image: NASA, ESA, and the Hubble Heritage Team (STScI/AURA)

Modelling PAH features in space

by Giacomo Mulas, Giuliano Malloci, and Christine Joblin

The basic picture

All astronomers know that Polycyclic Aromatic Hydrocarbons (PAHs) have been observed everywhere, in our and in other galaxies, out to cosmological distances. Yet, the characteristic infrared (IR) emission spectrum that we assign to "PAH" is still not attributed to specific species. One of the difficulties in analysing this spectrum is that we do not have yet catalogues of laboratory spectra of the infrared emission of isolated PAHs excited by UV radiation, which would be directly comparable to astronomical observations. In this subject, modelling is crucial to bridge the gap between what laboratory measurements and theoretical calculations can currently provide about PAHs and what astronomy can observe.

In the astronomical PAH model, PAHs are supposed to absorb mainly UV and visible photons, with rates ranging from about once per week in the diffuse ISM (for a PAH size about like that of ovalene, $C_{32}H_{14}$) to about once per hour in a bright photodissociation region (PDR) with a photon density four orders of magnitude larger. The absorption of a single photon brings the molecule from its ground electronic state to an excited electronic state. From there, it can relax in several ways: by emitting an electron, if the excitation energy is sufficient; it can undergo a series of radiationless transitions, traversing conical intersections, to vibrationally highly excited states of lower electronic states; or it can undergo a radiative transition, thereby emitting some of its energy via electronic fluorescence or phosphorescence. Once in a highly excited vibrational state of the ground electronic state, fast intramolecular transitions maintain the molecule in an ergodic state, with equal probability of being in any state compatible to its energy and angular momentum. From there, it can either fragment, if enough energy is localised on a bond to break it, or relax radiatively via delayed (so-called Poincaré) fluorescence and/or via vibrational transitions (infrared cooling). Some of the vibrational transitions are at very nearly the same wavelengths for all PAHs and therefore pile up, yielding the observable Aromatic Infrared Bands (AIBs). Collisions are usually much less frequent than UV-Visible photon absorption events;

therefore collisional de-excitation is by and large negligible. In the simplest approximation, one assumes that all absorbed energy goes irreversibly into populating vibrational levels, and gets entirely reemitted in vibrational transitions. In a way, in this simple approximation, one considers a PAH as a nanoscopic pebble that is heated by very diluted sunlight (in discrete ”chunks”, since each single photon heats it substantially, the so-called ”stochastic heating” producing random temperature spikes), first reaches internal thermal equilibrium and then cools down by thermal emission.

Given its isolated conditions, in all but the most intense radiation fields it will relax all the way down to its vibrational ground state, or very close to it. Its thermal emission spectrum can be obtained by the Kirchoffs law if its absorption spectrum at the same temperature is known. One therefore integrates this over the cooling curve, and thus estimates in this simple-, approximated way the IR emission spectrum of a PAH, provided one knows its electronic photo-absorption spectrum (to know how it absorbs), its vibrational absorption spectrum at all relevant temperatures (to know how it emits), and its T-dependent heat capacity.

The electronic photo-absorption spectrum of cold PAHs can be measured or estimated via standard theoretical methods (e.g. Time-Dependent Density Functional Theory (TD-DFT)) with acceptable accuracy (as far as energetic balance and IR emission are concerned) with reasonable computational costs for PAHs containing up to a little over 100 C atoms; and such data are nowadays available for an increasingly number of molecules through public databases. Similarly, the vibrational absorption spectra of PAHs of similar sizes at 0 K, in the harmonic approximation, can nowadays be routinely, and relatively cheaply, computed using standard techniques (DFT); and several databases are now available[1,2]. Considerable datasets of experimental absorption spectra at low temperatures are also available, which allow the gauging empirical correction factors to vibrational frequencies to account for the neglected anharmonicity. Much less laboratory data is also available at high T, which together with molecular dynamics simulations enable us to see the variations with temperature, mainly a T-proportional shift in frequency and broadening of the bands. Very few fully quantum calculations of fully anharmonic vibrational spectra of PAHs at 0 K and even less at high T are available, even if there are promising advancements in this direction. In any case, putting together the already available pieces one can obtain a rough quantitative estimate of the T-dependent spectrum of a PAH from the theoretical harmonic one. The T-dependent vibrational heat capacity can be derived in the harmonic approximation provided one knows all vibrational frequencies (including IR-inactive ones). One can thus produce in this way synthetic emission spectra of all individual PAHs for which all these ingredients are known, and their mixtures, under well-defined irradiation conditions, such as well-studied PDRs.

This procedure is applicable for all PAHs for which available online databases provide all the required ingredients, and the inventory of species included is steadily being extended to more PAHs and PAH derivatives (e.g. nitrogenated PAHs, superhydrogenated or dehydrogenated PAHs, PAHs with aliphatic side groups, deuterated PAHs and so on). Some of the useful databases already offer, or are in the process of getting ready to offer, their data via computer friendly interfaces like VAMDC[3], that can be queried in real time to obtain easily parsable results, so that models can always automatically use the most up to date version of the available spectral information with no need on the user’s part to manually check if new data became

available. Ultimately, one would like to be able to interpret spatial variations in the AIB spectrum within a given object and in general, differences among different ”types” of AIB spectra, e.g. with characteristically different widths, relative intensities and peak positions of some bands, to changes in PAH chemical composition, size distribution, excitation and charge states. It is not yet possible to interpret these changes in a precise way.

Models including ionisation and hydrogenation equilibrium

However, while such ”simple” models are now the baseline for whatever sensible interpretation of observed AIBs, or conversely to predict observable features of some specific PAH or PAH derivatives species or groups, a more complete modelling is needed if one wants to identify individual species, or to bring forward our understanding of PAHs in the more complete ”big picture” of interstellar physics and chemistry.

One approximation we need to overcome is that of assuming that all the energy absorbed via electronic transitions is simply, and completely, re-radiated via infrared cooling, and thus consider other relaxation channels, including ionisation, fragmentation, and electronic Poincaré fluorescence. All of these channels are in competition with vibrational relaxation, and should be studied simultaneously. The ionisation yield has been measured for a small number of species, but is known to be relatively small when the energy of the absorbed photon is only slightly above the ionisation threshold, and to increase up to almost unity a few eV above it. Few measurements of the electron recombination efficiency of PAH ions, especially with cold electrons, are also available. Laboratory studies of the photofragmentation of PAHs show that they can lose sidegroups (if present), hydrogen, C_2H_2, etc., if enough energy is available in a single bond. They also show that once a PAH has been completely, or almost completely, dehydrogenated, it then proceeds to further fragment, progressively destroying its carbon skeleton which may then isomerise to some more stable carbon cluster before being completely dissociated. Photofragmentation in PAHs proceeds in direct competition with radiative cooling, including delayed electronic fluorescence (whose importance increases with excitation energy), when most or all absorbed energy has been converted into vibrational energy in the electronic ground state. Experimental measurements, together with supporting quantum chemistry (e.g. dissociation channels, dissociation energies, transition points and barriers via DFT) and reactive molecular dynamics calculations, provide us with energy-dependent fragmentation rates. Putting together vibrational cooling rates, photoionisation yields, electron recombination rates, fragmentation rates, H attachment rates and the photoabsorption cross-sections, one can model the ionisation and hydrogenation balance of PAHs in a given environment. The results of this kind of modelling provide a sound understanding of the changes one observes in spatially resolved IR spectra of PDRs, where going from the bright dense PDR at the border of the molecular cloud towards the exciting young star, one observes first the spectrum of neutral PAHs, then that of cations, finally that of the very photostable species C_{60}/$C_{60}^{+[4,5]}$.

Linking PAH fluorescence/phosphorescence to AIBs

Electronic relaxation may happen immediately following a photon absorption event, in competition with the sequence of non-radiative transitions that in most cases gets the molecule, through a series of conical intersections, all the way to a highly vibrationally excited state of the ground electronic energy level. However, even after this happens, the molecule is in an ergodic state, where all states at the same energy and the same angular momentum are equally likely to be populated, including electronic excited states, making possible the delayed Poincaré fluorescence.

"Prompt" fluorescence is not very important to model PAH energetics: laboratory studies show that this is mostly relevant for neutral PAHs, possibly for doubly ionised ones, for which no specific studies are available, and almost completely negligible for PAH cations, for which radiationless relaxation to the ground electronic state appears to be extremely fast. Delayed fluorescence is important if high levels of excitation are possible, and in this case, as seen above, it can effectively compete with fragmentation. Such high excitations may occur if either very high-energy photons are sufficiently abundant or photon densities are high enough to make it sufficiently likely for a molecule to absorb additional photons when it still has some energy left from the previous absorption event.

In any case, being able to account for the emission from excited electronic states enables us to connect directly observations of the aromatic vibrational bands with other features such as the Blue Luminescence (BL) and the Extended Red Emission (ERE). Actually, if PAHs are producing the AIBs, they must be simultaneously contributing to some extent to the BL and the ERE. Indeed some specific neutral PAHs were proposed as carriers of the BL by its discoverers. And in that case, since energy-dependent laboratory measurements of the fluorescence and phosphorescence of those specific molecules were available, detailed modelling showed that those same molecules, if producing the observed BL, would also produce some specific IR bands well above the detection threshold of existing ISO observations of the same source, which failed to observe them[6].

Modelling PAH emission in the far infrared bands

Most of the astronomical studies on PAHs focus on their most prominent, most easily observed vibrational bands in the mid-IR. They are so bright because they involve either single bonds or small groups of bonds, and therefore are at very nearly the same wavelengths for all PAHs, whose individual emission thereby stacks up producing very high overall fluxes. However, in their cooling sequence, PAHs must radiate in **all** the IR-active bands, including the ones at lower frequency which are species-specific and change for every PAH, offering an attractive possibility to identify individual ones. But while the simple "extra-small pebble" emission model with a PAH in internal thermal equilibrium emission works well when the molecule is "hot" enough, which is the case when it emits in the higher energy modes, it breaks down at some point in the cooling sequence. The rate of intramolecular transitions maintaining internal thermal equilibrium decreases roughly proportionally with the density of vibrational scales, ex-

tremely steeply with excitation energy. Thus, at some point of the cooling sequence, internal redistribution suddenly becomes much slower than radiative transitions, so that thermal equilibrium breaks. The number of vibrational quanta in each vibrational mode is then frozen and all the remaining vibrational quanta in all accessible vibrational modes have no other way out but to be emitted, in IR-active or even IR-inactive transitions, unless something else happens, like the absorption of another photon. In a dilute radiation field, this means that the expected relative intensity of the bands emitted when the molecule is out of internal thermal equilibrium does not depend on their relative IR-activity, but only on the statistics governing their population near the decoupling energy. This can be properly accounted for by abandoning the thermal (macrocanonical) emission model in favour of a Monte Carlo (microcanonical) model. This was the approach with which the intensities of PAH emission in the far-IR was modelled[7], in the hope, thus far frustrated, to detect some individual such bands in Herschel observations of sources bright in the mid-IR PAH features but with a relatively low dust emission continuum, to reduce background and increase spectral contrast.

Modelling spectral band shapes

Furthermore, individual far-IR bands emitted by relatively cold PAHs would also show rotational structure, be it resolved or just a rotational envelope. The spectral shape of these bands is crucial for their spectral contrast, and therefore for their detectability. However, the rotation of an isolated PAH in space is very far from thermal equilibrium. Which is unfortunate, because if it were, it would be extremely cold, resulting in extremely sharp bands, easily detectable. Instead, rotation is driven by the exchange of angular momentum by the numerous photons emitted during the vibrational cooling sequences, and by internal radiationless transitions which, under internal thermal equilibrium conditions, brings the population of rotational levels at each J (total angular momentum) in thermal equilibrium with the thermal bath of the vibrational states. Then, in each cooling sequence, with decreasing energy, since also the Coriolis coupling terms that bring about the rotation-vibration thermal equilibrium scale with the density of vibrational states, at some point the rotational levels decouple. From that moment on, the population of rotational states is frozen and changes only via radiative transitions. Monte Carlo modelling can also account for the population of rotational states, and thereby produce at least a crude estimate, in the rigid or semi-rigid rotor approximation, of the rotational structures of individual vibrational bands. It turns out that for far-IR PAH bands the best spectral contrast would be provided by the sharp Q branches of the bands that have them, depending on their symmetry[8]. It becomes therefore important to be able to model in a quantitative way how sharp these Q branches would actually be. PAHs are typically rigid enough to make very small the broadening of Q branches due to centrifugal distortion, with the rotational populations resulting from the Monte Carlo simulations. Therefore, the main source of band broadening is vibrational anharmonicity. Indeed, as long as the modes are coupled, photons in the vibrational cooling sequence of an isolated PAH are not emitted in fundamental transitions, but are hot bands, they are not from the first excited state in one mode and the ground state. This means that they are slightly displaced with respect to the position of the fundamental transition, with the displacement depending on the detailed population of all vibrational states at the moment of the transition. Modelling this requires first the knowledge of the detailed anharmonic vibrational structure of the molecule

under study, as a function of the excitation energy. Unfortunately this is rather demanding, especially since large molecules like PAHs, with many vibrational modes clustering at characteristic frequencies, create a large number of Fermi and Darling-Dennyson resonances making the anharmonic analysis cumbersome even for not very large species. When these data are available, Monte Carlo models can relatively easily include them, resulting in the prediction of the detailed ro-vibrational structure of individual bands of individual molecules. This was indeed also done for the case mentioned above of testing the tentative attribution of the BL to specific small, neutral PAHs, to assess the observability of their predicted infrared bands.

Modelling PAH rotation, PAH radio emission and DIB structure

As another application of PAH modelling, one should consider the hypothesis of PAHs as carriers of the Diffuse Interstellar Bands (DIBs) in absorption in the visible. In this hypothesis, some DIBs would be caused by electronic transitions of individual PAHs. Indeed PAHs may have permitted transitions in the visible, even if usually much weaker than their $\pi \rightarrow \pi^*$ resonances in the UV, if they are either neutral and very big or ionised. While all laboratory studies so far showed that PAH cations have very broad bands, due to their extremely fast non-radiative transition relaxation to lower electronic states, large, neutral PAHs do show clearly distinguishable rotational envelopes. The same Monte Carlo modelling that can account for the population of rotational states of PAHs when emitting infrared photons, can also account for the population of rotational states when the molecule absorbs a visible photon from the electronic ground state, as is the case for DIBs. If one knows the rotational constants of the ground and excited electronic states involved, which can both be obtained from quantum chemistry calculations or derived from laboratory measurements, then it is possible to predict the rotational envelope of the transition in a given environment in space, and compare it with observed DIB profiles, offering a powerful test to confirm an identification or reject it[9].

Again linked with the population of rotational levels, we may consider the pure rotational emission of PAHs with a permanent dipole moment. While pure rotational transitions in PAHs with even a relatively large dipole moment, are so rare to have negligible effects on the population of rotational levels, they can be predicted by the same Monte Carlo modelling used above to predict the rotational envelopes of PAHs producing DIBs. If high quality rotational parameters are known for a PAH, enabling one to know the precise position of its rotational lines, Monte Carlo modelling can predict the emission intensities to attach to each of them, as a function of the column density of the given PAH. This was used for example to put upper limits on the column density of corannulene in the Red Rectangle[10].

Concluding remarks

Summing up, **modelling has much to offer to the study of PAHs in astronomy, and promises to do more, in bridging the gap between what can be measured in the laboratory or computed by theory, and what is observed in astronomical environments.** This is

especially true for processes that are extremely hard to reproduce in laboratory, such as e.g. the population of rotational states in an isolated molecule driven by a diluted series of visible-UV photon absorption events followed by vibrational cooling all the way down to the ground state. **Modelling is clearly crucial to link together, in a unified picture, all the several distinct observable features that a PAH, if present, must simultaneously have, possibly in different wavelength ranges, such as e.g. electronic fluorescence/phosphorescence (contributing to the BL and ERE) and absorption (contributing to DIBs) in the visible, emission in the infrared, rotational profiles, and so on, as illustrated in Figure 1.**

The key to the success of such modelling lies fundamentally in the increasingly easy accessibility of good modelling ”ingredients”, especially from large, publicly available online databases. Its main current limitation is conversely the lack of ”ingredients” which are difficult to come by, such as e.g. detailed anharmonic vibrational analysis of large PAHs at high temperatures, ionisation yields and electron recombination rates, etc.: **give us better ingredients, we will cook you a better model.**

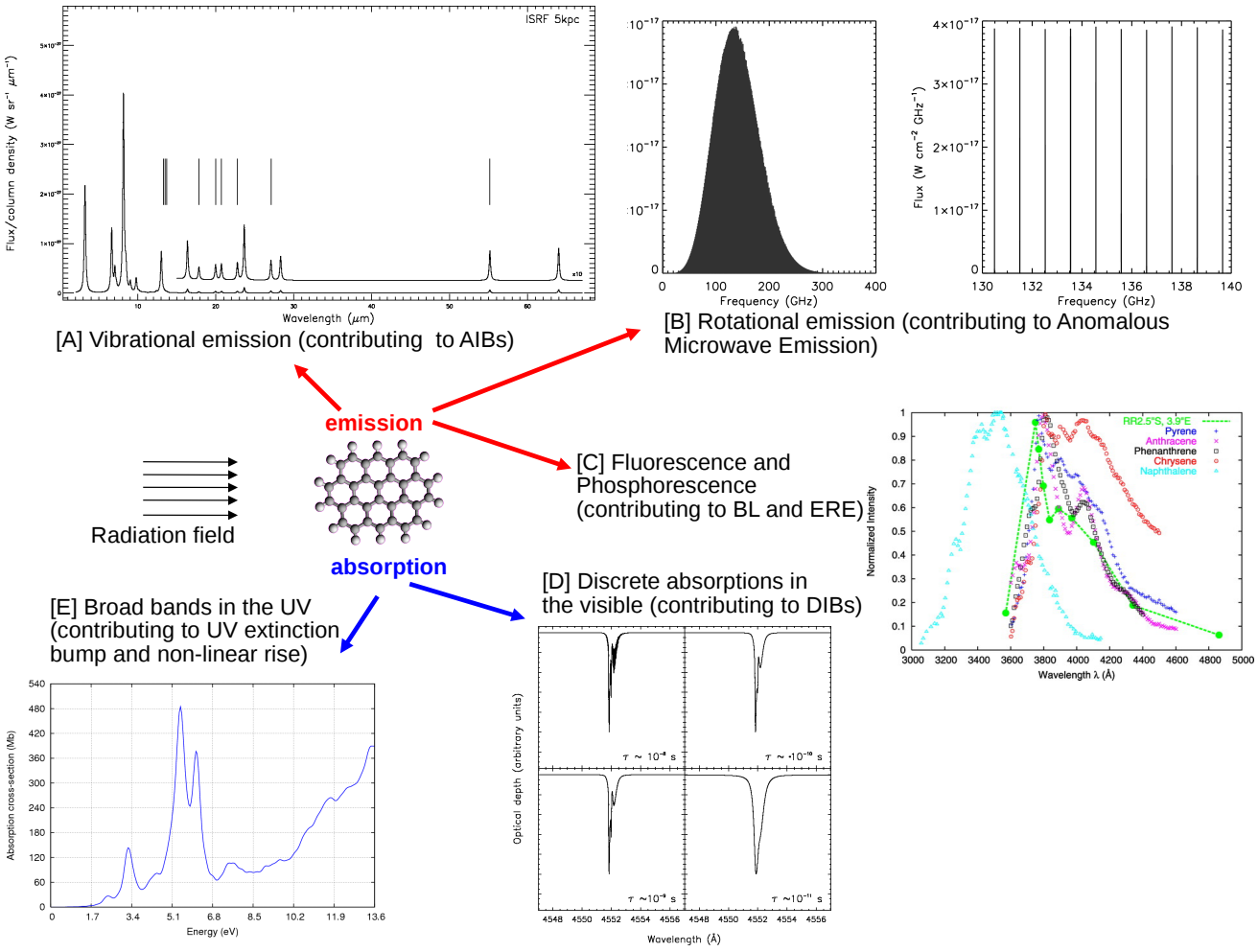

Figure 1 - *Linking the spectral features from PAHs in space. References:* ***[A]*** *Mulas et al. (2006) A&A 460, 93,* ***[B]*** *Pilleri et al. (2009) MNRAS 397, 1053,* ***[C]*** *Vijh et al. (2004) ApJ 606, L65* ***[D]*** *Malloci et al. (2003), A&A 410, 623,* ***[E]*** *Cecchi-Pestellini et al. (2008), A&A 486, L25.*

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Abstracts

Low temperature formation of nitrogen-substituted polycyclic aromatic hydrocarbons (PANHs) – barrierless routes to dihydro(iso)quinolines

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Meteorites contain bio-relevant molecules such as vitamins and nucleobases, which consist of aromatic structures with embedded nitrogen atoms. Questions remain over the chemical mechanisms responsible for the formation of nitrogen-substituted polycyclic aromatic hydrocarbons (PANHs) in extraterrestrial environments. By exploiting single collision conditions, we show that a radical mediated bimolecular collision between pyridyl radicals and 1,3-butadiene in the gas phase forms nitrogen-substituted polycyclic aromatic hydrocarbons (PANHs) 1,4-dihydroquinoline and to a minor amount 1,4-dihydroisoquinoline. The reaction proceeds through the formation of a van der Waals complex, which circumnavigates the entrance barrier implying it can operate at very low kinetic energy and therefore at low temperatures of 10 K as present in cold molecular clouds such as TMC-1. The discovery of facile de facto barrierless exoergic reaction mechanisms leading to PANH formation could play an important role in providing a population of aromatic structures upon which further photo-processing of ice condensates could occur to form nucleobases.

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Efficient electron-promoted desorption of benzene from water ice surfaces

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Desorption of benzene (C_6H_6) from solid water surfaces [compact amorphous solid water (c-ASW) and crystalline ice (CI)] during irradiation of ultrathin solid films with low energy (250-300 eV) electrons has been investigated. The observed desorption behaviour is complex but typically two desorption components, with particularly large cross-sections, were present in the observed signal. A fast component, with a cross-section up to 10^{-15} cm^2, is attributed to desorption of isolated C_6H_6 molecules that are hydrogen-bonded to small clusters of water (H_2O) molecules on the solid water surface. A slower component, with a cross-section of *ca.* 10^{-17} cm^2, is attributed mainly to desorption from larger C_6H_6 islands on the solid water surface. Possible desorption mechanisms are proposed and astrophysical implications are discussed.

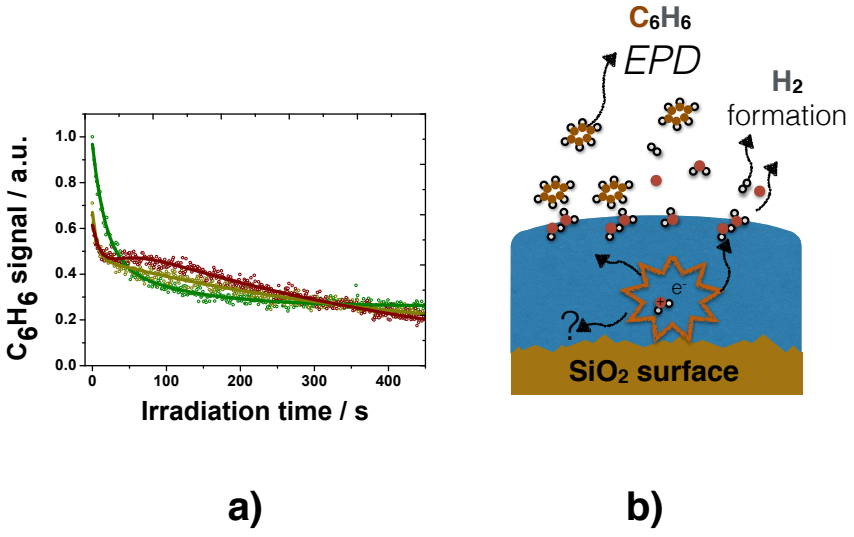

Figure 1: **a)** C_6H_6 EPD signal obtained for 5 L of C_6H_6 on H_2O ice. H_2O condensed at 110 K results in a compact amorphous film (c-ASW, in green), annealing this to 138 K allows the formation of a film partially crystalline (PCI, in dark yellow), while higher deposition temperatures (153 K) form a crystalline film (CI, in wine). Irradiation was conducted with 250 eV electrons and initial beam current of 180 nA. Fitted curves are displayed in full lines, while experimental points in open circles. A bi-exponential function was used for desorption traces from c-ASW and PCI, while a multi-exponential function best describes the remaining curve. **b)** Cartoon representing the formation of excitons in the solid H_2O bulk during electron irradiation and their migration to the vacuum interface leading to C_6H_6 desorption and H_2 formation.

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Laboratory Astrochemistry: Catalytic Conversion of Acetylene to Polycyclic Aromatic Hydrocarbons over SiC Grains

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Catalytic conversion reactions of acetylene on a solid SiC grain surface lead to the formation of polycyclic aromatic hydrocarbons (PAHs) and are expected to mimic chemical processes in certain astrophysical environments. Gas-phase PAHs and intermediates were detected in situ using time-of-flight mass spectrometry, and their formation was confirmed using GC-MS in a separate experiment by flowing acetylene gas through a fixed-bed reactor. Activation of acetylene correlated closely with the dangling bonds on the SiC surface which interact with and break the C-C PI bond. Addition of acetylene to the resulting radical site forms a surface ring structure which desorbs from the surface. The results of HRTEM and TG indicate that soot and graphene formation on the SiC surface depends strongly on reaction temperature. We propose that PAHs as seen through the UIR emission bands can be formed through decomposition of graphene-like material, formed on the surface of SiC grains in carbon-rich circumstellar envelopes.

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http://www.chemistry.hku.hk/download/Chem(201602)share/SiCpaperAR.pdf

Ab initio simulation of pyrene spectra in water matrices

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The absorption and emission spectra of free pyrene and pyrene in a water ice matrix were simulated ab initio. Water ice was mimicked by a large cluster of explicit water molecules. The optimum geometries of the ground and excited states, vibrational frequencies, and normal modes were calculated using DFT. The transition energies were calculated by XMCQDPT/CASSCF. Ab initio time-dependent Franck-Condon (FC) and time-independent Franck-Condon and Herzberg-Teller (FCHT) approximations were used for the vibronic profiles of the spectra. The absorption spectra of the free molecule and the molecule in the water cluster are well reproduced within the FC approximation. The fluorescence spectrum of the gas-phase pyrene cannot be satisfactorily reproduced within pure FC or within the FCHT approximation. However,

the fluorescence spectrum of pyrene in the water cluster is satisfactorily reproduced within the FC approximation. Both absorption and emission spectra of pyrene in the water cluster are broadened due to the translations and torques of pyrene in the solvent cage even at low temperatures. This broad but well structured spectrum shape should be taken into account in the identification of PAHs in cometary ice.

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Spectroscopic evidence for the formation of pentalene$^+$ in the dissociative ionization of naphthalene

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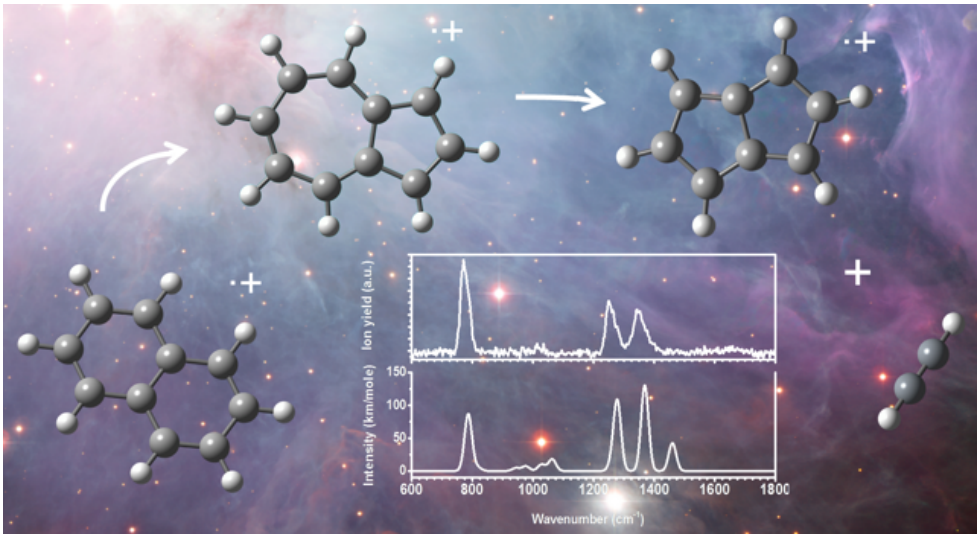

Figure 2

Although acetylene loss is well known to constitute the main breakdown pathway of polycyclic aromatic hydrocarbon (PAH) species, the molecular structure of the dissociation products remains only poorly characterized. For instance, the structure of the C_8H_6 product ion formed upon acetylene loss from the smallest PAH naphthalene ($C_{10}H_8$) has not been experimentally established. Several $C_8H_6^+$ isomers are conceivable, including phenylacetylene, benzocyclobutadiene, pentalene as well as a number of a-cyclic products. Here we present infrared (IR) spectroscopic evidence for the formation of the (anti-aromatic) pentalene structure using a com-

bination of tandem mass spectrometery and IR laser spectroscopy. The formation of pentalene is suggestive of facile 6- to 5-membered ring conversion, which possibly has implications for the PAH/fullerene interrelationship in energetic settings such as the interstellar medium and combustion environments.

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Single and Double Photoionization and Photodissociation of Toluene by Soft X-rays in Circumstellar Environment

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The formation of polycyclic aromatic hydrocarbons (PAHs) and their methyl derivatives occurs mainly in the dust shells of asymptotic giant branch (AGB) stars. The bands at 3.3 and 3.4 μm, observed in infrared emission spectra of several objects, are attributed C-H vibrational modes in aromatic and aliphatic structures, respectively. In general, the feature at 3.3 μm is more intense than the 3.4 m. Photoionization and photodissociation processes of toluene, the precursor of methylated PAHs, were studied using synchrotron radiation at soft X-ray energies around the carbon K edge with time-of-flight mass spectrometry. Partial ion yields of a large number of ionic fragments were extracted from single and 2D-spectra, where electron-ion coincidences have revealed the doubly charged parent-molecule and several doubly charged fragments containing seven carbon atoms with considerable abundance. *Ab initio* calculations based on density functional theory were performed to elucidate the chemical structure of these stable dicationic species. The survival of the dications subjected to hard inner shell ionization suggests that they could be observed in the interstellar medium, especially in regions where PAHs are detected. The ionization and destruction of toluene induced by X-rays were examined in the T Dra conditions, a carbon-rich AGB star. In this context, a minimum photodissociation radius and the half-life of toluene subjected to the incidence of the soft X-ray flux emitted from a companion white dwarf star were determined.

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ApJ 2016, in press

http://arxiv.org/abs/1601.06856

Announcements

Postdoctoral position at the University of Hawai'i at Manoa

Advertised by Prof. Ralf Kaiser

The Reaction Dynamics Group, Department of Chemistry, University of Hawai'i at Manoa, invites applications for a postdoctoral position in the area of reaction dynamics and combustion chemistry. The prime directive of the experimental studies is to investigate the formation of polycyclic aromatic hydrocarbons (PAHs) in combustion systems exploiting crossed molecular beams along with mass spectrometry (QMS; ReTOF) and ion imaging (Hawaii) and a pyrolytic micro reactor (Advanced Light Source, Lawrence Berkeley Laboratory). The appointment period is initially for one year, but can be renewed annually based on availability of funds and satisfactory progress. The salary is competitive and commensurate with experience. Successful applicants should have a strong background in one or more of the following: experimental reaction dynamics, molecular beams, combustion chemistry, UHV technology, pulsed laser systems. Solid communication skills in English (written, oral), a publication record in internationally circulated, peer-reviewed journals, and willingness to work in a team are mandatory. Only self-motivated and energetic candidates are encouraged to apply. Please send a letter of interest, three letters of recommendation, CV, and publication list to Prof. Ralf I. Kaiser (contact information below). A description of our current research group can be found at http://www.chem.hawaii.edu/Bil301/welcome.html.

The review of applications will start February 7, 2016, and it will continue until the position is filled.

Contact: Prof. Ralf Kaiser
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Honolulu, HI 96822-2275, USA
E-mail: ralfk@hawaii.edu

Two Faculty Positions in Astrophysics at Instituto de Astrofisica de Atacama, Copiapo (Chile)

Advertised by Mauro Barbieri

Application deadline: 18 March 2016 (positions will remain open until filled).

The Instituto de Astrofisica de Atacama (IAA) at the Universidad De Atacama (UDA) in Copiapo (Chile) invites applications for two faculty positions to join the IAA team. The successful candidates will join a group of five faculty working on a broad range of research topics and will have access to the Chilean Time in a broad array of facilities, including ALMA, VLT, Gemini, Magellan, LSST, GMT and the E-ELT.

We are particularly interested in candidates with strong experience in one or more of these fields:

- Origin, structure and evolution of planets, satellites, and minor bodies in the Solar System;
- Extrasolar Planets;
- Formation, structure and evolution of stars;
- Milky Way: stellar populations, star clusters, variable stars, galactic structure;
- Terrestrial Mars analogs;
- Astrobiology.

The positions carry teaching duties in astronomy at the undergraduate level, with a load of 6h per week. The working language is English. While knowledge of Spanish is not required (teaching can be done in English), the successful candidates are expected to teach in Spanish within two years. The appointment at UDA will be for three years, with a first probation year, and the position is further extendable subject to performance.

Applicants should have a PhD in astronomy or physics or related sciences completed at least 3 years prior to the starting day of the contract.

To receive full consideration, applications must be sent by Friday 18 of March 2016, although the positions will remain open until filled. Start date is expected to be October 2016.

Applications must be submitted by e-mail to Mauro Barbieri (mauro.barbieri@uda.cl), and they should include:

1. Cover letter
2. Curriculum Vitae

3. List of publications
4. Statement of recent research achievements (max. 2 pages)
5. An outline of future research (min. 2 pages, max. 10 pages)
6. The contact details of three referees (one needs to be the last employer, the others needs to be aware of the recent work of the candidate).

Questions may be addressed to the e-mail address below.
E-mail: mauro.barbieri@uda.cl

Relevant links:

Universidad de Atacama
http://www.uda.cl

Instituto de Astrofisica de Atacama
https://sites.google.com/site/grupoastrouda

Convocatoria Programa de Insercion de Investigadores en la UDA
http://www.vrip.uda.cl/frontend/noticia_completa/104

Webpage: http://eas.unige.ch/jobs.jsp?id=671

New Facebook group : ”Carbonaceous molecules in space”

Social networks play in increasing role in the communication and discussion of scientific results. At the initiative of O. Berné, J. Bouwman and A. Candian a new Facebook page has been created on the topic of carbonaceous molecules in space. This group is aimed at scientists interested in Polycyclic Aromatic Hydrocarbons, Carbon chains, Hydrocarbons, Fullerenes etc. in space, from the laboratory, theoretical and observational point of view. Recently published papers can be advertised there as well as conference announcements and photos, jobs etc. The group is opened to any professional interested in the field.

You can find the group’s page there:
https://www.facebook.com/groups/1009413999125549/?fref=ts

AstroPAH Newsletter

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astropah@strw.leidenuniv.nl

Next issue: 15 March 2016
Submission deadline: 4 March 2016