

# PAHs in Astronomy - A Review

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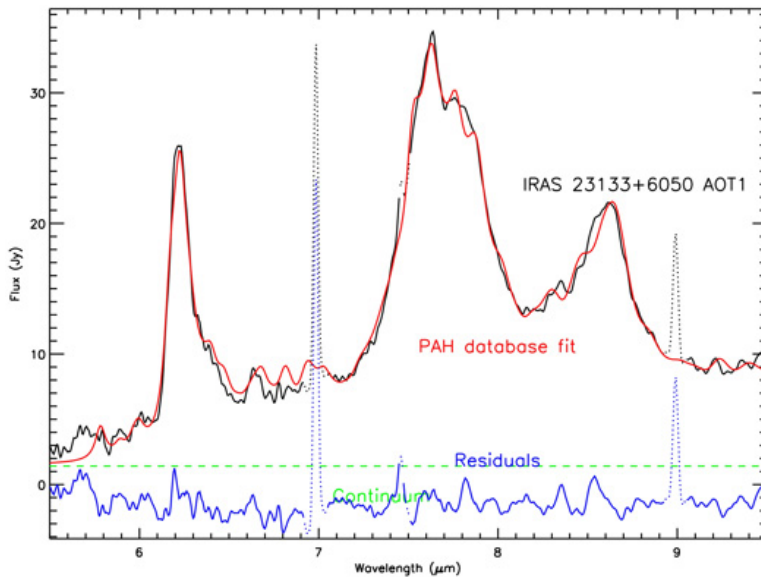
**Abstract.** Carbonaceous materials play an important role in space. Polycyclic Aromatic Hydrocarbons (PAHs) are a ubiquitous component of organic matter in space. Their contribution is invoked in a broad spectrum of astronomical observations that range from the ultraviolet to the far-infrared and cover a wide variety of objects and environments from meteorites and interplanetary dust particles to outer Solar System bodies to the interstellar medium in the local Milky Way and in other galaxies. Extensive efforts have been devoted in the past two decades to experimental, theoretical, and observational studies of PAHs. A brief review is given here of the evidence obtained so far for the contribution of PAHs to the phenomena aforementioned. An attempt is made to distinguish the cases where solid evidence is available from cases where reasonable assumptions can be made to the cases where the presence - or the absence - of PAHs is purely speculative at this point.

**Keywords.** Infrared: ISM, ultraviolet: ISM, ISM: molecules, ISM: dust, extinction, methods: laboratory, techniques: spectroscopic, line: identification, line: profiles, surveys, molecular data

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## 1. Overview

Carbon molecules and ions play an important role in space. Polycyclic Aromatic Hydrocarbons (PAHs) are an important and ubiquitous component of the organic materials. Twenty years have passed since the PAH model was put forward to account for the ubiquitous infrared (IR) emission bands associated with a wide range of interstellar environments in our local galaxy and in other galaxies (Leger & Puget 1984, Allamandola *et al.* 1985). The infrared bands are observed at 3.29, 6.2, 7.7, 8.7, 11.3, and 12.7  $\mu\text{m}$  and are often accompanied by minor, weaker, bands and underlying broad structures in the 3.1 - 3.7, 6.0 - 6.9, and 11 - 15  $\mu\text{m}$  ranges. In the model dealing with the interstellar spectral features, PAHs are present as a mixture of radicals, ions, and neutral species (Allamandola *et al.* 1999). The ionization states reflect the ionization balance of the medium while the size, composition, and structure reflect the energetic and chemical history of the medium. The proposed excitation (pumping) mechanism of the IR bands is a one-photon mechanism that leads to the transient heating of the PAH molecules and ions by stellar ultraviolet (UV), visible, and/or NIR photons. The IR bands are associated with the molecular vibrations of PAH structures present either as free molecules and ions (for the discrete bands) or as subunits of larger carbonaceous grains (for the broad, continuum-like structures). PAHs thus constitute the building blocks of interstellar dust grains and play an important role in mediating energetic and chemical processes in the interstellar medium (ISM). The PAH model has considerably evolved over the years (see Figure 1), thanks in large part to the extensive laboratory and theoretical efforts that have been devoted to this issue over the years. There is a wide consensus now, in the post-Spitzer era, that PAHs are the best candidates to account for the IR emission bands (Draine & Li 2007). The bands that were once dubbed the “unidentified” IR bands (UIR) are now



**Figure 1.** Least squares fit of the PAH spectra in the Ames' database to the ISO SWS spectrum of the H II Region IRAS 23133. From Cami *et al.* (2008)

routinely called the “PAH bands” and are used as probes of the ISM in extra-galactic environments (Smith *et al.* 2007).

PAHs are also thought to contribute to the interstellar extinction and to be among the carriers of the diffuse interstellar absorption bands (DIBs). The DIBs are ubiquitous spectral absorption features observed in the line of sight to stars that are obscured by diffuse or translucent interstellar clouds. Close to 500 bands have been reported to date spanning from the near UV to the near IR with bandwidths ranging from 0.4 to 40 Å (Tielens & Snow 1995, Snow & McCall 2006). DIBs are also detected in extragalactic environments (Cox *et al.* 2007, Cordiner *et al.* 2008). The present consensus is that the DIBs arise from gas-phase, organic molecules and ions that are abundant under the typical conditions reigning in the diffuse ISM. The PAH hypothesis is consistent with the cosmic abundance of carbon and hydrogen and with the required photostability of the DIB carriers against the strong VUV radiation field in the diffuse interstellar clouds (Salama *et al.* 1996). It should be noted, however, that DIBs that are unambiguously associated with specific neutral or ionized PAHs are yet to be found.

Photo-luminescence from charged PAH clusters has been advanced as the possible source of the extended red emission (ERE), a broad emission feature ranging from 540 to beyond 900 nm with a peak wavelength longward of 600 nm to beyond 800 nm, that is observed in many environments where both dust and UV photons are present (photo-dissociation regions found in the diffuse interstellar medium, reflection nebulae, planetary nebulae, and even in other galaxies). The carriers of the ERE are widespread throughout the diffuse interstellar medium of the Milky Way Galaxy and other galaxies (Rhee *et al.* 2007, Berné *et al.* 2008, Witt *et al.* 2008).

PAHs have been proposed as the carriers of the unknown fluorescence bands that were detected in the 280-400 nm range by the TKS spectrometer on board Vega in the coma of comet Halley (Moreels *et al.* 1994, Clairemidi *et al.* 2007). Although specific PAHs [anthracene ( $C_{14}H_{10}$ ), phenanthrene ( $C_{14}H_{10}$ ), and pyrene ( $C_{16}H_{10}$ )] were singled out in this case, the observed bands are too broad for unambiguous assignments and further confirmation should await higher resolution data. If verified, however, this finding would be the first detection of the signature of *specific* PAHs in space.

PAHs have also recently been tentatively invoked as trace components in the complex refractory organics that best model the low albedo surface materials of the moons of Saturn, Iapetus, and Hyperion (Cruikshank *et al.* 2007), and as a component of the complex organic materials that form in Saturn's rings (Cuzzi 2008).

Finally, PAHs have been unambiguously characterized in meteoritic samples (cf. Plows *et al.* 2003) and in interplanetary dust particles (cf. Clemett *et al.* 1993).

## 2. Laboratory and Theoretical Studies of PAHs

The major challenges that face the study of cosmic PAHs are of two orders. First, these studies must meet the general basic key requirements for laboratory astrophysics, i. e., insure that the laboratory measurements of the physical/chemical phenomena under consideration are relevant and that the experimental conditions accurately mimic (in a realistic way) the known physical and chemical conditions that exist in the specific space environments under study. Second, the nature of the samples must be properly reproduced. PAHs are refractory materials with low vapor pressure, are often toxic, and represent a particularly difficult challenge for laboratory studies. Theoretical studies are also challenging. Improved quantum chemistry models and programs must be developed to account for such large polyatomic molecular structures (Weisman *et al.* 2003).

For example, the harsh physical conditions reigning in IS clouds -low temperature, collisionless, strong UV radiation fields – are simulated in the laboratory by isolating the molecular PAH entities (neutral and ions) in cold inert-gas matrices (He, Ne, and Ar) or, in the most recent experiments, by forming molecular beams seeded with PAH molecules (Figure 2). Cold PAH ions and radicals are formed *insitu* from the neutral precursors in an isolated environment either through one-photon ionization or through soft penning ionization in a cold plasma expansion or “glow discharge” and probed with high-sensitivity cavity ringdown spectroscopy in the NUV-NIR range (Romanini *et al.* 1999, Biennier *et al.* 2003, 2004, Sukhorukov *et al.* 2004, Tan & Salama 2005a, b, 2006) or with laser depletion mass spectroscopy measurements (Bréchnignac & Pino 1999, Pino *et al.* 1999). Carbon nanoparticles are also formed during the short residence time of the precursors in the plasma and are characterized with time-of-flight mass spectrometry. These experiments provide unique information on the spectra of large carbonaceous molecules and ions in the gas phase that can now be directly compared to interstellar and circumstellar observations (DIBs, extinction curve). These findings, when combined with detailed investigations of the flow dynamics in the PDN (Remy *et al.* 2005, Biennier *et al.* 2006) and fed into a plasma modeling program (Broks *et al.* 2005a, b) that describes the electron density and energy, as well as the argon ion and metastable atom number density, permit a full characterization of the plasma and hold great potential for understanding the formation process of interstellar carbonaceous grains.

Almost ten years have passed since our last review of the status of the PAH model (Salama 1999). Substantial progress has been made in this past decade both in experimental and in theoretical studies of PAHs (neutrals and ions), allowing for more decisive comparisons with astronomical observations. In this chapter, we briefly review the advances made on the various fronts.

*PAHs in the infrared:* The current consensus is that the interstellar IR emission spectra correspond to the composite emission of vibrational modes of a complex mixture of molecular PAHs of different sizes (i.e., number of carbon atoms), structures (compact, linear, branched) and charge states (neutrals, positive and negative ions). The vibrational spectra of neutral and ionized PAHs were measured in solid inert-gas matrices of argon at low temperature (10 K) for an extended set of molecular structures containing up to 50 carbon atoms (Hudgins & Allamandola 2004, Mattioda *et al.* 2005). This extended

spectral database, combined with theoretical calculations, has allowed major progress in fitting the IR observational data that now permits one to take into account the subtle variations that are observed among the various regions of space probed by these bands as illustrated in Figure 1.

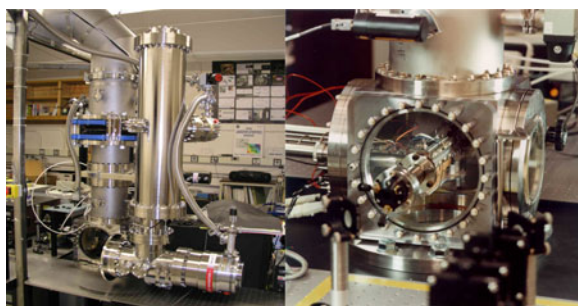
Despite their success in explaining the IR emission bands, PAH IR spectra alone cannot - by definition - lead to the identification of *specific* individual molecular PAH structures. The C-C and C-H vibrational frequencies measured in the mid-infrared mostly characterize chemical bonds that are present in almost all PAHs and have a weak dependence on the size and structure of the molecule, making it impossible to characterize specific PAH molecules and/or ions. The identification of individual PAH structures can only come from the detection of their skeleton modes in the far-infrared (FIR) range, their rotational spectra in the microwave, and/or from the detection of their electronic spectra in the UV and visible, and this, assuming that individual contributions can be deconvolved from the global distribution. The realization of these limitations has led to the development of new innovative approaches in laboratory astrophysics.

*PAHs in the far-infrared and microwave ranges:* FIR and sub-millimeter transitions probe skeleton motions and are a direct function of the size and the shape of the molecular structure, making them very interesting candidates for the detection of specific PAH structures in space. Interstellar PAHs should produce a forest of lines over a broad spectral range and the signature of specific PAHs might be detectable in the near future with instruments such as Herschel and SOFIA. This domain has been largely unexplored until recently when FIR spectra of a set of neutral PAHs have been obtained in absorption in solid inert-gas matrices of argon at low temperature (Mattioda *et al.* 2008) and in the gas phase via thermal emission (Pirali *et al.* 2006). The FIR spectra of cold neutral and ionized PAHs in the gas phase have recently been reported from resonantly enhanced multiphoton ionization (REMPI) and zero kinetic energy photoelectron (ZEKE) spectroscopy measurements (Zhang *et al.* 2008) opening the way for *direct* comparison with astronomical data when available.

Advances have also been observed in the microwave range, where the rotational spectra of cold neutral PAHs have recently been reported (Thorwirth *et al.* 2007). Although PAHs with only carbon and hydrogen atoms have weak dipole moments, nitrogen-containing PAHs have larger dipole moments that might be observable in this range, opening new prospects for the detection of specific PAHs.

*PAHs in the visible and ultraviolet:*

*PAH ions:* The electronic spectra of selected PAH ions were also measured in order to derive their *intrinsic* characteristics for comparison with interstellar spectra. Since



**Figure 2.** Configuration of the Laboratory Facility. *Right:* close-up view of the Chamber consisting of a Pulsed Discharge Nozzle coupled to a Cavity Ringdown Spectrometer apparatus and Reflectron time-of-flight mass spectrometer.

the discharge does not affect the vibrational temperature of the aromatic ions formed in cold plasma expansion (Remy *et al.* 2005, Biennier *et al.* 2006), detailed analysis of band profiles indicates that the vibronic bands are typically broad (FWHMs of the order of a few tens of  $\text{cm}^{-1}$ ), lack substructure and exhibit ultra fast relaxation lifetimes (a few tens to a few hundred femtoseconds). These features are characteristic of non-radiative intramolecular relaxation processes and explain the UV photon pumping mechanism that occurs in the ISM and the observations of the IR emission bands by radiative cascade. The characteristics of the PAH ion bands measured to date are recapitulated in Table 1 where they are compared to the strong broad DIB at 4428 Å that exhibits very similar characteristics. The 4428 Å DIB is an averaged Lorentzian profile resulting from measurements in the lines-of-sight of 35 highly-reddened O and early B stars with reddening,  $E(B-V)$  ranging from 1.0 to 2.5 mag, and located in the Cyg OB2 association (Snow *et al.* 2002). The preliminary conclusion that can be derived from this comparison is that if PAH ions contribute to the DIBs they contribute to a class of *broad* DIBs. The search for weaker broad DIBs has been inconclusive so far. This would tend to indicate the absence of these specific ions in the line of sights that were probed. The non-observation might also be due, however, to the difficulty of identifying weak broad features in the astronomical spectra. The case will be settled when dedicated surveys of broad DIBs with low error bars will be available for comparison with the laboratory data.

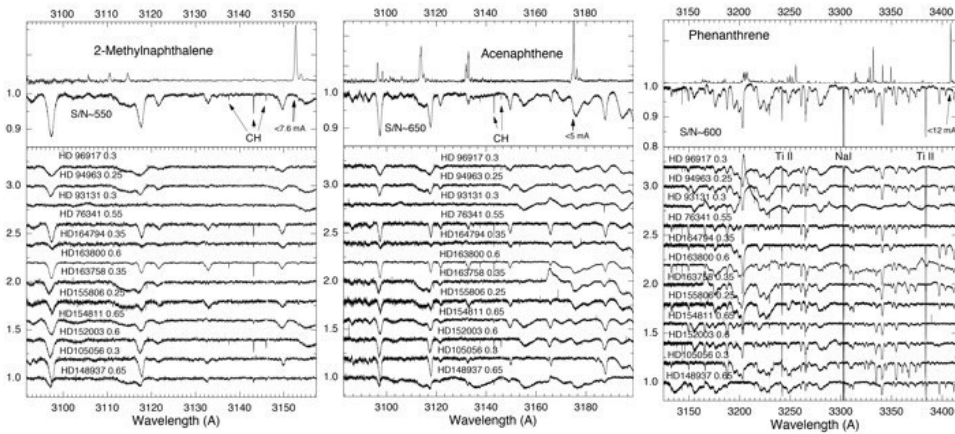
*Neutral PAHs:* The electronic spectra of cold (50 K rotational temperature) neutral methylnaphthalene ( $\text{C}_{11}\text{H}_{10}$ ), acenaphthene ( $\text{C}_{12}\text{H}_{10}$ ), phenanthrene ( $\text{C}_{14}\text{H}_{10}$ ), pyrene ( $\text{C}_{16}\text{H}_{10}$ ), perylene ( $\text{C}_{20}\text{H}_{12}$ ), pentacene ( $\text{C}_{22}\text{H}_{14}$ ), and benzoperylene ( $\text{C}_{22}\text{H}_{12}$ ) were measured in the gas-phase in order to compare with astronomical spectra (Tan & Salama

**Table 1.** Electronic state peak positions and band widths of cold gas-phase PAH ions measured in the laboratory are compared to the characteristics of the strong broad 4428 Å DIB

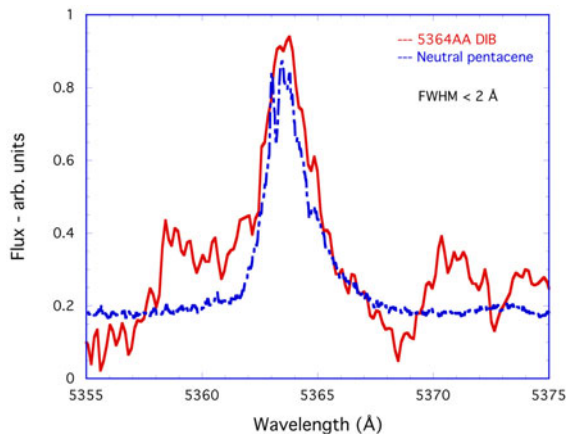
Molecular ion	Electronic State	$\lambda$ (Å)	$\Delta \lambda$ (Å)
Naphthalene <sup>+</sup> [ $\text{C}_{10}\text{H}_8^+$ ] <sup>a,1</sup>	$D_2$	6707.7	10
Naphthalene <sup>+</sup> [ $\text{C}_{10}\text{H}_8^+$ ] <sup>b,2</sup>	$D_3$	4548.5	19
Acenaphthene <sup>+</sup> [ $\text{C}_{12}\text{H}_{14}^+$ ] <sup>a,1</sup>	$D_2$	6462.7	22
Fluorene <sup>+</sup> [ $\text{C}_{13}\text{H}_{10}^+$ ] <sup>c,2</sup>	$D_3$	6201.7	53
Phenanthrene <sup>+</sup> [ $\text{C}_{14}\text{H}_{10}^+$ ] <sup>d,2</sup>	$D_2$	8919.0	12
Anthracene <sup>+</sup> [ $\text{C}_{14}\text{H}_{10}^+$ ] <sup>e,1</sup>	$D_2$	7087.6	47
Pyrene <sup>+</sup> [ $\text{C}_{16}\text{H}_{10}^+$ ] <sup>f,1</sup>	$D_5$	4362.0	28
Pyrene <sup>+</sup> [ $\text{C}_{16}\text{H}_{10}^+$ ] <sup>g,2</sup>	$D_4$	4803.3	30
Pyrene <sup>+</sup> [ $\text{C}_{16}\text{H}_{10}^+$ ] <sup>g,2</sup>	$D_2$	7786.6	97
Methylpyrene <sup>+</sup> [ $\text{C}_{17}\text{H}_{12}^+$ ] <sup>h,1</sup>	$D_5$	4411.3 (4413.3; 4409.3)	10
Pyrene(COH) <sup>+</sup> [ $\text{C}_{17}\text{H}_{10}\text{O}^+$ ] <sup>h,1</sup>	$D_8$	4457.8	20
Pyrene(COH) <sup>+</sup> [ $\text{C}_{17}\text{H}_{10}\text{O}^+$ ] <sup>h,1</sup>		4442.7	
Pyrene(COH) <sup>+</sup> [ $\text{C}_{17}\text{H}_{10}\text{O}^+$ ] <sup>h,1</sup>		4431.4	
4428 Å DIB <sup>i</sup>	$4428.4 \pm 1.4$	$17.3 \pm 1.64$	

Notes: <sup>1</sup>CRDS, <sup>2</sup>Laser Depletion MS, <sup>a</sup>Biennier *et al.* (2003), <sup>b</sup>Pino *et al.* (1999), <sup>c</sup>Bréchnignac *et al.* (2001), <sup>d</sup>Bréchnignac & Pino (1999), <sup>e</sup>Sukhorukov *et al.* (2004), <sup>f</sup>Biennier *et al.* (2004), <sup>g</sup>Pino (1999), <sup>h</sup>Tan & Salama (2006), <sup>i</sup>Snow *et al.* (2002)

2005a, b, Rouillé *et al.* 2004, 2007). Typical spectra are shown in Figures 3 & 4. Neutral PAHs exhibit narrower bands than the ions (FWHMs are of the order of only a few  $\text{cm}^{-1}$ ) with a profile that is *closely* similar to the profile of the narrower DIBs. The case is strikingly illustrated in the comparison of the 5363 Å band of neutral pentacene,  $\text{C}_{22}\text{H}_{14}$ , with the narrow ( $< 2$  Å FWHM) 5364 Å DIB detected with the echelle spectrograph of the OHP 2m-telescope (Figure 4). Note that  $\text{C}_{22}\text{H}_{14}$  exhibits another band of similar strength at 5340 Å where only a weaker feature is found in the astronomical spectra. Additional comparisons are being performed between laboratory spectra and the astronomical spectra of extensive sets of reddened O and B stars observed with the ELODIE/OHP and the UVES/VLT telescopes in the 3100 Å to 5400 Å range. The stars have reddening  $E(B-V)$  ranging from 0.3 to 1.35 mag. Features can be detected at the 0.2% level when co-adding all spectra. From these comparisons, we can derive upper limits to the abundances of individual PAHs in the observed lines of sight. Values of the order of  $10^{-4}$  to  $10^{-6}$  are derived for the fraction of cosmic carbon locked up in these PAHs (Cami *et al.* 2005, Galazutdinov *et al.* 2008). These preliminary results await comparison with improved modelling of stellar lines in the NUV.



**Figure 3.** Comparison of jet-cooled neutral PAH spectra in the NUV-Visible to the ESO/VLT/UVES spectra of reddened O and B stars. (Galazutdinov *et al.* 2008)



**Figure 4.** Comparison of band profiles of jet-cooled pentacene ( $\text{C}_{22}\text{H}_{14}$ ) with CRDS and the 5363.8 Å DIB measured with the OHP echelle spectrograph (see text). The laboratory band (dotted line) was slightly shifted in wavelength for illustration purposes. Taken from Salama (2008).

*Discharge products and formation of carbon particles:* We have identified the formation of CH as one of the high-energy plasma fragmentation products formed in the PDN through the measurement of its (A-X) (0-0) absorption band. We have simultaneously observed an increase in the extinction of the CRD signal caused by the formation of carbon nanoparticles in the plasma and the formation of soot on the electrodes of the PDN source. Analysis of the soot with  $\mu\text{L}^2\text{MS}$  has shown the formation of larger PAH particles in the discharge (Biennier *et al.* 2005). These preliminary findings hold some potential for exploring the formation (and destruction) processes of carbon-bearing molecules in space and are the subject of investigations in this and in other laboratories as evidenced by presentations at this symposium (contributions by Pino *et al.*, Brunetto *et al.*, Saito *et al.*).

### 3. Implications

This brief overview of Laboratory Astrophysics studies applied to the characterization of PAHs in space indicates that tremendous progress has been made in the past decade leading to laboratory data that can now be *directly* compared to the astronomical observations. These preliminary results demonstrate the power of the laboratory approach associating cold molecular beams and plasma sources with sensitive high-resolution spectroscopy (CRDS, REMPI, ZEKE) and mass spectrometry (e.g. RETOF-MS) techniques for generating and characterizing laboratory analogs of large interstellar organic molecules. The laboratory spectra of cold PAHs are decongested, making it possible *for the first time* to perform unambiguous searches for specific PAH molecules in astronomical spectra and derive meaningful upper limits for their abundances. These experiments also provide first hand data on the spectroscopy and on the molecular dynamics of *free*, cold, large complex organic molecules and ions in the gas phase. We are now, for the first time, in the position to directly search for *individual* PAH molecules and ions in astronomical spectra.

This new generation of laboratory experiments opens a new page and offers tremendous opportunities for the data analysis of upcoming space missions that have the potential to lead to the identification of *specific* PAHs in space. Herschel and SOFIA will soon pioneer observations in the FIR. The Cosmic Origins Spectrograph (COS) due to be installed on the Hubble Space Telescope in the next servicing mission will search for the signature of large aromatic molecules and ions in the UV extinction of highly reddened stars. Finally, the new generation of laboratory experiments that couples mass spectrometry instruments to molecular beam and high-sensitivity spectroscopy instruments also provide a powerful tool for a better understanding of the formation mechanisms of carbonaceous dust nanoparticles from molecular precursors in the circumstellar shells of carbon-rich stars. This is the topic of future exciting research.

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## Discussion

ZIURYS: When you use an argon matrix you get a matrix shift that can move the band frequencies around. Are you going to update your database with the gas phase data?

SALAMA: If you are talking about the infrared work in argon matrices, the shift is small when you compare to the limited gas phase data that is available and that has been measured by Rich Saykally and his group at UCB. In their measurements, shifts in band positions are of the order of a few wavenumbers (less than 5 wavenumbers) and band profiles are only slightly broader in Ar matrices as compared to the gas phase. So the matrix perturbation is not a big issue for the infrared spectra. This observation has actually led the authors to conclude that the argon matrix data are sufficiently similar to the gas phase data in the infrared to compare the bands with reasonable accuracy. This is, however, not true in the UV and visible range where matrix perturbation is a real issue. The electronic spectra measured in this range using even the least perturbing neon matrices show larger shifts and band broadenings compared to the gas phase. So, I think that although data measured in the gas phase is definitely always preferable, the problem is minor in the infrared. This is not the case for the electronic transitions that fall in the UV-Visible range where the energies involved are higher and result in stronger matrix-induced perturbations dictating the need to transition to the gas phase as I discussed in my presentation.



Group picture at the University of Hong Kong.