

PAH IN THE LABORATORY AND INTERSTELLAR SPACE

Thomas J. Wdowiak, Gregory C. Flickinger, and David A. Boyd
Physics Department, University of Alabama at Birmingham,
UAB Station, Birmingham, Alabama 35294 USA

ABSTRACT. The hypothesis that polycyclic aromatic hydrocarbons (PAH) are a constituent of the interstellar medium, and a source of the infrared emission bands at 3.3, 6.2, 7.7, 8.6, and 11.3 microns is being studied using PAH containing acid insoluble residue of the Orgueil CI meteorite and coal tar. FTIR spectra of Orgueil PAH material that has undergone thermal treatment, and a solvent insoluble fraction of coal tar that has been exposed to hydrogen plasma are presented. The ultraviolet excited luminescence spectrum of a solvent soluble coal tar film is also shown. Comparison of the laboratory measurements with observations appears to support the interstellar PAH hypothesis, and demonstrates the process of dehydrogenation expected to take place in the interstellar medium.

The presence of polycyclic aromatic hydrocarbon molecules (PAH) in the interstellar medium is inferred from the observation of infrared emission bands at 3.3, 6.2, 7.7, 8.6, and 11.3 microns. (for a review of the field see "Polycyclic Aromatic Hydrocarbons and Astrophysics", ed. A. Leger, L. d'Hendecourt, and N. Boccara, D. Reidel, 1987). Demonstration that this assignment is correct is important because it would mean PAH is a major form of interstellar carbon and that PAH molecules could play a role in charge exchange reactions leading to chemical pathways radically different from what has been considered previously. The latter situation leads to new estimates of abundances of interstellar molecules, such as formaldehyde in dark clouds, that are orders of magnitude greater than previous results. (Lepp and Dalgarno 1988) The difficulty in making definite the PAH assignment is that the kinds of PAH samples generally available to the experimenter from supply houses and laboratory sources are probably not of the type considered to exist in the interstellar medium. The 11.3 micron emission band mandates PAH molecules that have single hydrogen atoms per aromatic ring (Bellamy 1975, Cohen, Tielens, and Allamandola 1985), while most laboratory samples have 2, 3, or 4 hydrogen atoms per ring. Also, interstellar PAH molecules must be composed of >20 carbon atoms in order to survive the interstellar ultraviolet radiation field (Leger and Puget 1984). Laboratory experiments with PAH candidates having >20 carbon atoms are difficult because of low solubility and low volatility. While available pure PAH samples are useful for exploring basic mechanisms, we have turned our attention toward PAH in carbonaceous chondrites and the PAH products of the coking process, pyrolysis, plasma chemistry, and combustion with the intent of determining if the PAH assignment for the UIR bands is reasonable.

The acid insoluble residue of the Orgueil (CI) carbonaceous chondrite has been shown to have substantial aromatic content (Cronin, Pizzarello, and Frye 1987). After vacuum treatment it exhibits an infrared absorption spectrum similar to that observed in emission from the Orion Nebula (Wdowiak, Flickinger, and Cronin, 1988). The Orion emission spectrum in the 5 to 14 micron region and the KBr pellet absorption spectrum of Orgueil

acid insoluble residue after vacuum heating to 500C are shown in Figure 1. The Orgueil FTIR spectrum has had a continuum subtracted to remove the effect of scattering in the KBr pellet, revealing the maximum of the broad absorption "hump" is at ~7.8 microns in addition to the peaks at 6.2 and 11.3 microns. The coincidence of the wavelength of the heated treated residue "hump" maximum and the observed 7.7 micron emission band is interesting.

The Orgueil acid insoluble residue has other interesting IR spectral features besides those shown in Figure 1. Figure 2 shows the heat treated Orgueil acid insoluble residue has absorption bands at 16 and 19.6 microns (625 cm^{-1} and 510 cm^{-1}). These features are intrinsic to the residue and are evident in untreated material. They are probably due to bending of the PAH aromatic structure and are of interest as a candidate for the cause of the broad 25 micron band emission observed with IRAS (Hauser et al., 1984; Lynch et al., 1988). Because of the absence of a 10 micron (1000 cm^{-1}) band one can conclude the 16 micron (625 cm^{-1}) and 19.6 micron (510 cm^{-1}) bands are not due to silicate material that has escaped being dissolved by HF. Sandford and Walker (1985) have published an IR spectrum of an interplanetary dust particle (IDP "Conehead") having bands at 16.8 micron (595 cm^{-1}) and 23.1 micron (433 cm^{-1}) attributed to an hydrous Al_2O_3 or Fe_2O_3 . The Orgueil 16 micron (625 cm^{-1}) and 19.6 micron (512 cm^{-1}) absorption features could therefore be due to microgram amounts of mineral in the milligram amount of sample residue.

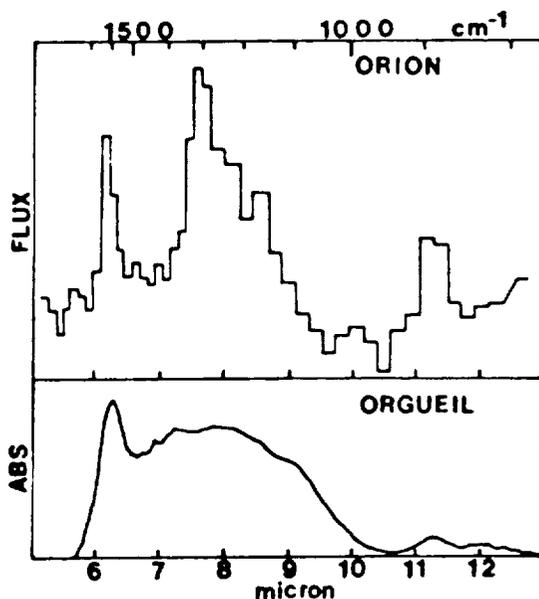


Fig. 1 Orion Bar (Allamandola et al. 1987) and heat treated Orgueil PAH residue.

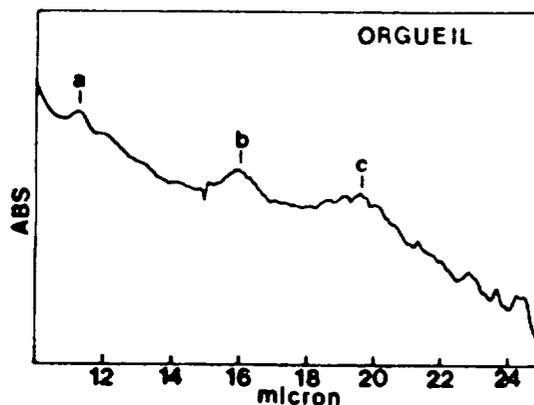


Fig. 2 Orgueil heat treated PAH residue a-11.3, b-16 and c-19.6 micron bands.

Coal tar prepared by coking coal at 1400 K in the absence of air is utilized as a PAH mixture that is an analog to interstellar PAH mixtures. Bulk coal tar mixed with acetone was filtered and the filtrate evaporated afterwards to concentrate a solvent soluble fraction used to prepare air dried films. As the solvent is evaporated away a dramatic spectral shift of $\sim 2000\text{\AA}$ from blue to orange-red occurs in the near ultra-violet excited luminescence. The solvent soluble fraction coated on a substrate as a film and excited with ultraviolet radiation exhibits luminescence having a spectral signature in the 5500\AA to 7500\AA range similar to that of the Red Rectangle and other dusty regions (Figure 3). This result suggests the Red Rectangle emission is due to excited-dimer (excimer) emission of PAH molecules clumped together (Wdowiak 1986). In the excimer process which requires adjacent PAH molecules (as in the film), an excited dimer is formed from an excited singlet molecule and an unexcited one. This is followed by a radiative transition emitting light at longer wavelengths than single molecules would, followed by rapid dissociation into monomers. Duley and Williams (1988) have demonstrated PAH clumps would have an infrared emission spectrum similar to that of free molecules, making the excimer process plausible for the source of the optical emission of objects such as the Red Rectangle which also exhibits IR band emission (Russell, Sofier, and Willner 1978).

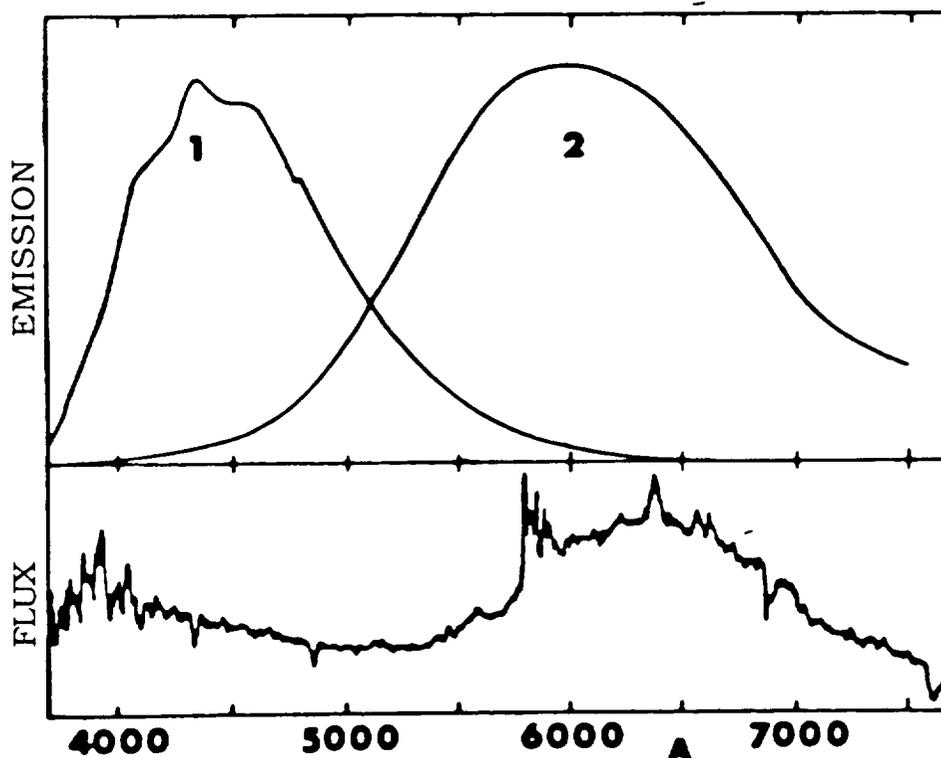


Fig. 3 Luminescence of 3070\AA excited coal tar in ethyl alcohol (1) and as a film on quartz (2) corrected for R928 PMT sensitivity shown with the spectrum of the Red Rectangle (Schmidt, Cohen, and Morgan 1980).

The coal tar residue obtained in the filtering process was washed repeatedly with benzene to remove soluble material and then air dried prior to pressing it into KBr pellets or subjecting it to further processing. The solvent insoluble fraction of coal tar has infrared spectral characteristics similar, but not identical to that of the heat treated acid insoluble residue of the Orgueil meteorite. In particular the presence of 3.3 micron (3030 cm^{-1}) absorption and other features longward of 11.3 micron (885 cm^{-1}) suggests it is more hydrogenated. An experiment was performed to try to simulate in a gross, but rapid manner the effect of H atom, H ion, and ultraviolet exposure on interstellar PAH. The benzene insoluble coal tar residue was placed in a boat, and subjected to a microwave excited hydrogen plasma at a pressure of 1.5 Torr for 35 minutes. The processing reduced the strength of the 13.4 micron (746 cm^{-1}) band, probably associated with aromatic rings having 3 or 4 adjacent hydrogens per ring, relative to the 11.3 micron (885 cm^{-1}) band associated with 1 hydrogen per ring (Figure 4). This experiment may demonstrate why the 11.3 micron interstellar emission band dominates the 10 to 15 micron region, by simulating the dehydrogenation expected to take place in the interstellar environment.

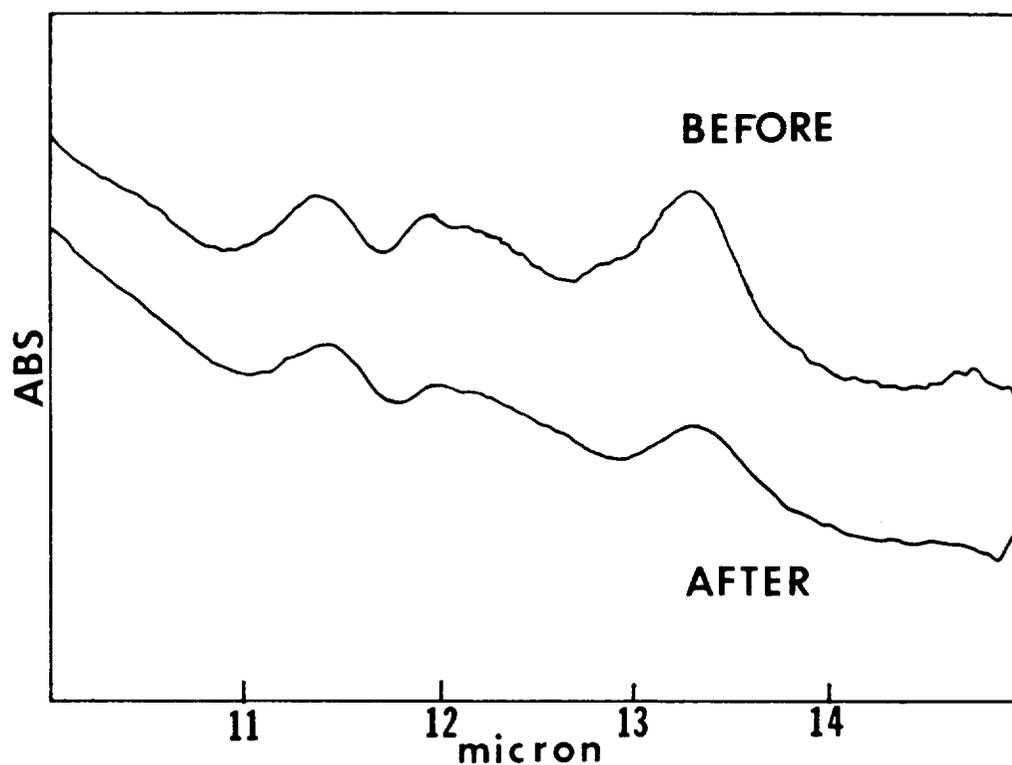


Fig. 4 FTIR spectra in the 10 to 15 micron region of the solvent insoluble fraction of coal tar before and after being subjected to a hydrogen plasma environment.

Comparison of the laboratory measurements discussed here and observations indicates the linking of the IR emission bands to a PAH source is not inconsistent with our laboratory experience. However a laboratory analog that exhibits precisely all of the spectral features of a source such as the Red Rectangle (HD 44179) still eludes the laboratory worker and is troubling. It may be that the PAH species have a special character, or that there is stratification of various populations of PAH species in a unique manner in the source of IR emission and no single analog or analog system will suffice. Still to be exploited are the structured features superimposed upon the Red Rectangle 5500A - 7500A emission "hump" (Schmidt, Cohen, and Margon 1980, Warren-Smith, Scarrott, and Murdin 1981). Those features may be due to simple radicals or ions trapped in relatively inert ices such as CO or N₂ (Wdowiak 1981) or are the signatures of complex molecules. Perhaps even stimulated emission may be involved. What is needed are observations of the Red Rectangle quality of other similar sources. This work was supported by NASA grant NAGW-749.

- Allamandola, L.J., Tielens, A.G.G.M., and Barker, J.R.: 1987 in *Polycyclic Aromatic Hydrocarbons and Astrophysics* (ed. Leger, A., d'Hendecourt, L., and Boccardo, N. D. Reidel).
- Bellamy, L.J.: 1985, *The Infra-red Spectra of Complex Molecules* (Chapman and Hall, London).
- Cohen, M., Tielens, A.G.G.M., and Allamandola, L.J.: 1985, *Ap.J.* 299, 193.
- Cronin, J.R., Pizzarello, S., and Frye, J.S.: 1987, *Geochim. Cosmochim. Acta* 51, 299.
- Duley, W.W. and Williams, D.A.: 1988, *M.N.R.A.S.* 231, 969.
- Hauser, M.G. et al.: 1984, *Ap.J.* 278, L 115.
- Leger, A. and Puget, L.L.: 1984, *Astron. Astrophys.* 137, L5.
- Lepp, S. and Dalgarno, A.: 1988, *Ap.J.* 324, 553.
- Lynch, D.K., Hackwell, J.A., Wesselius, P., Olling, R., and Isreal, F.P.: 1988, *Bull. Am. Astron. Soc.* 20, 732.
- Sandford, S.A. and Walker, R.M.: 1985, *Ap.J.* 291, 838.
- Schmidt, G.D., Cohen, M., and Margon, B.: 1980, *Ap.J.* 239, L133.
- Russell, R.W., Soifer, B.T., and Williams, S.P.: 1978, *Ap.J.* 220, 568.
- Warren-Smith, R.F., Scarrott, S.M., and Murdin, P.: 1981, *Nature* 292, 317.
- Wdowiak, T.J.: 1981, *Nature* 293, 724.
- Wdowiak, T.J.: 1986, in *Interrelationships Among Circumstellar, Interstellar, and Interplanetary Dust* (NASA CP 2403), A41.
- Wdowiak, T.J., Flickinger, G.G., and Cronin, J.R.: 1988, *Ap.J.* 328, 175.

