



Synthesis of Complex Organics in Planetary Nebulae

Sun Kwok^{1,2}, SeyedAbdolreza Sadjadi² and Yong Zhang^{2,3}

¹Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, Vancouver, Canada

²Laboratory for Space Research, The University of Hong Kong, Hong Kong, China

³School of Physics & Astronomy, Sun Yat Sen University, Zhuhai, China
email: sunkwok@hku.hk

Abstract. A family of unidentified infrared emission (UIE) bands is widely observed in planetary nebulae. We suggest that the carriers of the UIE bands are mixed aromatic/aliphatic organic nanoparticles (MAONs) synthesized over thousand-year time scales in the nebulae. The possible chemical pathways of synthesis is discussed. These organics are ejected into the interstellar medium and could have enriched the primordial Solar System, leading to the reservoir of complex organics in comets, asteroids, planetary satellites, and interplanetary dust particles.

Keywords. stars: AGB and post-AGB, ISM: molecules, planetary nebulae: general

1. Introduction

Planetary nebulae (PNe) have long been recognized as sources of heavy element enrichment of the Galaxy. Advances in infrared and millimeter-wave astronomical spectroscopy have led to the realization that PNe are also major distributors of molecules and solids in the interstellar medium. Gas-phase molecules and various inorganic solids such as silicates, silicon carbide, and refractory oxides have been detected in the circumstellar envelopes of asymptotic giant branch (AGB) stars, the immediate progenitors of planetary nebulae. In spite of the very low density conditions, molecules and solids are formed in the circumstellar environment over very short ($\sim 10^3$ yr) time scales (Kwok 2004).

The discovery of complex organics in PNe was totally unexpected. A family of unidentified infrared emission (UIE) bands at 3.3, 6.2, 7.7, 8.6, and 11.3 μm , superimposed on an underlying continuum, was first detected in the young planetary nebula NGC 7027 (Russell, Soifer, & Willner 1977). Soon after the discovery, the 3.3 μm feature was identified by Roger Knacke as due to C–H stretching mode of aromatic compounds (Knacke 1977). This would be the first identification of organic compounds in an astronomical source, but the interpretation was not accepted at the time.

The UIE bands have since been detected in many PNe, as well as in reflection nebulae, diffuse interstellar medium, and external galaxies. In some active galaxies, the amount of energy emitted in the UIE bands can be as high as 20% of the total energy output of the galaxy (Smith et al. 2007). Since the carrier is synthesized in situ, PNe are the best objects to study their origins. While the UIE bands are strong in young PNe, they are not seen in AGB stars. The best way to determine when the carriers of the UIE bands are synthesized is to study proto-planetary nebulae (PPNe), the missing link between AGB and PNe. After the discovery of about 30 PPNe (Hrivnak, Kwok, & Volk 1989; Kwok 1993), we proceeded to take infrared spectroscopy of these objects. In addition to the UIE

bands, the 3.4 μm feature (identified as C–H stretching mode of aliphatic compounds) were found in the spectra of PPNe (Geballe et al. 1992; Hrivnak et al. 2007). Also found were broad plateau emission features around 8 and 12 μm (Kwok, Volk, & Hrivnak 1999), which we proposed as the result of superpositions of in-plane and out-of-plane bending modes of aliphatic compounds (Kwok, Volk, & Bernath 2001).

Subsequent observations, especially by the *Infrared Space Observatory* (ISO) and *Spitzer* telescopes show that the UIE phenomenon consists of major emission features at 3.3, 6.2, 7.7, 8.6, and 11.3 μm , minor emission features at 3.4, 6.9, 12.1, 12.4, 12.7, 13.3, 15.8, 16.4, 17.4, 17.8, and 18.9 μm and strong, broad emission plateaus features at 6–9, 10–15, and 15–20 μm . The 3.3 and 11.3 μm features are generally attributed to C–H stretching and C–H out-of-plane bending modes of aromatic compounds, and the 3.4 and 6.9 μm attributed to C–H stretching and bending modes of aliphatic compounds (Duley & Williams 1981). The origin of the strong features at 6.2, 7.7, 8.6 μm features is less clear, and are possibly due to coupled vibrational modes of complex organics. A successful model must be able to explain all these properties. The key question is: what is the chemical structure of the carrier?

2. The PAH hypothesis

After the development of millimeter-wave astronomy and the wide detection of molecules through their rotational transitions, the polycyclic aromatic hydrocarbon (PAH) molecules became the most popular hypothesis for the UIE phenomenon. In the PAH hypothesis, the UIE features are the result of infrared fluorescence from small (~ 50 C atoms) gas-phase PAH molecules being pumped by far-ultraviolet photons. However, the PAH hypothesis has a number of problems. PAH molecules are primarily excited by UV with little absorption in the visible, but UIE features are seen in PPNe and reflection nebulae with no UV background radiation. The predicted strong and narrow electronic transitions of PAH molecules in the UV are not seen in interstellar extinction curves. The upper limits of PAH/H of 10^{-10} – 10^{-8} derived from UV absorption spectroscopy are orders of magnitude lower than the abundance needed to account for the infrared bands (Clayton et al. 2003; Salama et al. 2011; Gredel et al. 2011). PAH molecules are well studied in the laboratory by chemists (Schlemmer et al. 1994; Cook et al. 1996; Cook & Saykally 1998), who found “No PAH emission spectrum has been able to reproduce the UIE spectrum w.r.t. either band positions or relative intensities” (Wagner, Kim, & Saykally 2000). The PAH model predicts that the UIE band ratios are strongly dependent on the UV background as individual UIE bands are assumed to arise from different neutral or ionized PAHs (Hudgins and Allamandola 2004; Draine et al. 2011), but the profiles and peak wavelengths of UIE bands are found to be independent of temperature of exciting star (Uchida et al. 2000).

The initial identification of the PAH model was based on the 3.3 and 11.3 μm features but there are no obvious counterparts in PAH molecules for the 6.2, 7.7, and 8.6 μm features. To quote Cook & Saykally (1998): “In order to reproduce the narrow 6.2 and 11.2 μm UIR bands, the carriers must consistently exhibit bands at these positions with a consistency similar to that which is observed with the 3.3 μm emission. In addition, the carriers of the UIRs must, in general, exhibit an absence of strong bands in the gap between the 6.2 and 7.7 μm UIR features. The PAHs used in these model spectra simply do not meet these criteria; hence they do not reproduce the details of the UIR spectra”. Based on a comparison between the astronomical UIE spectra with the laboratory spectrum of coronene, Léger and Puget (1984) assign the 6.2 μm band to C–C stretch and the 8.6 μm to C–H in-plane bending mode of PAH molecules. Peeters (2011) assigns the infrared bands between 6.1 and 6.5 μm to pure aromatic C–C stretching modes, bands from 6.5 to 8.5 μm to coupled C–C stretching and C–H in-plane bending modes, and

bands between 8.3 to 8.9 μm to C–H in-plane bending modes. However, all C–C stretching modes are very weak in comparison to the C–H modes in neutral PAH molecules. In order to explain the prominence of the features, PAH ions are suggested to be responsible for the UIE features in the 6–9 μm region (Hudgins and Allamandola (2004)).

In part to address the above list of problems, the PAH hypothesis has been revised to incorporate different ionization states and large sizes to increase the absorption cross sections in the visible. The molecular size range has been extended to >1,000 atoms (Peeters et al. 2021). The PAH molecules are also modified to include dehydrogenation, superhydrogenation, and minor aliphatic side groups (Li & Draine 2012). Heteroatoms (defined as those atoms other than C or H) such as N are also introduced to explain the 6.2 μm band (Hudgins & Allamandola 1999).

By using the NASA Ames PAH database and fitting routines (Boersma et al. 2014), the PAH model can fit astronomical observations by including a mixture of PAH of different sizes, structures (compact, linear, branched) and ionization states, as well as artificial broad intrinsic line profiles. However, the number of free parameters in these fits is so large that this procedure has been shown to be able to fit any artificial spectra (Zhang & Kwok 2015).

3. Mixed aromatic/aliphatic organic nanoparticles as carriers of the UIE bands

Amorphous organic solids are often the natural results of combustion. When a mixture of hydrocarbon gases is subjected to energy injection (laser ablation/pyrolysis, electric discharge, photolysis, radio waves), the evaporated condensates collected in cooled substrates are often amorphous carbonaceous compounds. The infrared spectra of these laboratory-synthesized organics show general similarities to the astronomical UIE spectra (Dischler et al. 1983; Herlin et al. 1998) (Figure 1). A recent experiment designed to simulate molecular and solid synthesis in circumstellar low-temperature and low-density conditions yielded the production of simple molecules such as acetylene and ethylene, as well as carbonaceous solids such as amorphous carbon nanograins and aliphatic carbon clusters (Martinez et al. 2020).

As an alternative to the PAH hypothesis, a mixed aromatic-aliphatic model (MAON) has been proposed (Kwok & Zhang 2011, 2013). MAONs consist of small units of aromatic rings linked by aliphatic chains, as well as heteroatoms such as O, N, and S. A typical nanoparticle may contain multiple of structures shown in Figure 2.

As the vibrational spectra of complex organics are not known, we have made initial studies to identify the vibrational mode of all major bands using quantum chemistry techniques. We start with PAH molecules with aliphatic side groups (Sadjadi, Zhang, & Kwok 2015) and proceed to study the nature of the 3.3/3.4, 6.2, and 11.3 μm UIE bands (Sadjadi, Zhang, & Kwok 2015; Hsia et al. 2016; Sadjadi, Zhang, & Kwok 2017). From the study of a small number of MAON-like molecules, we find that many spectral bands are due to coupled vibrational modes and their origin is not straight forward to interpret (Sadjadi, Kwok, & Zhang 2016). Further work is needed to explore the spectral properties of MAON-like molecules.

4. PAH vs MAON

There are fundamental differences between the chemical structures of PAHs and MAONs and these distinctions are not just semantics. For example, is the carrier of UIE free-flying molecules or solids? Is the carrier purely aromatic or has a mixed sp^2/sp^3 structure? Is the geometry two or three dimensional? Is the carrier small (< 50 C) or large ($\sim 10^3$ C)? Does it consist of pure C and H or does it also contain impurities? Is

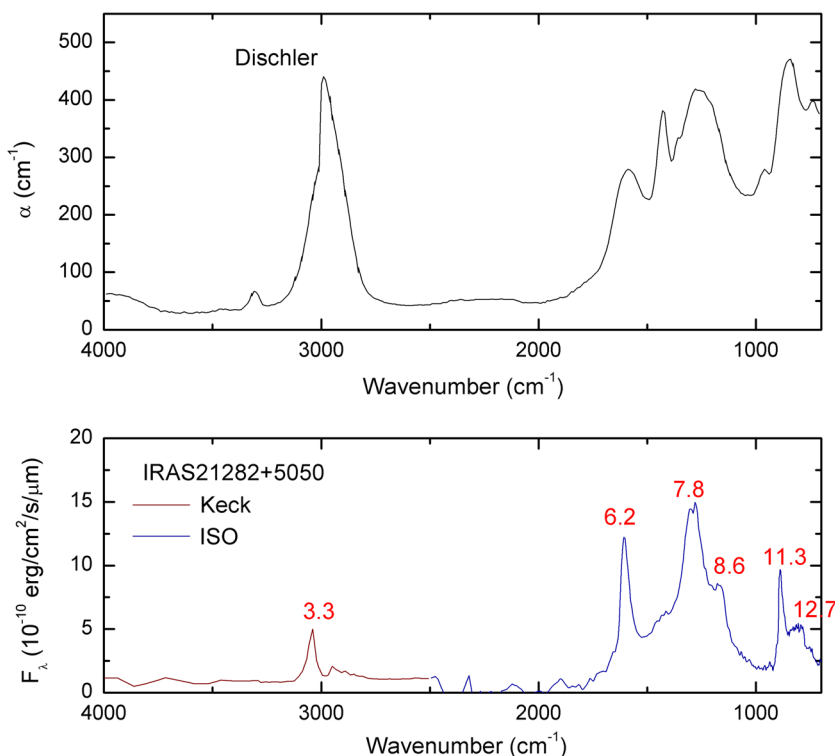


Figure 1. Laboratory infrared spectra of hydrogenated amorphous carbon (top, Dischler et al. 1983) compared to the astronomical spectrum of the planetary nebula IRAS 21282+5050 (bottom panel). The UIE bands are labeled by their wavelengths in μm .

the structure made of pure rings or with a variety of functional side groups? Is the chemical structure regular with repeatable patterns or amorphous with aromatic islands with variable sizes and aliphatic chains with random length and orientations? We hope with time that these distinctions will be clarified and the carrier of the UIE bands identified.

5. Circumstellar synthesis of complex organics

Acetylene (C_2H_2) is commonly detected in evolved carbon stars through its ν_5 fundamental band at $13.7 \mu\text{m}$ (Volk, Xiong, & Kwok 2000). Polymerization of C_2H_2 leads to the formation of diacetylene (C_4H_2) and triacetylene (C_6H_2) in PPNe, culminating in the formation of benzene (C_6H_6). During the PPNe phase, benzene molecules are clustered together to form islands of aromatic rings. Various aliphatic side groups (CH_2 , CH_3 , $(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$...) are attached to the peripheral of the rings, linking the aromatic islands together with aliphatic bridges. With the onset of photoionization during the PNe phase, there could be a loss of peripheral H and progressive formation of larger clusters into MAONs.

6. Implications

PPNe, PNe, and novae are the only astronomical objects that we have direct observations of organic synthesis. As chemical synthesis takes place in an expanding circumstellar envelope, the time scale of synthesis is limited by the dynamical timescale of expansion. In PPNe and PNe, chemical evolution leading to complex organic compounds is observed to take place over only a few thousand years. If complex organics are routinely made by

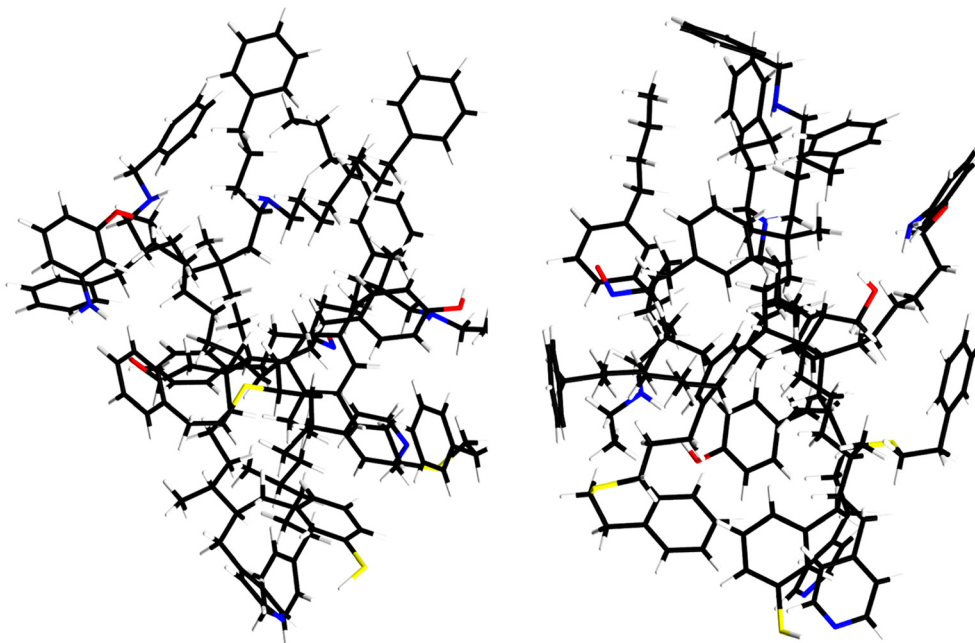


Figure 2. Two views of the molecule $C_{169}H_{225}N_7O_4S_3$. The MAON structure is characterized by a highly disorganized arrangement of small units of aromatic rings linked by aliphatic chains. The C atoms are shown in black, H atoms in white, O in red, N in blue, and S in yellow. A typical MAON particle may consist of multiple structures similar to this one.

old ordinary Sun-like stars and distributed throughout the Galaxy by PNe, these stellar organics may have spread throughout the Galaxy and have even possibly enriched the primordial Solar System. The fact that macro-organics with MAON-like structures have been identified in meteorites, comets, interplanetary dust particles, and planetary satellites suggests that there may be a stellar-Solar System connection (Kwok 2016). It is also plausible that the early Earth may have inherited some of these stellar organics (Kwok 2017). The possible role of stellar organics on the origin of life on Earth represents a fascinating topic for future investigations.

Acknowledgment

We thank Ryszard Szczerba and the Local Organizing Committee for organizing a wonderful conference. This work is supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

References

- Boersma, C., Bauschlicher, C. W., Jr., Ricca, A., et al. 2014, *ApJS*, 211, 8
- Clayton, G. C., Gordon, K. D., Salama, F., et al. 2003, *ApJ*, 592, 947
- Cook, D. J., & Saykally, R. J. 1998, *ApJ*, 493, 793
- Cook, D. J., Schlemmer, S., Balucani, N., et al. 1996, *Nature*, 380, 227
- Dischler, B., Bubenzer, A., & Koidl, P. 1983, *Solid State Commun*, 48, 105
- Draine, B. T., Li, A., Hensley, B. S., et al. 2021, *ApJ*, 917, 3
- Duley, W. W., Williams, D. A. 1981, *Mon. Not. R. Astron. Soc.* 196, 269
- Geballe, T. R., Tielens, A. G. G. M., Kwok, S., Hrivnak, B. J. 1992, *ApJ*, 387, L89
- Gredel, R., Carpentier, Y., Rouillé, G., et al. 2011, *A&A*, 530, 26
- Herlin, N., Bohn, I., Reynaud, C., et al. 1998, *A&A*, 330, 1127

- Hrivnak, B. J., Kwok, S., & Volk, K. M. 1989, *ApJ*, 346, 265
- Hrivnak, B. J., Geballe, T. R., Kwok, S. 2007, *ApJ*, 662, 1059
- Hsia, C. H., Sadjadi, S., Zhang, Y., Kwok, S. 2016, *ApJ*, 832, 213
- Hudgins, D. M., & Allamandola, L. J. 1999, *ApJ*, 513, L69
- Hudgins, D. and Allamandola, L. J. 2004, in *Astrophysics of Dust*, Witt, A. N., Clayton, G. C., and Draine, B. T. (eds.), ASP Conf. Ser. vol. 309, p. 665
- Knacke, R. F. 1977, *Nature*, 269, 132
- Kwok, S. 1993, *Ann. Rev. Astr. Ap.*, 31, 63
- Kwok, S. 2004, *Nature*, 430, 985
- Kwok, S. 2016, *Astr. Ap. Rev.*, 24, 8
- Kwok, S. 2017, *Nature Astronomy*, 1, 642
- Kwok, S., Volk, K., & Bernath, P. 2001, *ApJ*, 554, L87
- Kwok, S., Volk, K., & Hrivnak, B. J. 1999, *A&A*, 350, L35
- Kwok, S., & Zhang, Y. 2011, *Nature*, 479, 80
- Kwok, S., & Zhang, Y. 2013, *ApJ*, 771, 5
- Léger, A., Puget, J. L. 1984, *A&A*, 137, L5
- Li, A., and Draine, B. T. 2012, *ApJ*, 760, L35
- Martínez, L., Santoro, G., Merino, P., et al. 2020, *Nature Astronomy*, 4, 97
- Peeters, E. 2011, in *IAU Symposium 280 The Molecular Universe*, Cernicharo, J. & Bachiller, R. (eds), CUP, p. 149
- Peeters, E., Mackie, C., Candian, A., Tielens, A. G. G. M. 2021, *Acc. Chem. Res.*, 54, 1921
- Russell, R. W., Soifer, B. T., & Willner, S. P. 1977, *ApJ*, 217, L149
- Sadjadi, S., Kwok, S., Zhang, Y. 2016, *IOP J. Phys. Conf. Ser.* 728, 062003
- Sadjadi, S., Zhang, Y., & Kwok, S. 2015 *ApJ*, 801, 34
- Sadjadi, S., Zhang, Y., & Kwok, S. 2017 *ApJ*, 845, 123
- Salama, F., Galazutdinov, G.A., Krelowski, J., et al. 2011, *ApJ*, 728, 154
- Schlemmer, S., Cook, D., Harrison, J., et al. 1994, *Science*, 265, 1686
- Smith, J. D. T., Draine, B. T., Dale, D. A., et al. 2007, *ApJ*, 656, 770
- Uchida, K. I., Sellgren, K., Werner, M. W., & Houdashelt, M. L. 2000, *ApJ*, 530, 817
- Volk, K., Xiong, G.-Z., & Kwok, S. 2000, *ApJ*, 530, 408
- Wagner, D. R., Kim, H., & Saykally, R. J. 2000, *ApJ*, 545, 854
- Zhang, Y., & Kwok, S. 2015, *ApJ*, 798, 37