Residue from Vacuum Ultraviolet Irradiation of Benzene Ices: Insights into the Physical Structure of Astrophysical Dust

K K Rahul[a], S Karthik[a, $], J K Meka[a,$], A Das[b], V Chandrasekaran[c], B N Rajasekhar[d], J. –I. Lo[e], B.-M. Cheng[e], P Janardhan[a], A Bhardwaj[a], N J Mason[f], B Sivaraman[a,*]

[a] Physical Research Laboratory, Ahmedabad, India.

[b] Indian Centre for Space Physics, Kolkata, India.

[c] Vellore Institute of Technology, Vellore, India.

[d] Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai, India.

[e] National Synchrotron Radiation Research Center, Hsinchu, Taiwan.

[f] School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 UK.

Abstract

We have irradiated benzene ices deposited at 4 K on a cold, interstellar dust analog with vacuum ultraviolet (9 eV) irradiation for periods lasting from several hours to nearly a day, after which the irradiated ice was warmed to room temperature. Vacuum ultraviolet photoabsorption spectra of the aromatic residue left at room temperature were recorded and showed the synthesis of benzene derivatives. The residue was also imaged using an electron microscope and revealed crystals of various sizes and shapes. The result of our experiments suggest such geometrically shaped dust particles may be a key component of interstellar dust.

* Corresponding author: Email - bhala@prl.res.in
[$] Equally contributed to this work.

Introduction

The surfaces of Cold Interstellar Dust (CID) is now thought to provide the main sites for the synthesis of complex molecules in the interstellar medium. The icy mantles of such CIDs are composed of a mixture of molecules which may be processed by a variety of energetic particles (e.g. UV photons, cosmic rays) leading to the formation of even more complex molecules. The majority of these synthesized molecules are latterly released into the gas phase by thermal desorption allowing them to be identified most commonly by microwave and millimeter spectroscopy. However, if the synthesized molecule does not sublime, even at higher temperatures (say around 300 K), then a residue remains on the existing dust surface which may then be further processed. To-date most of the experimental work has focused on understanding the chemical composition of the icy mantles and residues that were left behind from energetic processing and, to the best of our knowledge, the physical structures of the residues that are synthesized *in situ* have been only partially explored.

Though there exist a plethora of molecules to study we have focused our attention on the simple aromatic molecule benzene, C_6H_6, since it has an important place in the list of astrochemical molecules due to its ring structure that is the basis for all the polycyclic aromatic hydrocarbon (PAH), the caged carbon molecules (such as Fullerenes) and also has the ability to create aromatic dust. In fact, the discovery of benzene in the interstellar medium (ISM) (Cernicharo, Heras et al. 2001) was a major stepping stone in associating PAH molecules with the unindentified bands in the infrared where in the ultraviolet where the 3.28 μm band observed in the ISM was assigned to the aromatic component of the hydrocarbon content (Chiar, Tielens et al. 2000). Furthermore, the co-existing and much more intense 3.4 μm band has been identified as a characteristic feature of amorphous hydrogenated carbon (a-C:H) dust particles containing mixtures of aromatic and amorphous hydrogenated carbon (Chiar, Tielens et al. 2013). Most recently Mixed Aromatic / Aliphatic Nanoparticles (MAONs) have been proposed to explain other spectral signatures that are observed in the ISM (Kwok and Zhang 2011).

Many laboratory experiments have been carried out to understand the formation of aromatic molecules and also their dissociation both in pure (Callahan, Gerakines et al. 2013 and references therein) and in mixtures of ices (James, Jones et al. 2019 and references therein). While irradiating a pure benzene ice using keV protons the most intense infrared (IR) band of benzene was found to grow in intensity which was attributed to the synthesis of an aromatic residue (Strazzulla and Baratta 1991). Callahan et al. 2013 (Callahan, Gerakines et al. 2013) suggested that this residue may contain molecules such as polyphenyls. However, to-date the structure of the residue resulting from benzene ice irradiation has not been reported. Here, we present results on the physical structure of the residue obtained from the Vacuum UltraViolet (VUV) photon irradiation of benzene ices.

Experiment

The experiments were performed using the high flux beamline BL 03 on the Taiwan Light Source (TLS) at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. VUV light was dispersed with a cylindrical grating monochromator (focal length of 6 m) on a bending magnet beam line of a storage ring (1.5 GeV). More details of the experimental station can be found in the earlier publications (Lu, Chen et al. 2005, Lu, Chen et al. 2008). VUV transmission spectra were recorded before and after deposition of the molecular ice to obtain the incident (I_o) and transmitted (I_t) intensities from which absorbance are calculated using the Beer–Lambert law. The minimum cut off wavelength is determined by the material used for the entrance and exit windows, in this case, lithium fluoride (LiF). In all the spectra a step size of 1 nm was used.

Benzene was deposited on a LiF substrate cooled to 4 K using a Sumitomo RDK helium cryostat, the base pressure of chamber was 3.7 E-8 Torr. The pressure in the gas line filled with benzene vapour was 31 Torr. Since the aim of our experiment was to synthesize enough of the residue to allow images to be recorded we prepared quite a thick sample by depositing benzene onto the LiF substrate for 15 min at pressure of 7 E-8 Torr in the chamber. The photo-absorption spectrum of pure benzene ice was recorded, then the ice was irradiated with 9 eV (137.8 nm) photons for a minimum of 9 hours and up to a maximum of 25 hours. Spectra were recorded after irradiation and the irradiated ice was then warmed to 300 K, with spectra recorded at 10 K intervals. After reaching 300 K the sample was left prior to being removed from the chamber and coated with a 5 nm gold / palladium coating before being placed in the sample mount of a Field Emission Scanning Electron Microscope (FE-SEM).

Result and Discussion

The VUV spectrum of benzene ice formed at 4 K is shown in Figure 1(a) and the spectral signatures observed were found to be in good agreement with those previously reported in literature (Dawes, Pascual et al. 2017, James, Jones et al. 2019). However, since the purpose of the experiment was to understand the physical structure of aromatic residue, which requires a large amount of residue after irradiation, a very thick ice had to be prepared before irradiation at 4 K, thus the most intense absorption bands of benzene in the 140 nm – 220 nm were saturated but the rest of the characteristic bands of benzene ice that appear at 240 nm – 275 nm were clearly seen. Upon irradiation using 9 eV photons, the spectral signature in the 220 nm – 280 nm region was observed to alter, with a broad continuum (Fig 1(b)), a strong indication of chemical processing to have occurred in the irradiated ice, being seen. The ice was then warmed up at the rate of 5 K min^{-1} and at 140 K most of the benzene was found to sublime. Upon further warming the ice up to room temperature, 300 K, a residue was observed only on the irradiated spot on the surface of the LiF window. The VUV spectrum of the residue recorded at 300 K had a broad absorption in the 120 nm – 300 nm range with distinct peaks at 195 nm and 254 nm. The

195 nm peak is in good agreement with residues reported previously in benzene irradiated ices. However, in this work an additional band was observed at 254 nm that could be due to the unsaturated or saturated carbon chain attached to the main aromatic ring for the characteristic band observed at 195 nm. Strazzulla et al 1991 (Strazzulla and Baratta 1991) have discussed that when benzene ices were irradiated by keV protons under astrochemical icy condition and probed using IR spectroscopy, the intensity of the 688 cm^{-1} benzene peak intensifies upon irradiation, which was thought to be a characteristic signature of other synthesised aromatic compounds such as polyphenyls (Callahan, Gerakines et al. 2013). Therefore, by comparing the residue spectrum in Fig 1(c) with that of pure styrene ($C_6H_5CH=CH_2$) ice formed under the similar conditions, we propose that the peak observed at 254 nm could be from aromatic molecules having a hydrocarbon chain attached to the aromatic ring. Even in the irradiated mixtures of benzene and carbon dioxide ices, benzene derivatives were reported (Fig 1(d)) (James, Jones et al. 2019).

The LiF windows containing residues were then detached from the cold head and gold / palladium coated before mounting on to the FE-SEM imaging stub. SEM images were taken at the centre of the window where photon irradiation was carried out. Several small white dots were seen at the irradiation spot (Fig 2a). By further zooming in, we observed flat, two dimensional micrometre-sized flakes (Fig 2(b)). At places close to these sites, we also observed some three dimensional particles, resembling cubes (Fig 2(c)), of about a micrometre in scale. The image shown in Fig 2(d), was observed to have a distinctive geometrical shape. Looking around the irradiation site for more particles, we could see similar cubic features and in addition features surrounded by small stick or rod shaped particles (Fig 2(e)) of approximately 100 nm. A spherical particle was also found and it was also observed to be surrounded by such micron sized rod like features. For the ice irradiated for nearly 25 hours, the residue was again found to contain such cubical particles along with a thin sheet of residue (Fig 3(a-f)). The micron sized cubical particles were found as separate pieces as well as being embedded within the thin sheet. In addition, we observed rods that are half a micron thick and a few micron long, especially even "T" shaped rods (Fig 3(c, d)) were present. Apart from the cubical particles and rods, we also observe particles resembling a "triangular prism" that are a few micrometre thick (Fig 3(e)) and nearly 10 µm long. At other sites in the residue, we also found many micro rods embedded on to the sheet (Fig 3(f)).

Conclusion

In an attempt to understand the physical nature of the residue from benzene ice irradiation we irradiated a benzene ice formed at 4 K using 9 eV photons for 9 and 25 hours, which after warming the ice to room temperature left a residue that was imaged using a FE-SEM. The VUV spectrum of the residue was observed to have aromatic and side chain absorption features from which we ascertain the residue

should be a benzene derivative. Images of the residue revealed many micron sized particles of different geometrical shapes, such as cubes, rods and spheres. Besides such features sheets embedded with micro-rods were also observed. To the best of our knowledge, this is the first report showing the formation of geometrical shapes like cubes, rods and spheres from the irradiated residue of aromatic molecule. The results have implications in our understanding on the physical nature of the interstellar dust, especially the MAONs. In our future experiments we will be investigating the residues from the photon irradiation of icy non-aromatic cyclic molecules.

Acknowledgements

KKR, ESK, JKM, PJ, AB and BS would like to acknowledge the support from Department of Space, Government of India. BS and BNRS thank the support from Sir John Mason Academic Trust for the support in running the synchrotron experiments. BS, NJM and BMC acknowledges the support from NSRRC for the beamtime grant to carry out the irradiation experiments. The authors would like acknowledge the FE-SEM imaging facilities at IIT-Gandhinagar and Inter University Accelerator Center (IUAC), Delhi.

Figure captions

[1] Shows the VUV spectra of (a) pure benzene ice deposited at 4 K on a LiF window, (b) of irradiated benzene ice and as a function of temperature until 300 K, (c) the residue compared with styrene ice and (d) the residue at 300 K in comparison with the residue spectra at 200 K reported by James et al (James , Jones et al. 2019).

[2] Shows the FE-SEM images of (a) particles left after irradiation for nearly 9 hours on top of the LiF window, (b) flakes, (c & d) cubes, (e) cube surrounded by rod shaped particles and (f) spherical particle surrounded by small particles.

[3] Shows the FE-SEM images of particles left after irradiation for nearly 25 hours on top of the LiF window, (a) cubes embedded on a sheet, (b) separate cubes, (c) “T” shaped micro rod, (d) joint micro rods, (e) particle resembling triangular prism and (f) micro rods that are embedded on a sheet.

References

Callahan, M. P., P. A. Gerakines, M. G. Martin, Z. Peeters and R. L. Hudson (2013). "Irradiated benzene ice provides clues to meteoritic organic chemistry." Icarus **226**(2): 1201-1209.

Cernicharo, J., A. M. Heras, A. G. G. M. Tielens, J. R. Pardo, F. Herpin, M. Guélin and L. B. F. M. Waters (2001). "*Infrared Space Observatory's* Discovery of C4H2, C6H2, and Benzene in CRL 618." The Astrophysical Journal **546**(2): L123-L126.
Chiar, J. E., A. G. G. M. Tielens, A. J. Adamson and A. Ricca (2013). "The structure, origin, and evolution of interstellar hydrocarbon grains." The Astrophysical Journal **770**(1): 78.
Chiar, J. E., A. G. G. M. Tielens, D. C. B. Whittet, W. A. Schutte, A. C. A. Boogert, D. Lutz, E. F. van Dishoeck and M. P. Bernstein (2000). "The Composition and Distribution of Dust along the Line of Sight toward the Galactic Center." The Astrophysical Journal **537**(2): 749-762.
Dawes, A., N. Pascual, S. V. Hoffmann, N. C. Jones and N. J. Mason (2017). "Vacuum ultraviolet photoabsorption spectroscopy of crystalline and amorphous benzene." Physical Chemistry Chemical Physics **19**(40): 27544-27555.
James, R. L., N. C. Jones, S. V. Hoffmann and A. Dawes (2019). "VUV spectroscopy of an electron irradiated benzene : carbon dioxide interstellar ice analogue." RSC Advances **9**(10): 5453-5459.
Kwok, S. and Y. Zhang (2011). "Mixed aromatic–aliphatic organic nanoparticles as carriers of unidentified infrared emission features." Nature **479**(7371): 80-83.
Lu, H.-C., H.-K. Chen, B.-M. Cheng, Y.-P. Kuo and J. F. Ogilvie (2005). "Spectra in the vacuum ultraviolet region of CO in gaseous and solid phases and dispersed in solid argon at 10 K." Journal of Physics B: Atomic, Molecular and Optical Physics **38**(20): 3693-3704.
Lu, H.-C., H.-K. Chen, B.-M. Cheng and J. F. Ogilvie (2008). "Absorption spectra in the vacuum ultraviolet region of small molecules in condensed phases." Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **71**(4): 1485-1491.
Strazzulla, G. and G. A. Baratta (1991). "Laboratory study of the IR spectrum of ion-irradiated frozen benzene." Astronomy and Astrophysics **241**: 310-316.

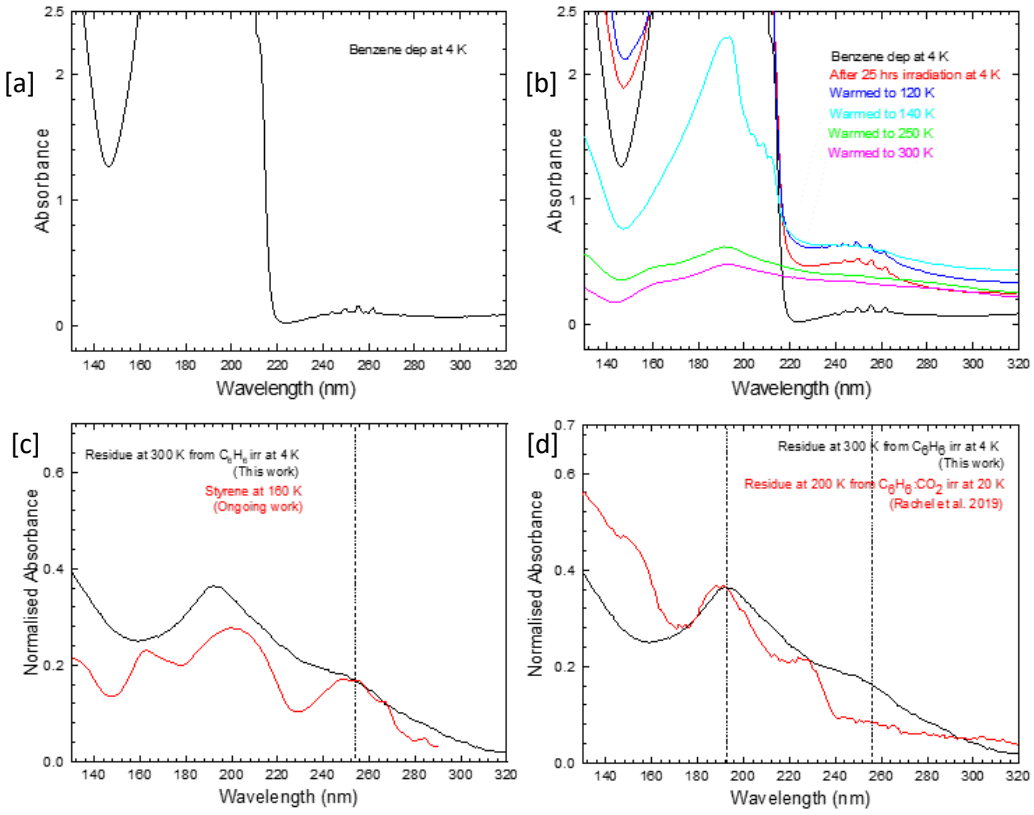

Figure 1

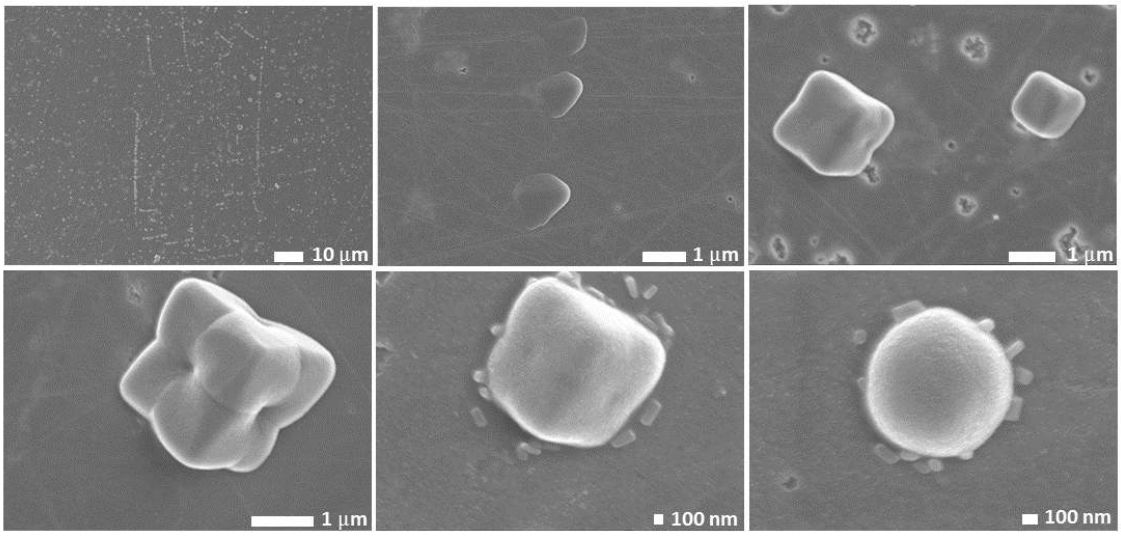

Figure 2

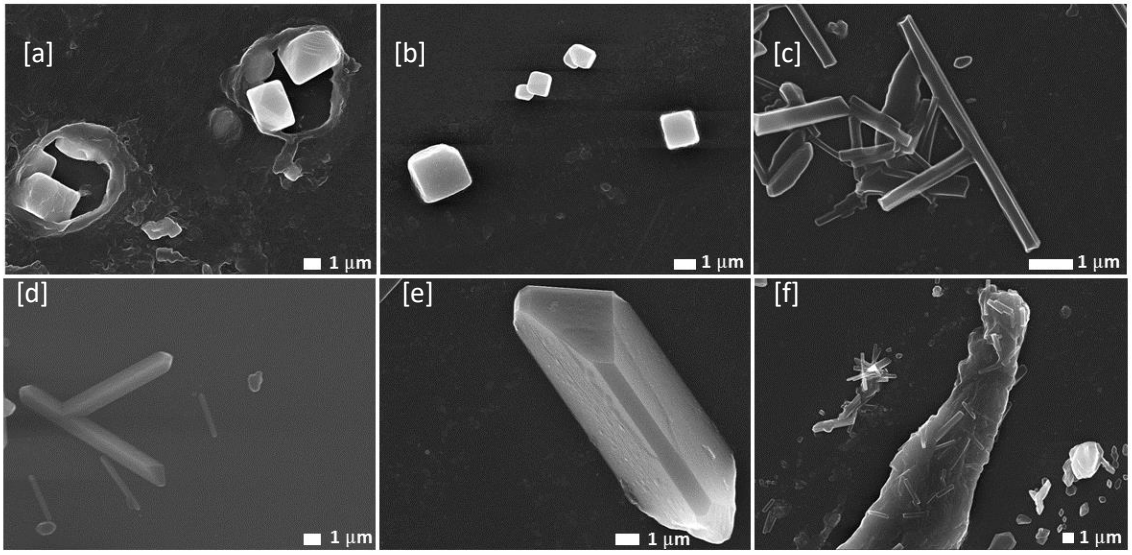

Figure 3