DFT study of five-membered ring PAHs

Gauri Devi¹, Mridusmita Buragohain¹*, Amit Pathak²,

¹Department of Physics, Tezpur University, Tezpur 784 028, India,
ms.mridusmita@gmail.com, *Corresponding author
²Department of Physics, Banaras Hindu University, Varanasi 221 005, India
(amitpah@gmail.com)

Abstract
This work reports a ‘Density Functional Theory’ (DFT) calculation of PAH molecules with a five-member ring to determine the expected region of infrared features. It is highly possible that fullerene molecule might be originated from five-membered ring PAH molecules in the ISM. Effect of ionization and protonation on five-membered ring PAH molecule is also discussed. A detail vibrational analysis of five-membered ring PAH molecule has been reported to further compare with observations and to identify any observational counterpart.

Keywords: PAH, Interstellar molecules, IR spectra, Unidentified infrared bands, Astrochemistry

INTRODUCTION
Polycyclic Aromatic Hydrocarbons (PAHs) are suspected to be one of the stable and largest aromatic compounds present in the interstellar medium (ISM) of the Milky Way and external galaxies. The ubiquitous presence of PAHs has been established through numerous observations of the unidentified infrared (UIR) emission bands in the mid-IR (Tielens, 2008, and references therein). PAH molecules, being stable, can survive acute conditions of the ISM in its regular as well as in ionized or de-hydrogenated phase. These properties help to understand the total carbon budget of the universe. PAHs, because of their ubiquitous presence, may provide some clues to some of the hitherto unsolved problems of astronomical spectroscopy, e.g. the 3.4 μm absorption feature (Sellgren et al., 1994), the far-UV steep of the interstellar extinction curve (Li and Draine, 2001), the 217.5 nm bump (Henning and Salama, 1998) and the diffuse interstellar bands (Salama et al., 1999) that appear as absorption features in the visible region of the interstellar extinction curve. PAHs are also believed to contribute to the understanding of the formation of molecular hydrogen and other carbon based molecular systems (Pauzat et al., 2011). PAHs can also contribute to the energetics and the interstellar chemistry.

A PAH structure basically consists of fused benzenoid rings with de-localized electrons. In some cases, these molecules may consist of five-membered ring with a pl...
nar (fluoranthene, C_{16}H_{10}) or a non-planar structure (corannulene, C_{20}H_{10}). PAH molecules with five-member ring have significant interstellar implications in view of the fact that non-planar systems belong to polar molecules and are involved with rotational transitions (Pilleri et al., 2009). Recently discovered C_{60} and C_{60}^+ (Sellgren et al., 2010; Campbell et al., 2015; Ehrenfreund and Foing, 2015) in the reflection nebula NGC 7023 have attracted attentions towards five-membered ring PAHs because of their possibility to help formation of fullerenes or vice versa. In the top-down model of formation of fullerenes from a PAH molecule, intermediate is a five-membered ring PAH (Berné and Tielens, 2012; Mackie et al., 2015) which might show important spectral characteristics in a UV irradiated source. C_{60} are originally proposed to be the carrier of Diffuse Interstellar Bands (DIBs) in the near-infrared (Campbell et al., 2015; Ehrenfreund and Foing, 2015), but still awaits its confirmation because of the non-availability of a suitable gas phase spectrum. High resolution spatially resolved spectra of these sources might also show the spectral signatures of PAHs with five-member rings. Previous studies on interstellar PAHs reveal that large PAH cations undergo fragmentation through rapid H-loss, leaving the molecule in a fully dehydrogenated form (Ekern et al., 1998; Zhen et al., 2014). The process of fragmentation depends on various factors including the size, compactness and the binding energy of the molecules. Non-compact, linear and comparatively small size PAH molecules are likely to lose a C_2 unit forming a pentagon ring, even before all the peripheral H atoms are lost (Ekern et al., 1998; West et al., 2014).

Motivated by the facts that the spectra of C_{60} and C_{60}^+ have close connections with the PAHs with five-member rings, this study proposes to use Density Functional Theory (DFT) to understand the spectroscopic properties of the different forms of PAHs with five-member rings along with their protonated and cationic counterparts.

**COMPUTATIONAL APPROACH**

Density Functional Theory (DFT) is commonly used to study large molecules as it is computationally efficient, viable and the results closely match those of experiments. Use of this computational methods helps to calculate the harmonic frequencies and intensities of vibrational modes of PAHs in various forms including size, composition and charge states (Langhoff, 1996; Bauschlicher et al., 1997; Bauschlicher and Langhoff, 1997; Langhoff et al., 1998; Hudgins et al., 2001, 2004; Pathak and Rastogi, 2005, 2006, 2007; Pathak and Sarre, 2008; Pauzat, 2011; Candian et al., 2014; Buragohain et al., 2018). The present work uses DFT in combination with a B3LYP functional, along with the 6-311G** basis set used for the purpose of optimization of the molecular structures of PAHs. The optimized geometry has been used to obtain the vibrational frequencies of various modes of PAHs. The use of the large basis set such as the 6-311G** has certain advantages in reducing the overestimation compared to the smaller basis sets and shows good agreement with experiment. But it is also beset with one disadvantage, viz., it does not support the use of the single scaling-factor for the entire range of the vibrational modes (Langhoff, 1996). Upon comparing the theoretical frequencies with laboratory spectroscopic experimental data, three different scaling factors have been determined. The scaling factors obtained are 0.974 for the C-H out-of-plane (oop) mode, 0.972 for
the C-H in-plane and C-C stretching modes and 0.965 for the C-H stretching mode \cite{Buragohain2015, Buragohain2016}. Necessary calibration for the selected PAH variants are incorporated prior to obtaining the spectra. The PAH samples selected for the present works include Corannulene (C_{20}H_{10}), Fluoranthene (C_{18}H_{10}), Benzo-ghi-Fluoranthene (C_{18}H_{10}), Benzo[alaceanthrylene (C_{20}H_{12}) with their pentagon ring at the centre, Azulene (C_{10}H_{8}), Acenaphthylene (C_{12}H_{8}), Fluorene (C_{13}H_{10}) and Benzo-ghi-Fluoranthene with pentagon ring at the edge. The normalized or the relative intensities (\text{Int}_{\text{rel}}) and the computed wavelengths of bands are used to plot a Gaussian profile with the FWHM of 30 cm\(^{-1}\). We have used GAMESS \cite{Schmidt1993} and QChem for our calculation \cite{Shao2015}.

RESULTS AND DISCUSSION

In Fig. 1, the IR spectra of neutral coronene (C_{24}H_{12}) and neutral corannulene (C_{20}H_{10}) are compared with their cationic and protonated forms. The obtained features are the characteristics of various vibrational modes in the respective molecules. Coronene is a compact and very stable PAH molecule due to delocalization of electrons and the aromatic bondings between all adjacent atoms. Corannulene is a five-membered ring PAH with a comparatively less symmetric structure, non planar and a close member to coronene. In neutral coronene, the dominant features appear at \sim 3.3 \mu m and \sim 12 \mu m due to C-H stretching and C-H out of plane vibration respectively. Ionization of a PAH molecule results in a decrease in the intensity of the 3.3 \mu m with an increase of features in the 6-10 \mu m region \cite{Tielens2008}. This is indeed seen for a coronene cation as shown in Fig. 1b. Protonated coronene shows a similar pattern as that of a coronene cation, but with an increase in the total intensity of features due to lower symmetry of the structure. In addition, a 3.4 \mu m feature due to the stretching of the aliphatic C-H bond is also present for a protonated coronene that is observationally detected in various sources in the ISM.

Neutral corannulene (Fig. 1d) shows all the features that are also obtained for a coronene molecule with an additional overlapping out of plane feature at 15.3 \mu m (integrated \text{Int}_{\text{rel}} 0.39). Upon ionization, corannulene cation not only shows an increase in the intensity of 6-10 \mu m region, but a tremendous increase in the number of features (Fig. 1e). This characteristic is not observed from the cation of a regular six-membered ring PAH molecule, for example: coronene. These intense features arise due to a combination of C-C stretching and C-H in plane bending in which pentagon ring also takes part. However, a direct effect of pentagon ring is rarely present. In this 6-10 \mu m region features of a corannulene cation, the most intense feature appears at 9.4 \mu m (\text{Int}_{\text{rel}} 1). Beyond 10 \mu m, the features are mostly characteristics of C-H out of plane vibrational modes. Protonation usually results in breaking of the symmetry of the molecule which eventually leads to more number of features with significant intensity. However, protonated corannulene shows comparatively less intense features (Fig. 1f) compared to its ionized and neutral forms in spite of being protonated. The 3.4 \mu m
Figure 1: Theoretical IR spectra of (a) coronene (C_{24}H_{12}), (b) coronene cation (C_{24}H_{12}^+), (c) protonated coronene (HC_{24}H_{12}^+), (d) corannulene (C_{20}H_{10}), (e) corannulene cation (C_{20}H_{10}^+), (f) protonated corannulene (HC_{20}H_{10}^+)
Figure 2: Theoretical IR spectra of (a) Fluoranthene (C$_{16}$H$_{10}$), (b) Fluoranthene cation (C$_{16}$H$_{10}^{+}$), (c) protonated Fluoranthene (HC$_{16}$H$_{10}^{+}$), (d) Benzo-ghi-Fluoranthene (C$_{18}$H$_{10}$), (e) Benzo-ghi-Fluoranthene cation (C$_{18}$H$_{10}^{+}$), (f) protonated Benzo-ghi-Fluoranthene (HC$_{18}$H$_{10}^{+}$), (g) Azulene (C$_{10}$H$_{8}$), (h) Azulene cation (C$_{10}$H$_{8}^{+}$) and (i) protonated Azulene (HC$_{10}$H$_{8}^{+}$).

A feature is indeed present in the IR spectra of protonated corannulene. The complete list of wavelength and Int$e$$l$ of the modes are given as supplementary material to the paper.

We are also considering comparatively smaller PAHs for our study as smaller PAHs are more prone to form a pentagon ring followed by a loss of C$_{2}$ unit as compared to large size PAHs. The obtained IR spectra are shown in Fig. 2. Like any other neutral PAHs, neutral Fluoranthene, neutral Benzo-ghi-Fluoranthene and neutral Azulene show intense features for C−H stretching (3 $\mu$m region) and C−H out of plane (beyond 10 $\mu$m region). 6-10 $\mu$m region is comparatively less intense for neutral Benzo-ghi-Fluoranthene as expected whereas Fluoranthene and Azulene in their neutral forms show moderately intense 6-10 $\mu$m region. Ionization usually enhances features in the 6-10 $\mu$m region. In our study however, only cationic Benzo-ghi-Fluoranthene seems to show this behavior with an exception for Fluoranthene and Azulene. Ionization of Fluoranthene though leads to an increasing number of features, the intensity of
the individual features seem to be less as compared to its neutral counterpart (Fig. 2b). Also, the most intense feature is present at 11.4 \( \mu m \) (Int\(_{rel} \sim 1 \)) due to C−C stretching of the central five member ring in combination with C−C−C in plane modes. Another C−C−C in plane feature appears at 15.1 \( \mu m \) (Int\(_{rel} \sim 0.68 \)) variation in intensity from that of neutral Azulene. region. However, cationic Fluoranthene shows Ionization of Fluoranthene though leads to an increasing number of features, the intensity of the (Fig. 2b). Protonated form of Fluoranthene shows the expected characteristics; i.e., less intense 3 \( \mu m \) region with significant 6-10 \( \mu m \) region. Cationic Benzo-ghi-Fluoranthene shows a rich 6-10 \( \mu m \) spectra with the most intense feature appearing at 6.8 \( \mu m \) (Int\(_{rel} \sim 1 \)). These are inherent of C−C stretching and C−H in plane vibrational modes, with an involvement from both five and six member rings. In addition, an overlapping 10-13 \( \mu m \) region is present due to C−H out of plane with a partial contribution from C−C−C in plane vibrational modes. Protonated Benzo-ghi-Fluoranthene shows a similar spectral effect as that of protonated Corannulene, where the number of spectral features in the 6-10 \( \mu m \) region decreases with a decrease in the total intensity in comparison to its respective cations. Another striking difference for protonated Benzo-ghi-Fluoranthene is that the C−H out of plane intensity at 11-13 \( \mu m \) decreases, whereas the same feature appears significantly for its neutral and cationic form. In the 6-10 \( \mu m \), cationic Azulene shows a slight decrease in numbers with insignificant variation in intensity from that of neutral Azulene. Protonated Azulene shows rich spectra in 6-10 \( \mu m \) region; the most intense feature appears at 7.2 \( \mu m \) (Int\(_{rel} \sim 1 \)) due to C−C stretching of the pentagon ring in combination with C−C and C−H in plane vibrational mode.

Fig. 3 shows the IR spectra of neutral Acenaphthylene, neutral Fluorene and neutral Benzo[a]aceanthrylene. The obtained spectra show similar features as that of Figs. 2a, 2d and 2g. However neutral Acenaphthylene and neutral Benzo[a]aceanthrylene show additional overlapping out of plane features at 12.1 \( \mu m \) and 11.4 \( \mu m \) (Int\(_{rel} \sim 1 \)) respectively. Although ionization has increased the number of features in the 6-10 \( \mu m \) region, the increase in the intensity of the features in 6-10 \( \mu m \) is not appreciable as compared to its neutral counterpart in Fig. 3a; most intense features appear at 9.2 \( \mu m \) and 6.4 \( \mu m \) (Int\(_{rel} \sim 1 \)) due to the C−C stretching and C−H in plane mode of vibration. Protonated Acenaphthylene shows prominent features in 6-10 \( \mu m \) region with three most intense features at 6.2 \( \mu m \), 6.8 \( \mu m \) and 7.1 \( \mu m \) (Int\(_{rel} \sim 1 \)) due to C−C stretching mode of pentagon ring in combination with C−H in plane mode of vibration. Cationic Fluorene shows no significant 6-10 \( \mu m \) in spite of being ionised. Most intense feature in this case appear at 6.4 \( \mu m \) (Int\(_{rel} \sim 1 \)) due to the C−C stretching and C−H in plane mode of vibration. Protonation of Fluorene has increased both the number and intensity of the features with most intense features at 6.3 \( \mu m \), 6.1 \( \mu m \) and 6.7 \( \mu m \) (Int\(_{rel} \sim 1 \)) due to C−C stretching of the pentagon ring, 6-member rings and C−H in plane vibration mode. Cationic Benzo[a]aceanthrylene shows a tremendous increase in the number and intensity of the features in 6-10\( \mu m \) region; the most intense feature appears at 7.1 \( \mu m \) (Int\(_{rel} \sim 1 \)) due to C−C stretching of the pentagon ring in combination with C−H in plane vibration mode. Protonated Benzo[a]aceanthrylene has shown comparatively less intensity features even though the number of features are increased. The most intense feature appears at 7.7 \( \mu m \) due to the C−C stretching of pentagon ring combined with C−C−C in plane vibration mode.
Figure 3: Theoretical IR spectra of (a) Acenaphthylene (C_{12}H_{8}), (b) Acenaphthylene cation (C_{12}H_{8}^+), (c) protonated Acenaphthylene (HC_{12}H_{8}^+), (d) Fluorene (C_{13}H_{10}), (e) Fluorene cation (C_{13}H_{10}^+), (f) protonated Fluorene (HC_{13}H_{10}^+), (g) Benzo[a]aceanthrylene (C_{20}H_{12}), (h) Benzo[a]aceanthrylene cation (C_{20}H_{12}^+) and (i) protonated Benzo[a]aceanthrylene (HC_{20}H_{12}^+).
Figure 4: Theoretical IR spectra of Benzo-ghi-Fluoranthen (C\textsubscript{18}H\textsubscript{10}) with the pentagon ring at the centre: (a) neutral form (C\textsubscript{18}H\textsubscript{10}), (b) cationic form (C\textsubscript{18}H\textsubscript{10}\textsuperscript{+}) and (c) protonated form (HC\textsubscript{18}H\textsubscript{10}\textsuperscript{+}). The theoretical IR spectra for the neutral, cationic and protonated forms of the Benzo-ghi-Fluoranthen (C\textsubscript{18}H\textsubscript{10}) when the pentagon ring is at the edge are given in (d), (e) and (f) respectively.
As observed from the IR spectra obtained in Fig. 4, it is clear that neutral Benzo-ghi-Fluoranthene with the pentagon ring at the edge shows a rich 6-10 $\mu$m region as compared to the neutral Benzo-ghi-Fluoranthene with the pentagon ring at the centre. These features are due to C–C stretching and C–H in plane vibrational modes with contribution from both five and six member rings; the most intense feature appears at 6.7 $\mu$m ($\text{Int}_{\text{rel}} \sim 1$). With ionization, Benzo-ghi-Fluoranthene with the pentagon ring at the centre shows a rich 6-10 $\mu$m region similar to the cationic Benzo-ghi-Fluoranthene with pentagon ring at the edge. The most dominant feature of cationic Benzo-ghi-Fluoranthene with pentagon ring at the centre appears at 6.9 $\mu$m ($\text{Int}_{\text{rel}} \sim 1$) due to C–C in plane stretching in combination with C–H in plane mode of vibration. In ionized Benzo-ghi-Fluoranthene with the pentagon ring at the edge, there is a slight increase in the intensity of the features, but the number of features are almost the same. However, reverse is the situation in the case of protonation. Protonated Benzo-ghi-Fluoranthene with the pentagon ring at the edge shows a tremendous number of features and increase in intensity of the features in 6-10 $\mu$m region. The most intense features are at 6.4 $\mu$m, 6.8 $\mu$m, 8.9 $\mu$m and 9.6 $\mu$m ($\text{Int}_{\text{rel}} \sim 1$) due to C–C in plane stretching of the pentagon ring and six member ring.

We are providing the complete list of position and intensity of bands as supplementary material to the paper.

CONCLUSION

Five-membered ring PAH molecules are important, particularly in ionized forms in the ISM in view of its possible relation in the formation of $C_{60}^+$. We have carried out DFT study for some selected five-membered ring PAH molecules to understand its spectral characteristics and to find correlation with the observed AIBs, if any. Five-membered ring PAHs do not show any specific extraordinary feature which we can assign to be exclusively coming from the pentagon ring. However, indirect effect of pentagon ring is indeed present which are evident particularly for cations of five-membered ring PAHs. Any PAH cations are expected to produce intense features in the 6-10 $\mu$m region. These features grow even more intense for a five-membered ring PAH cations. This might be an indirect effect coming from the involvement of a pentagon ring. Our study shows some specific spectral characteristics for a neutral five-membered ring PAH (Benzo-ghi-Fluoranthene with the pentagon ring at the edge), that can probably be attributed to the location of the pentagon ring present in it. Interestingly, protonated forms of five-membered ring PAHs show moderate 6-10 $\mu$m region whereas for a PAH containing only six-member ring, a broad and intense 6-10 $\mu$m region is seen. In such a scenario, 6-10 $\mu$m region stands as a strong tool that might be used for the observational search of five-membered ring PAHs in the ISM. A detail study in terms of size and shape is indeed required to draw a concrete conclusion. This study might also be helpful to understand the formation of interstellar fullerenes from five-membered ring PAHs.
Acknowledgements

AP acknowledges financial support from ISRO Respond grant (ISRO/RES/2/401/15-16) and DST EMR grant, 2017. AP thanks the Inter-University Centre for Astronomy and Astrophysics, Pune for associateship. AP and MB acknowledge financial support from DST JSPS grant (DST/INT/JSPS/P-238/2017).

REFERENCES

Bauschlicher, C. W., Langhoff, S. R., Jul. 1997. The calculation of accurate harmonic frequencies of large molecules: the polycyclic aromatic hydrocarbons, a case study. Spectrochimica Acta Part A: Molecular Spectroscopy 53, 1225–1240.

Bauschlicher, C. W., Langhoff, S. R., Sandford, S. A., Hudgins, D. M., Mar. 1997. Infrared Spectra of Perdeuterated Naphthalene, Phenanthrene, Chrysene, and Pyrene. Journal of Physical Chemistry A 101, 2414–2422.

Berné, O., Tielens, A. G. G. M., Jan. 2012. Formation of buckminsterfullerene (C60) in interstellar space. Proceedings of the National Academy of Science 109, 401–406.

Buragohain, M., Pathak, A., Sarre, P., Gour, N. K., Mar. 2018. Interstellar dehydrogenated PAH anions: vibrational spectra. MNRAS474, 4594–4602.

Buragohain, M., Pathak, A., Sarre, P., Onaka, T., Sakon, I., Nov. 2015. Theoretical study of deuteronated PAHs as carriers for IR emission features in the ISM. MNRAS454, 193–204.

Buragohain, M., Pathak, A., Sarre, P., Onaka, T., Sakon, I., Nov. 2016. Mid-infrared vibrational study of deuterium-containing PAH variants. Planet. Space Sci.133, 97–106.

Campbell, E. K., Holz, M., Gerlich, D., Maier, J. P., Jul. 2015. Laboratory confirmation of C_{60}^{+} as the carrier of two diffuse interstellar bands. Nature523, 322–323.

Candian, A., Sarre, P. J., Tielens, A. G. G. M., Aug. 2014. Polycyclic Aromatic Hydrocarbons with Armchair Edges and the 12.7 \mu m Band. ApJ791, L10.

Ehrenfreund, P., Foing, B., 2015. Astrochemistry: Fullerene solves an interstellar puzzle. Nature 523 (7560), 296–297.

Ekern, S. P., Marshall, A. G., Szczepanski, J., Vala, M., 1998. Photodissociation of gas-phase polycyclic aromatic hydrocarbon cations. The Journal of Physical Chemistry A 102 (20), 3498–3504.

Henning, T., Salama, F., Dec. 1998. Carbon in the Universe. Science 282, 2204.

Hudgins, D. M., Bauschlicher, Jr., C. W., Allamandola, L. J., Mar. 2001. Closed-shell polycyclic aromatic hydrocarbon cations: a new category of interstellar polycyclic aromatic hydrocarbons. Spectrochimica Acta 57, 907–930.
Hudgins, D. M., Bauschlicher, Jr., C. W., Sandford, S. A., Oct. 2004. The Impact of Deuteration on the Infrared Spectra of Interstellar Polycyclic Aromatic Hydrocarbons. ApJ614, 770–780.

Langhoff, S. R., 1996. Theoretical infrared spectra for polycyclic aromatic hydrocarbon neutrals, cations, and anions. The Journal of Physical Chemistry 100 (8), 2819–2841.

Langhoff, S. R., Bauschlicher, C. W., Hudgins, D. M., Sandford, S. A., Allamandola, L. J., 1998. Infrared spectra of substituted polycyclic aromatic hydrocarbons. The Journal of Physical Chemistry A 102 (9), 1632–1646.

Li, A., Draine, B. T., Jun. 2001. Infrared Emission from Interstellar Dust. II. The Diffuse Interstellar Medium. ApJ554, 778–802.

Mackie, C. J., Peeters, E., Bauschlicher, Jr., C. W., Cami, J., Feb. 2015. Characterizing the Infrared Spectra of Small, Neutral, Fully Dehydrogenated Polycyclic Aromatic Hydrocarbons. ApJ799, 131.

Pathak, A., Rastogi, S., Jun. 2005. Computational study of neutral and cationic catacondensed polycyclic aromatic hydrocarbons. Chemical Physics 313, 133–150.

Pathak, A., Rastogi, S., Aug. 2006. Computational study of neutral and cationic peri-condensed polycyclic aromatic hydrocarbons. Chemical Physics 326, 315–328.

Pathak, A., Rastogi, S., Jul. 2007. Theoretical infrared spectra of large polycyclic aromatic hydrocarbons. Spectrochimica Acta Part A: Molecular Spectroscopy 67, 898–909.

Pathak, A., Sarre, P. J., Nov. 2008. Protonated PAHs as carriers of diffuse interstellar bands. MNRAS391, L10–L14.

Pauzat, F., Mar. 2011. Computational IR Spectroscopy for PAHs: from the early years to the present status. In: Joblin, C., Tielens, A. G. G. M. (Eds.), EAS Publications Series. Vol. 46 of EAS Publications Series. pp. 75–93.

Pauzat, F., Lattelais, M., Ellinger, Y., Minot, C., Apr. 2011. The interstellar carbonaceous aromatic matter as a trap for molecular hydrogen. MNRAS412, 2729–2734.

Pilleri, P., Herberth, D., Giesen, T. F., Gerin, M., Joblin, C., Mulas, G., Malloci, G., Grabow, J.-U., Brüken, S., Surin, L., Steinberg, B. D., Curtis, K. R., Scott, L. T., Aug. 2009. Search for corannulene (C_{20}H_{10}) in the Red Rectangle. MNRAS397, 1053–1060.

Salama, F., Galazutdinov, G. A., Krelowski, J., Allamandola, L. J., Musaev, F. A., Nov. 1999. Polycyclic Aromatic Hydrocarbons and the Diffuse Interstellar Bands: A Survey. ApJ526, 265–273.
Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S., Windus, T. L., Dupuis, M., Montgomery, J. A., 1993. General atomic and molecular electronic structure system. Journal of Computational Chemistry 14 (11), 1347–1363.

Sellgren, K., Smith, R. G., Brooke, T. Y., Sep. 1994. The 3.2-3.6 micron spectra of monoceros R2/IRS-3 and Elias 16. ApJ433, 179–186.

Sellgren, K., Werner, M. W., Ingalls, J. G., Smith, J. D. T., Carleton, T. M., Joblin, C., Oct. 2010. C_{60} in Reflection Nebulae. ApJ722, L54–L57.

Shao, Y., Gan, Z., Epifanovsky, E., Gilbert, A. T. B., Wormit, M., Kussmann, J., Lange, A. W., Behn, A., Deng, J., Feng, X., Ghosh, D., Goldey, M., Horn, P. R., Jacobson, L. D., Kaliman, I., Khaliullin, R. Z., Kús, T., Landau, A., Liu, J., Pryanov, E. I., Rhee, Y. M., Richard, R. M., Rohrdanz, M. A., Steele, R. P., Sundstrom, E. J., Woodcock III, H. L., Zimmerman, P. M., Zuev, D., Albrecht, B., Alguire, E., Austin, B., Beran, G. J. O., Bernard, Y. A., Berquist, E., Brandhorst, K., Bravya, K. B., Brown, S. T., Casanova, D., Chang, C.-M., Chen, Y., Chien, S. H., Closer, K. D., Crittenden, D. L., Diedenhofen, M., DiStasio Jr., R. A., Dop, H., Dutoi, A. D., Edgar, R. G., Fatehi, S., Fusti-Molnar, L., Ghyssels, A., Golubeva-Zadorozhnaya, A., Gomes, J., Hanson-Heine, M. W. D., Harbach, P. H. P., Hauser, A. W., Hohenstein, E. G., Holden, Z. C., Jagau, T.-C., Ji, H., Kaduk, B., Khystyaev, K., Kim, J., Kim, J., King, R. A., Klunzinger, P., Kosenkov, D., Kowalczyk, T., Krauter, C. M., Lao, K. U., Laurent, A., Lawler, K. V., Levchenko, S. V., Lin, C. Y., Liu, F., Livshits, E., Lochan, R. C., Luenser, A., Manohar, P., Manzer, S. F., Mao, S.-P., Mardirossian, N., Marenich, A. V., Maurer, S. A., Mayhall, N. J., Oana, C. M., Olivares-Amaya, R., O’Neill, D. P., Parkhill, J. A., Perrine, T. M., Peverati, R., Pieniazek, P. A., Prociuk, A., Rehn, D. R., Rosta, E., Russ, N. J., Sergueev, N., Sharada, S. M., Sharma, S., Small, D. W., Sodt, A., Stein, T., Stück, D., Su, Y.-C., Thom, A. J. W., Tsuchimochi, T., Vogt, L., Vydrov, O., Wang, T., Watson, M. A., Wenzel, J., White, A., Williams, C. F., Vanovschi, V., Yeganeh, S., Yost, S. R., You, Z.-Q., Zhang, I. Y., Zhang, X., Zhou, Y., Brooks, B. R., Chan, G. K. L., Chipman, D. M., Cramer, C. J., Goddard III, W. A., Gordon, M. S., Hehre, W. J., Klamt, A., Schaefer III, H. F., Schmidt, M. W., Sherrill, C. D., Truhlar, D. G., Warshel, A., Xua, X., Aspuru-Guzik, A., Baer, R., Bell, A. T., Besley, N. A., Chai, J.-D., Dreuw, A., Dunietz, B. D., Furlani, T. R., Gwaltney, S. R., Hsu, C.-P., Jung, Y., Kong, J., Lambrecht, D. S., Liang, W., Ochsenfeld, C., Rassolov, V. A., Slipchenko, L. V., Subotnik, J. E., Van Voorhis, T., Herbert, J. M., Krylov, A. I., Gill, P. M. W., Head-Gordon, M., 2015. Advances in molecular quantum chemistry contained in the q-chem 4 program package. Mol. Phys. 113, 184–215.

Tielens, A. G. G. M., Sep. 2008. Interstellar Polycyclic Aromatic Hydrocarbon Molecules. ARA&A46, 289–337.

West, B., Useli-Bacchitta, F., Sabbah, H., Blanchet, V., Bodi, A., Mayer, P. M., Joblin, C., 2014. Photodissociation of pyrene cations: Structure and energetics from c16h10+ to c14+ and almost everything in between. The Journal of Physical Chemistry A 118 (36), 7824–7831.
Zhen, J., Castellanos, P., Paardekooper, D. M., Linnartz, H., Tielens, A. G. G. M., Dec. 2014. Laboratory Formation of Fullerenes from PAHs: Top-down Interstellar Chemistry. ApJ797, L30.