Fragmentation and isomerization of polycyclic aromatic hydrocarbons in the interstellar medium: coronene as a case study

Tao Chen1,*, Yi Luo1,2,⋆⋆, and Aigen Li3,⋆⋆⋆

1 School of Engineering Sciences in Chemistry, Biotechnology and Health, Department of Theoretical Chemistry and Biology, Royal Institute of Technology, 10691, Stockholm, Sweden
2 Hefei National Laboratory for Physical Science at the Microscale, Department of Chemical Physics, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, 230026 Anhui, China
3 Department of Physics and Astronomy, University of Missouri, Columbia, MO 65211, USA

December 19, 2019

ABSTRACT

Aims. Due to the limitations of current computational technology, the fragmentation and isomerization products of vibrationally-excited polycyclic aromatic hydrocarbon (PAH) molecules and their derivatives are poorly studied. In this work, we investigate the intermediate products of PAHs and their derivatives as well as the gas-phase reactions relevant to the interstellar medium, with coronene as a case study.

Methods. Based on the semi-empirical method of PM3 as implemented in the CP2K program, molecular dynamics simulations are performed to model the major processes (e.g., vibrations, fragmentations, and isomerizations) of coronene and its derivatives (e.g., methylated coronene, hydrogenated coronene, dehydrogenated coronene, nitrogen-substituted coronene, and oxygen-substituted coronene) at temperatures of 3000 K and 4000 K.

Results. We find that the anharmonic effects are crucial for the simulation of vibrational excitation. For the molecules studied here, H2, CO, HCN, and CH2 are the major fragments. Following the dissociation of these small units, most of the molecules could maintain their ring structures, but a few molecules would break completely into carbon chains. The transformation from hexagon to pentagon or heptagon may occur and the heteroatomic substitutions (e.g., N- or O-substitutions) facilitate the transformation.

Key words. astrochemistry, molecular data, molecular processes, ISM: molecules, methods: laboratory: molecular, (ISM:) photon-dominated region (PDR)

1. Introduction

Polycyclic aromatic hydrocarbon (PAH) molecules are commonly thought to be responsible for the distinctive set of aromatic infrared (IR) emission features at 3.3, 6.2, 7.7, 8.6 and 11.3 μm seen in a wide variety of astrophysical environments (Leger & Puget 1984 Allamandola et al. 1985). In the interstellar medium (ISM), PAHs are vibrationally excited by ultraviolet (UV) and visible stellar photons (Li & Draine 2002). Following the photo-excitation, electronic relaxation takes place predominantly by nonradiative processes, in which the intramolecular vibrational energies are redistributed randomly over all accessible vibrational degrees of freedom of the electronic ground state of the molecules (Allamandola et al. 1989). The vibrational de-excitation occurs from these vibrationally hot molecules, which lead to the aromatic IR emission bands (Tielens 2008). Besides the IR emission, fragmentation is a competing process for a vibrationally excited molecule. However the timescales are very different for these two processes. The fragmentation resulted from photo-driven processes takes place in a timescale of picoseconds (ps), and the loss of H, H2, or C2nHx usually dominates the experimental mass spectra of PAH fragmentation (West et al. 2014 Chen et al. 2018 Zhen et al. 2018). As the redistribution of the absorbed energy and the subsequent fragmentations are random, such a process is usually called statistical fragmentation (Chen et al. 2014 2015).

In addition to photo-driven processes, PAHs are also subjected to energetic ions from stellar winds or supernova explosions (Micelotta et al. 2010). Motivated by this astrophysical interest, the ion-induced fragmentation and molecular growth processes have recently been extensively investigated (Zettergren et al. 2013 Seitz et al. 2013 Stockett et al. 2014a,b Chen et al. 2014 Delaunay et al. 2015 Chen et al. 2015). At low energies (with center-of-mass energy less

* Email: taochen@kth.se
** Email: luo@kth.se
*** Email: lia@missouri.edu
than 1 keV), energetic ions lead to the loss of H and C atoms. The chemical routes and fragmentation products are expected to appreciably differ from that of photo-driven processes (i.e., the statistical fragmentation). This process is called non-statistical fragmentation (Stockett et al. 2014b; Chen et al. 2014, 2015), in which, single C-losses are commonly observed (Stockett et al. 2014, 2015). Non-statistical fragmentation occurs approximately thousand times faster than the statistical fragmentation, i.e., at a timescale of femtoseconds (fs).

At high center-of-mass energies (≥10 keV) of ion-induced dissociation, the statistical fragmentation is dominant, i.e., H-·H2-· and C2nH2- losses are most commonly detected on the experimental mass spectra (Zettergren et al. 2013; Seitz et al. 2013; Delaunay et al. 2013; Chen et al. 2015). This process is crucial for a PAH molecule to reach high internal energy or temperature, which can not be reached through the absorption of single photons below the Lyman limit. The main drawback with the experiments is that only the mass-to-charge ratios can be measured and no detailed information about the products, the intermediate fragments, and the reaction processes can be recorded. To compensate such a drawback, static quantum chemical calculations, e.g., density functional theory (DFT, are performed to reveal the possible structures and reactions associated with a product. The reaction pathways for the formation of H and H2 from PAHs have been revealed through static DFT (Paris et al. 2014; Chen et al. 2015; Castellanos et al. 2018). However, the static methods rely heavily on the empirical knowledge about complex systems/reactions, e.g., the mechanism for C2nH1-· losses or complete fragmentation of carbon skeletons, can hardly be explored using the static methods, instead, molecular dynamics simulations are widely performed to investigate the detailed fragmentation processes (Martín-Somer et al. 2016; Krasnokutski et al. 2017; Trinquier et al. 2017; Simon et al. 2018; Rapacioli et al. 2018; Chen & Luo 2019). In this work, we apply molecular dynamics simulations to investigate the vibrations, H-migrations, dissociations, and isomerizations of PAHs, with coronene (C24H12), a highly symmetric PAH species, as a case study.

In astronomical environments, PAH molecules may include substituents like N in place of C (e.g., see Hudson et al. 2005; Mattioda et al. 2008) and O in place of C (e.g., see Bauschlicher Jr 1998). Observationally, the C–C stretch peaks at wavelengths as short as 6.2 μm, in contrast, both experimental and computational spectra of pure PAHs reveal that it often occurs at ≥6.3 μm. The subtle variations in the peak wavelength of the 6.2 μm C–C emission band are commonly attributed to polycyclic aromatic nitrogen heterocycles — PAHs with one or more nitrogen atoms substituted into their carbon skeleton (Hudgins et al. 2005; Mattioda et al. 2008). In regions with intense UV radiation, small PAHs with fewer than 25 carbon atoms are expected to be partially dehydrogenated (e.g., see Tielens et al. 1987; Mallochi et al. 2008). In H-rich, UV-poor benign regions, PAHs may be superhydrogenated and their edges contain excess H atoms (e.g., see Bernstein et al. 1996; Thrower et al. 2012; Sandford & Bernstein 2013). They may also contain one or several methyl sidegroups revealed by the detection in many PAH sources of a weak satellite emission feature at 3.4 μm which always accompanies the 3.3 μm emission feature (see Yang et al. 2017 and references therein). Finally, experiments have shown that UV photolysis of low-temperature coronene-ice mixtures in dense molecular clouds would lead to the addition to PAHs of various functional groups (Bernstein et al. 1999; Gibb et al. 2000; Bernstein et al. 2002), including methyl (–CH3), methoxy (–OCH3), cyano (–CN), isocyano (–NC), alcohol (–OH), and ketone (>C=O).

To explore the effect of the structural complexities of PAHs on their fragmentation and isomerization processes, we therefore also examine seven derivatives of coronene, including methylated coronene, hydrogenated coronene, dehydrogenated coronene, N-substituted coronene, O-substituted coronene, carbonylc coronene and methoxycoronene (see Figure 1).

This paper is organized as follows. Section 2 shows the importance of the anharmonic effects, without such effects taken into account neither dissociation nor isomerization could be accurately studied. Section 3 elaborates the various relevant fragmentation processes. In Section 4 we show a new H roaming route. Section 5 explores the formation of pentagon and heptagon in PAH derivatives. Finally, we summarize the major results in Section 6.

2. Anharmonicity

For harmonic oscillators, the vibrational energy levels on the parabolic potential energy surface are equally separated (see Figure 2 for illustration), which can be calculated from the following:

\[ E_{\text{har}}(n) = \sum_{i=1}^{3N-6} \hbar \nu_i \left( n_i + \frac{1}{2} \right), \]

where \( \hbar \) is the Planck constant, \( \nu_i \) is the frequency of the \( i \)-th vibrational mode (for a non-linear molecule of \( N \) atoms, there will be \( 3N - 6 \) vibrational modes), and \( n_i \equiv (n_1, n_2, \ldots) \) is the quantum number representing the state of each vibrational mode. The fundamental vibrational frequency of a molecule corresponds to the transition from the ground

\( ^1 \) The 3.3 μm PAH emission band, commonly seen even in UV-intense reflection nebulae, planetary nebulae, and H II regions (Tielens 2008), arises predominantly from small PAHs of ~20–30 carbon atoms [see Figure 7 of Draine & Li (2007)]. Exposed to the intense UV radiation in these regions, compact, pericondensed PAH molecules like coronene, ovalene, circumcoronene are more likely to survive than catetocondensed PAHs with an open, irregular structure. Therefore, in this work we consider coronene as a case study.

\( ^2 \) More recently, Andrews et al. (2016) modeled the physical and chemical processes of coronene, circumcoronene and circumcoronene in the north-west photodissociation region (PDR) of the reflection nebula NGC 7023 where the UV starlight intensity is ~3600 times that of the local ISM. They found that coronene would be fully dehydrogenated in the NGC 7023 PDR. Montillaud et al. (2013) found that coronene would be fully dehydrogenated even in the diffuse ISM.
level \((n = 0)\) to the first vibrational excitation level \((n = 1)\). The zero point energy is \(E_{\text{har}}(0) = (1/2) \sum h\nu_i\). The transitions from \(n = 0\) to \(m > 1\) are called overtones, and the transitions from \(n \geq 1\) to \(m > n\) are called hot transitions or hot bands.

According to eq.1, a molecule with harmonic bonds could reach infinite energy \(E_{\text{har}}(n \to \infty)\) without bond breaking. However, this is not the case in reality. Molecules do dissociate at highly excited vibrational states (Chen et al. 2015; Chen & Luo 2019). The potential energy surface is not a perfectly parabolic shape, instead, it is a non-symmetric open well (i.e., anharmonic potential, see Figure 2), which allows a molecule to break up above certain vibrational states. On the anharmonic potential energy surface, the energy levels are unequally separated (see Figure 2 for illustration), which can be estimated from the following formula (Burcl et al. 2003):

\[
E_{\text{anh}}(n) = \sum_i h\nu_i \left( n_i + \frac{1}{2} \right) + \sum_{i \leq j} \chi_{ij} \left( n_i + \frac{1}{2} \right) \left( n_j + \frac{1}{2} \right),
\]

where \(\chi_{ij}\) the anharmonic coupling which describes the interactions (mode couplings) or resonances among various vibrational modes, can be approximated as a 2-dimensional matrix, and most of its elements are negative, which leads to the anharmonic energy levels \(E_{\text{anh}}(n)\) lower than the corresponding harmonic energy levels \(E_{\text{har}}(n)\). Moreover, due to mode couplings, combination bands (two or more fundamental vibrations are excited simultaneously) show up, and the positions and intensities of the fundamental bands also change (Chen 2018). The band shifting and broadening have been seen in the vibrational spectra calculated by molecular dynamics simulations (Chen 2019), suggesting that anharmonicity and mode couplings are intrinsically included in the molecular dynamics simulations.

3. Fragmentation

Figure 4 shows the experimental mass spectrum of coronene following collisions with \(\text{He}^+\) (Chen et al. 2015). Large amounts of H losses and fragmentations of the carbon skeleton are clearly seen. The mechanism for H losses has been studied in detail (Chen et al. 2015; Castellanos et al. 2018). However, due to the complex isomerization and dissociation features at highly excited vibrational states, the reaction pathway for the fragmentation of the carbon skeleton remains uncharted. Here, we investigate such reactions using molecular dynamics simulations.

It has been reported that the fragmentation only becomes important for temperatures exceeding \(\sim 2200\) K, regardless of the PAH size and the excitation agent (Chen et al. 2015). Therefore, we simulate vibrational excitations starting from 3000 K. We should note that, as shown in Figure 3 for a coronene molecule at a vibrational temperature of \(T \gtrsim 3000\) K, its vibrational energy has to exceed \(\sim 20\) eV. This indicates that the fragmentation process described here would be mostly applicable to UV-intense regions where PAHs are excited by multiple photons or hostile environments where PAHs are collisionally excited by energetic particles. As the energy can be randomly redistributed across all degrees of freedom, such simulations correspond to statistical fragmentations. The simulations are performed using the Quickstep module of the CP2K program package (VandeVondele et al. 2003). The semi-empirical method of PM3 (Stewart 1989) is utilized for electronic structure calculations. It has been shown that such methods are capable of producing reasonable
Internuclear distance

| Energy |
|--------|
| $E_{\text{har}}(1)$ |
| $E_{\text{har}}(2)$ |
| $E_{\text{har}}(3)$ |
| $E_{\text{har}}(4)$ |
| $E_{\text{har}}(5)$ |

Internuclear distance

| Energy |
|--------|
| $E_{\text{anh}}(1)$ |
| $E_{\text{anh}}(2)$ |
| $E_{\text{anh}}(3)$ |
| $E_{\text{anh}}(4)$ |
| $E_{\text{anh}}(5)$ |

Harmonic potential

Anharmonic potential

Dissociation energy

Fig. 2. Harmonic and anharmonic potentials. Harmonic potentials can be described by a parabolic function, which is a symmetric well and closes in both sides. A molecule does not break up with such a harmonic potential. Anharmonic potential is an asymmetric and open well. At certain vibrational states, a molecule dissociates.

vibrational spectra for large compact PAHs (Chen 2019) and high-temperature dissociation pathways for linear PAHs (Chen & Luo 2019). Canonical ensembles (NVT) are performed at multiple temperatures with the Nose-Hoover chain thermostat (Nose 1984b) and Martyna et al. (1992). Starting from optimized geometries of the individual molecules, the systems are equilibrated for 10 ps. The production simulations are subsequently run for 50 ps, at a time step of 0.1 fs.

Figure 5 shows the snapshots from molecular dynamics simulations for 1-hydrocoronene and O-substituted coronene at 3000 K. At such a temperature, no fragment is observed for other molecules. As demonstrated in Figure 5, due to the addition of an extra H atom to a peripheral carbon, the corresponding C–H bond converts from aromatic to aliphatic, which weakens the strength of the connection and eventually leads to the first break up of the C–H bond at 0.28 ps. In comparison to a pristine coronene which breaks up the first C–H bond at 4000 K, the hydrogenated coronene is less stable. This phenomenon is consistent with a recent finding that additional H atoms do not protect PAH molecules from fragmentation (Gatchell et al. 2015). At 0.54 ps a hydrogen atom migrates from the body of the newly formed carbon chain to the unsaturated carbon, and at 0.55 ps a new C–H bond is formed. At 1.26 ps, a hydrogen atom on the head of the carbon chain is dissociated, i.e., sp$^3$ C–C or sp$^2$ C=C bonds tend to form sp C≡C bonds by removing H atoms (Chen & Luo 2019). At the end of the simulation (50 ps), a smaller PAH (with only one ring broken) attached with an $-$CH$_2$ sidegroup is formed, which agrees with the results reported recently for linear PAHs (Chen & Luo 2019).

For the O-substituted coronene, one of the C–O bond breaks up at first at 8.08 ps. Similar to 1-hydrocoronene, the hydrogen atom linked to the other side of the C–O bond migrates to the unsaturated carbon to form a new C–H bond. A CO molecule is formed at 13.82 ps and dissociates from the maternal molecule. No other fragment is observed and no ring is broken until the end of the simulation (50 ps). This process is consistent with the experimental and theoretical studies of the photodissociation of bisanthenequinone cations, in which the CO-loss was found to be the lowest dissociation channel (Chen et al. 2018).

The other molecules dissociate at 4000 K. Again, as shown in Figure 5, such a high vibrational temperature can only be achievable for PAHs vibrationally excited by multiple photons or energetic particles. Figure 6 shows the fragmentation processes of coronene, 1-methylcoronene, coronene with a H-loss, N-substituted coronene, coronene with a hydrogen atom substituted by an oxygen atom, and 1-methoxycoronene. For coronene, a H$_2$-loss is observed, it is very similar to the reaction pathway as reported in the literature, i.e., H$_2$ is formed via H migration without breaking the ring (Paris et al. 2014; Chen et al. 2015; Castellanos et al. 2018). For 1-methylcoronene, the C–CH$_3$ bond breaks at 0.25 ps. In the meantime, one of the hydrogen atoms on the methyl group moves to the carbon atom connected with $-$CH$_3$. At 0.31 ps, a bare coronene molecule is formed and a CH$_2$-loss is observed simultaneously. No more fragment is found until the end of the simulation. However, one of the peripheral hexagons transforms to a pentagon attached with a $-$CH$_2$ sidegroup (see the last cell in the second row of Figure 6 for details).

Both coronene and 1-methylocoronene maintain the pristine aromatic structures, i.e., most of the rings do not break at 4000 K. However, the situation is different for the coronene with a H-loss. At 1.46 ps, three rings are broken to carbon chains, and a hydrogen atom is released. At 3.58 ps, all the rings are broken, and a C$_5$H$_2$ molecule and a longer carbon chain...
Temperature $T$ for coronene with vibrational energy $E$, calculated from its vibrational mode spectrum (see Draine & Li 2001). For coronene to attain a vibrational temperature of $T \gtrsim 2200$, 3000 and 4000 K, its vibrational energy $E$ has to exceed, respectively, $\sim 13.2$, 20.0, and 28.5 eV. This can only be achieved for PAHs excited by multiple photons or energetic particles.

chain are dissociated from each other. Subsequently, a H-loss from the longer chain is observed at 5.22 ps. At 6.59 ps, a $C_{3}H_{2}$ molecule is separated from the longer chain. The molecule is fragmented completely to multiple carbon chains and H atoms.

Fig. 4. Mass spectrum of coronene following collisions with 11.25 keV He$^+$. The highest peaks correspond to the single and double ionizations of coronene without fragmentation on the experimental time scale of $\sim 10 \mu$s. The left and right zoom-ins respectively show the intensity distributions for the losses of different numbers, $n$, of H atoms from the coronene dications and cations. The loss of an even number of H atoms is more favorable than the loss of an odd number of H atoms. Other peaks are due to the fragmentation of the carbon skeleton in one or several steps. See Chen et al. (2015) for details.
1-hydrocoronene:

| Time (ps) | 0 ps | 0.28 ps | 0.54 ps | 0.55 ps | 1.26 ps | 50 ps |
|-----------|------|---------|---------|---------|---------|-------|

O-substituted coronene:

| Time (ps) | 0 ps | 8.08 ps | 8.23 ps | 8.24 ps | 13.82 ps | 50 ps |
|-----------|------|---------|---------|---------|----------|-------|

Fig. 5. Fragmentation of 1-hydrocoronene (top) and O-substituted coronene (bottom) at 3000 K. The orange text in the cells indicates the fragment(s) which are located far away from the maternal molecule.

For the N-substituted coronene, HCN is formed at 0.425 ps. No more fragment is found until the end of the simulation. However, the maternal molecule isomerizes to a smaller PAH attached with carbon chains. The fragmentation of the coronene with a hydrogen atom substituted by an oxygen atom is also violent. At 0.585 ps, five rings are broken, and a CO unit is released from the main body. At 0.815 ps, a hydrogen atom is dissociated. At 1.275 ps, a C_5H_2 molecule is separated. Similar to the case for the coronene with a H-loss, the molecule is dissociated completely to multiple carbon chains, CO and H atoms. One-methoxycoronene is the largest molecule in this study, which contains 40 atoms. At 6.66 ps, a H_2 molecule is released from the methoxyl group. At 15.07 ps, another H_2 molecule is dissociated and the carbon atom on the methoxyl group migrates from the oxygen atom to a neighboring carbon atom, i.e., a –CO unit is formed. As discussed above for both O-substituted coronene and 1-carbonylcoronene, the C–CO bond always breaks before C–H and C–C bonds. At 21.84 ps, a CO-loss is observed. Thereafter, no more fragment is found and no rings break until the end of the simulation.

4. Hydrogen roaming

The roaming of hydrogen atoms is crucial for the formation of aliphatic bonds and H_2 molecules (Paris et al. 2014; Chen et al. 2015; Castellanos et al. 2018). Previous studies have reported hydrogen roaming on the periphery of PAHs. In this study, we find a new roaming route. Figure 7 shows the hydrogen roaming on the carbon skeleton of N-substituted coronene. Two hydrogen migrations are demonstrated: at 4.53 ps, one hydrogen atom is located at the end of a carbon chain, the other one is bound to an inner carbon atom belonging to a pentagon. At 4.545 ps, the carbon atom located at the end of the carbon chain dissociates from the carbon chain, and at 4.55 ps, it migrates to a nearby unsaturated carbon atom belonging to a hexagon. At 4.62 ps, the hydrogen atom located at the inner carbon atom migrates to the carbon chain which transfers a hydrogen atom to a nearby carbon atom at 4.55 ps. At 4.635 ps, all the peripheral carbon atoms become saturated with hydrogen atoms.

5. Formation of pentagon and heptagon

Figure 8 shows the formation of pentagons in the photodissociation of bisanthenequinone cations (Bq^+), in which the Bq^+ cation does not dehydrogenate, but instead fragments via the sequential loss of two neutral carbonyl groups (–CO), causing the formation of pentagons. In addition, the molecule transforms into a bowl-shaped one following the loss of the second –CO group. Such process is proposed to be an important step for the formation of fullerenne in the ISM (Chen et al. 2018). Similar reactions can also be found in Figure 6 and Figure 7.

Figure 9 shows another example of pentagon formation in the N-substituted coronene. At 0.325 ps, a HCN molecule is dissociated from the maternal molecule, which opens two hexagons and form two short carbon chains. At 0.335 ps, one carbon chain closes up to form a pentagon. Then at 0.395 ps another pentagon is formed due to the close up of the other carbon chain. These processes are similar to the formation of pentagons in Bq^+ (Chen et al. 2018). Recent work has also shown that the loss of a HCN molecule in nitrogen-containing PAHs offers a facile pathway towards pentagon formation (de Haas et al. 2017).

Article number, page 6 of 10
Apart from pentagons, we find the formation of heptagon in 1-methoxycoronene. Following the loss of two H₂ molecules, an unsaturated carbon (C=C) and a –CO functional group are formed (see Figure 10 and the last line in Figure 6). At 19.5 ps, the bond linking the C=C and –CO units breaks. As shown above, the unsaturated carbon is very reactive, which always tends to form covalent bonds with a neighboring atom. At 19.53 ps, the unsaturated carbon atom bends towards the neighboring carbon atom, and at 19.54 ps, a heptagon is formed.

6. Concluding Remarks

To date, more than 200 molecules have been identified in the ISM. To understand the origin and evolution of astronomically-relevant molecules, the time-of-flight (TOF) mass spectroscopy experiments in combination with the static quantum chemical calculations are commonly performed. However, such combination can hardly predict intermediate or temporary products/states of the studied molecules, especially when the molecules are vibrationally excited by photons, electrons or stellar winds from nearby stars. In this work, using molecular dynamics simulations, various fragmentation and isomerization features of coronene and its seven functionalized derivatives have been investigated at high temperatures. It is found that most of these molecules do not dissociate at 3000 K, except hydrogenated coronene and oxygen-substituted coronene. These two molecules release hydrogen atoms and CO units at 3000 K. Due to the loss of hydrogen, one of the peripheral ring in hydrogenated coronene breaks, i.e., a six-ring attached with a –C₂H unit structure is formed. However, the structure of the oxygen-substituted coronene remains closed (i.e., no open rings) following the loss of CO. The other six molecules dissociate at 4000 K: (i) bare coronene releases a H₂ molecule without breaking any ring; (ii) 1-methylcoronene releases a CH₂ unit and forms a pentagon bonded with a –CH₂ unit at the end of the simulation;
**N-substituted coronene:**

![Diagram of N-substituted coronene](image)

3.945 ps  4.53 ps  4.545 ps  4.55 ps  4.62 ps  4.635 ps

**Fig. 7.** Hydrogen roaming on C\textsubscript{22}H\textsubscript{10} fragment produced by ejection of HCN from nitrogen-substituted coronene.

![Mass spectrum](image)

**Fig. 8.** Mass spectrum of bisanthenequinone cation (Bq\textsuperscript{+}) following irradiation by laser. The three major peaks respectively represent Bq\textsuperscript{+}, [Bq-CO]\textsuperscript{+} and [Bq-2CO]\textsuperscript{+} (from right to left). The optimized structures of the molecules are shown beside each peak. See Chen et al. (2018) for details.

0.25 ps  0.285 ps  0.325 ps  0.335 ps  0.385 ps  0.395 ps

**Fig. 9.** Formation of pentagons in nitrogen-substituted coronene.

(iii) dehydrogenated coronene (i.e., coronene with a H atom loss) breaks completely to H atoms and carbon chains; (iv) nitrogen-substituted coronene releases a HCN unit and breaks two rings; (v) coronene with a H atom substituted by an oxygen atom dissociates to H, CO and carbon chains of various sizes; and (vi) 1-methoxycoronene releases two H\textsubscript{2} molecules and one CO unit, however, no ring breaks till the end of the simulation. The ring structures with carbon-chain attached and the formations of pentagons and heptagons are commonly observed in the simulations, especially in heteroatomic substituted molecules. The heteroatomic substitutions (e.g., nitrogen- and oxygen-substitutions) play a key role in the formation of pentagons or heptagons. We note that the vibrational temperatures of 3000 and 4000 K examined in this work can not be easily achieved by small PAHs through the absorption of single stellar photons [see Figure 13 of Draine & Li (2001) and Figure 4 of Draine & Li (2007)]. For coronene to attain such high vibrational temperatures, it
1-methoxycoronene:

![Diagram showing formation of heptagons in 1-methoxycoronene.](image)

19.44 ps 19.49 ps 19.5 ps 19.51 ps 19.53 ps 19.54 ps

**Fig. 10.** Formation of heptagons in 1-methoxycoronene.

has to be excited by multiple photons or by energetic particles. Therefore, the processes elaborated in this work mainly apply to PAHs in UV-intense regions where they are excited by multiple photons or in hostile environments where they are collisionally excited by energetic particles. Also, this is further complicated by the fact that coronene should be fully dehydrogenated in PDRs (see Andrews et al. [2016]) and even in the diffuse ISM (see Montillaud et al. [2013]).

**Acknowledgements**

We thank the referee for his/her very helpful comments and suggestions. This work is supported by the Swedish Research Council (Contract No. 2015-06501). The calculations were performed on resources provided by the Swedish National Infrastructure for Computing (SNIC) at the High Performance Computing Center North (HPC2N). AL is supported in part by NASA 80NSSC19K0572 and NSF AST-1816411.

**References**

- Allamandola, L., Tielens, A. G. G. M., & Barker, J. 1985, The Astrophysical Journal, 290, L25
- Allamandola, L., Tielens, A. G. G. M., & Barker, J. 1989, The Astrophysical Journal Supplement Series, 71, 733
- Andrews, H., Candian, A., & Tielens, A. 2016, Astronomy & Astrophysics, 595, A23
- Bauschlicher Jr Jr. C. W. 1998, Chemical Physics, 233, 29
- Bernstein, M. P., Elsila, J. E., Dworkin, J. P., et al. 2002, The Astrophysical Journal, 576, 1115
- Bernstein, M. P., Sandford, S. A., & Allamandola, L. J. 1996, The Astrophysical Journal Letters, 472, L127
- Bernstein, M. P., Sandford, S. A., Allamandola, L. J., et al. 1999, Science, 283, 1135
- Burc, R., Handy, N. C., & Carter, S. 2003, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 59, 1881
- Castellanos, P., Candian, A., Zhen, J., Linnartz, H., & Tielens, A. G. G. M. 2018, Astronomy & Astrophysics, 616, 1
- Chen, T. 2018, The Astrophysical Journal Supplement Series, 238, 18
- Chen, T. 2019, Astronomy & Astrophysics, 622, A152
- Chen, T., Gatchell, M., Stockett, M. H., et al. 2014, The Journal of Chemical Physics, 140, 224306
- Chen, T., Gatchell, M., Stockett, M. H., et al. 2015, The Journal of Chemical Physics, 142, 144305
- Chen, T., & Luo, Y. 2019, Monthly Notices of the Royal Astronomical Society, 486, 1875
- Delaunay, R., Gatchell, M., Rousseau, P., et al. 2015, The Journal of Physical Chemistry Letters, 6, 1536
- Draine, B. T. & Li, A. 2001, The Astrophysical Journal, 551, 807
- Drain, B. T. & Li, A. 2007, The Astrophysical Journal, 657, 810
- Gatchell, M., Stockett, M. H., de Ruette, N., et al. 2015, Physical Review A, 92, 050702
- Gibb, E. L., Whittet, D., Schute, W. A., et al. 2000, The Astrophysical Journal, 536, 347
- Hugoniot, D. M., Bauschlicher Jr Jr. C. W., & Allamandola, L. 2005, The Astrophysical Journal, 632, 316
- Krausokutski, S. A., Huisken, P., Jäger, C., & Henning, T. 2017, The Astrophysical Journal, 836, 32
- Leger, A. & Puget, J. 1984, Astronomy & Astrophysics, 137, L5
- Li, A. Draine, B. T. 2002, The Astrophysical Journal, 572, 232
- Manzi, G., Mulas, G., Cecchi-Pestellini, C., & Joblin, C. 2008, Astronomy & Astrophysics, 489, 1183
- Martín-Sömer, A., Yáñez, M., Hase, W. L., Gaigeot, M.-P., & Spezia, R. 2016, Journal of Chemical Theory and Computation, 12, 974
- Martyna, G. J., Klein, M. L., & Tuckerman, M. 1992, The Journal of Chemical Physics, 97, 2635
- Mattioda, A. L., Rutter, L., Parkhill, J., et al. 2008, The Astrophysical Journal, 680, 1243
- Micelotta, E., Jones, A., & Tielens, A. 2010, Astronomy & Astrophysics, 510, A36
- Montillaud, J., Joblin, C., & Toublan, D. 2013, Astronomy & Astrophysics, 552, A15
- Nosé, S. 1984a, Molecular Physics, 52, 255
- Nosé, S. 1984b, The Journal of Chemical Physics, 81, 511
- Paris, C., Alcalá, M., Martín, F., & Díaz-Tendero, S. 2014, The Journal of Chemical Physics, 140, 204307
- Rapacioli, M., Czaux, S., Foley, N., et al. 2018, Physical Chemistry Chemical Physics, 20, 22427
- Sandford, S. A. & Bernstein, M. P. 2013, The Astrophysical Journal Supplement Series, 205, 8
- Seitz, F., Zettergren, H., Rousseau, P., et al. 2013, The Journal of Chemical Physics, 139, 034309
- Simon, A., Champeaux, J.-P., Rapacioli, M., et al. 2018, Theoretical Chemistry Accounts, 137, 106
- Stewart, J. J. 1989, Journal of Computational Chemistry, 10, 209
- Stockett, M. H., Gatchell, M., Alexander, J. D., et al. 2014a, Physical Chemistry Chemical Physics, 16, 21980
Stockett, M. H., Gatchell, M., de Ruette, N., et al. 2015, International Journal of Mass Spectrometry, 392, 58
Stockett, M. H., Zettergren, H., Adoui, L., et al. 2014b, Physical Review A, 89, 032701
Thrower, J., Jørgensen, B., Friis, E. E., et al. 2012, The Astrophysical Journal, 752, 3
Tielens, A. G. G. M. 2008, Annu. Rev. Astron. Astrophys., 46, 289
Tielens, A. G. G. M., Seab, C., Hollenbach, D., & McKee, C. F. 1987, The Astrophysical Journal, 319, L109
Trinquier, G., Simon, A., Rapacioli, M., & Gadéa, F. X. 2017, Molecular Astrophysics, 7, 37
VandeVondele, J., Krack, M., Mohamed, F., et al. 2005, Computer Physics Communications, 167, 103
West, B., Useli-Bacchitta, F. Sabbah, H., et al. 2014, The Journal of Physical Chemistry A, 118, 7824
Yang, X. J., Glaser, R., Li, A., & Zhong, J. X. 2017, New Astronomy Reviews, 77, 1
Zettergren, H., Rousseau, P., Wang, Y., et al. 2013, Physical Review Letters, 110, 185501
Zhen, J., Chen, T., & Tielens, A. G. G. M. 2018, The Astrophysical Journal, 863, 128