Published in final edited form as:

J Phys Chem A. 2018 March 08; 122(9): 2361–2375. doi:10.1021/acs.jpca.7b11467.

Infrared Spectroscopy of Matrix-Isolated Neutral and Ionized Anthracoronene in Argon[†]

A. L. F. de Barros^{‡,¶}, A. L. Mattioda[¶], J. M. Korsmeyer[§], and A. Ricca^{¶,||}

[‡]Centro Federal de Educação Tecnológica Celso Suckow da Fonseca, Av. Maracanã 229, 20271-110 Rio de Janeiro, RJ, Brazil

[¶]NASA Ames Research Center, Mail Stop 245-6, Moffett Field, CA 94035-1000, USA

[§]Scripps College, 1030 Columbia Ave., Claremont, CA 91711, USA

^{||}Carl Sagan Center, SETI Institute, 189 Bernardo Ave., Mountain View, CA 94043, USA

Abstract

The matrix-isolated mid-IR (MIR) spectrum of neutral and ionized anthracoronene (C₃₆H₁₈, AnthCor) in argon has been measured experimentally, compared to the spectrum of its parent molecules, coronene and anthracene, and analyzed by comparison to a theoretical spectrum computed using density functional theory (DFT). The experimental and theoretical band positions generally agree within 0–10 cm⁻¹. Anthracoronene exhibits extremely intense cation and anion bands around 1330 and 1318 cm⁻¹. The intensity of these two bands approaches what is traditionally observed in the entire 1000–1600 cm⁻¹ range for a typical PAH cation or anion. The matrix-isolated Near-IR (NIR) through Overlap Region (OVR) spectrum of ionized AnthCor in argon has been reported for the first time and compared to the spectrum of its parent molecules, coronene and anthracene. AnthCor cation contains a very strong electronic transition around 6175 cm⁻¹, placing it outside the range of the electronic transitions typically observed for PAHs. Anthracoronene is one of the few PAHs studied to-date which has exhibited the formation of anions upon UV photolysis.

Graphical Abstract

[†]Infrared Spectroscopy of Anthracoronene

Correspondence to: A. L. F. de Barros; A. L. Mattioda.

1- Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are relevant to terrestrial biosciences and astrophysics. On earth, many PAHs have been found to be carcinogenic as well as damaging to reproductive and immune systems in animals¹. Additional research has found that PAHs in aquatic and terrestrial ecosystems can be biodegraded by microorganisms via catabolic pathways^{1–3}. Moreover, PAHs are the most abundant aromatic molecular species in space and they have been observed in reflection nebulae, planetary nebulae, Hii regions, comet nuclei, icy satellites, outer planet rings, and the interstellar medium (ISM)^{4–6}. Furthermore, deuterium enrichments found in meteorites suggest that some Solar System PAHs originated from the ISM⁷.

PAH interstellar infrared emissions are nonthermal in nature, and are produced by the radiative cooling of the PAH molecule after absorbing UV photons^{8,9}. Wherever there is a radiation source strong enough to excite PAH vibrational modes, strong signatures in the mid-infrared (MIR) can be observed at 3.3, 6.2, 7.7, 8.6, 11.2, and 12.7 μm .

In order to determine which PAHs are the source for these interstellar infrared emissions, infrared spectroscopic data of PAHs under interstellar conditions must be collected. Additional laboratory data measured in the UV/visible/near-IR are also needed to provide further evidence of the presence of PAHs. The following experiments have been conducted in an argon (Ar) matrix at a low pressure and temperature. The argon matrix isolates the PAH molecules from each other, avoiding intermolecular interactions and simulating a quasi-gas-phase environment. In this work, the mid-infrared (MIR) spectra of neutral and ionized anthracoronene, $\text{C}_{36}\text{H}_{18}$, as well as near-infrared (NIR) and overlap (OVR) spectra of ionized anthracoronene are reported for the first time. Comparisons are made between the IR spectra of anthracoronene and those of coronene and anthracene, since anthracoronene is a combination of both molecules (Figure 1). In addition to increasing our understanding of PAH vibrational spectroscopy, another purpose of this paper is to summarize the MIR, OVR and NIR spectroscopic properties of anthracoronene for future astrophysical experiments.

2- Experimental and Theoretical Methodologies

2.1- Laboratory Methods

The matrix isolation UV irradiation techniques used in this study have been well described in previous works, so only a brief account of the experimental technique will be given here ^{10–13}. Samples were prepared by the vapor co-deposition of anthracoronene and an over abundance of argon (Ar) onto a 18 K CsI window suspended in a high vacuum chamber ($P \sim 10^{-8}$ Torr) as shown in Figure 2. The sample sublimation temperature (see Fig.2) was monitored by thermocouplers mounted on the Pyrex tube. The solid anthracoronene ($C_{36}H_{18}$) sample was vaporized at a temperature of approximately 329°C. Argon gas was added via an adjacent length of liquid N_2 -cooled copper tubing, at a flow of 50 cm³, freezing simultaneously onto the cold window. The conditions were optimized to produce an Ar:PAH ratio in excess of 1000:1. An infrared spectrum of the deposited sample was recorded once a sufficient amount of neutral material was accumulated (~8% transmission of the strongest features).

The deposited argon matrix-isolated AnthCor (anthracoronene) was irradiated by UV photons using a microwave discharge lamp with flowing H_2 gas at a dynamic pressure of 150 mTorr. The spectrum from the lamp includes the combined 121.6 nm Lyman- α (10.2 eV) and 160 nm (7.8 eV) molecular hydrogen emission bands. The VUV radiation from the lamp enters the sample chamber through a MgF_2 window. The photon flux of the lamp was $(2 \pm 0.5) \times 10^{14}$ photon/(s cm²), as calculated by the actinometry measurement method (details in Mattioda et al.⁹, de Barros et al.¹⁴). The UV lamp had a forward power of 100 W and a reflected power of < 2 W.

Mid-infrared spectra (7000 – 400 cm⁻¹, 1.43 – 25 μ m) were collected on a Biorad Excalibur FTS 4000 FTIR spectrometer using a liquid nitrogen-cooled MCT-B detector in combination with a KBr beam splitter. The NIR spectra (15000 – 9000 cm⁻¹, 0.66 – 1.11 μ m) spectra were collected using a NIR source, quartz beam splitter, and a silicon detector. The spectra between 11000 and 7000 cm⁻¹ (0.91 – 1.43 μ m), referred to as the overlap (OVR) region were collected using the spectrometer's NIR source in conjunction with a quartz beam splitter and a liquid nitrogen-cooled MCT-B detector (typically used for the mid-IR). The number of scans was chosen to optimize both the signal-to-noise ratio as well as time requirements of each experiment. Spectra were collected with a MIR resolution of 0.5 cm⁻¹ (sensitivity of 2), NIR resolution of 1 cm⁻¹ (sensitivity of 1), and OVR resolution of 1 cm⁻¹ (sensitivity of 2). Background spectra were taken on the cold sample window before the AnthCor and argon deposition. MIR spectra were collected after 0, 2, 4, 8, 16, and 32 minutes of UV radiation exposure, and rationed against the MIR background spectra. Plotting the integrated band areas of newly formed species during these photolysis intervals permits the segregation of the anthracoronene anion and cation bands from rogue photo-products such as O_3 (1039 cm⁻¹) and HA_r^{2+} (904 cm⁻¹) as the IR vibrational bands due to different photo-products will grow in at different rates.

Since rogue photo-products are typically small molecular species without electronic transitions in the NIR or OVR, spectra the NIR and OVR region spectra were only taken

after 32 minutes of VUV processing of the sample and rationed against their respective backgrounds to identify the electronic transitions in anthracoronene

Baseline corrections, spectral subtraction, filtering, determination of band positions and intensities were obtained using the Agilent Resolutions Pro software version 4.0, by BioRad. All tabulated results were determined from unaltered data.

2.2- Theoretical Methods

The geometry optimizations and the harmonic frequency calculations were performed using density functional theory (DFT). We used the hybrid B3LYP functional^{17,18}, in conjunction with the cc-pVTZ basis set¹⁹ and the Gaussian09 suite of programs²⁰. The computed harmonic frequencies were scaled to lower frequencies using three scaling factors, namely 0.964 for C-H stretches, 0.979 for the 4–9 microns region, and 0.975 for the region greater than 9 microns. The scaling factors were obtained by fitting to 25 IR bands obtained from gas-phase experiments, namely to the 17 IR allowed bands determined by Pirali et al.²¹ (the 16 bands in Table 1 and the band at 1601 cm⁻¹ shown in Figure 2 of Pirali et al.²¹), the four A_g and the two B_{2g} bands summarized by Behlen et al.²² and the one A_u and one B_{1g} bands summarized by Cané et al.²³. The integrated band intensities, in km mol⁻¹, were broadened in wavenumber space by 3 cm⁻¹ to produce synthetic spectra that were comparable with experimental band widths. The calculations did not include overtones, combination band and resonances, which are expected to be weak compared with fundamentals. The vibrational modes were visualized using the interactive molecular graphics tool Jmol (<http://jmol.sourceforge.net>). The structure of the anthracoronene molecule, showing the benzene rings with the solo (non adjacent C-Hs, (1)), duo (two adjacent C-Hs, (2)) and quartet (four adjacent C-Hs, (4)) C-H groups, is given in Figure 1.

3- Results and Discussions

3.1- Neutral A-values

The A-values (molar absorptivity or integrated band strengths) of the experimentally measured AnthCor bands were determined by summing all theoretical absolute intensities between 1600 and 500 cm⁻¹ (6.25 and 20.0 μm, respectively). The experimental integrated band strength, A_i^{exp}, of AnthCor mode *i* in cm molecule⁻¹, is then obtained by scaling the experimental band area by the sum of theoretical absolute intensities between 1600 and 500 cm⁻¹, as shown in Equation (1):

$$A_i^{exp} = \frac{\int_{v_{i,1}}^{v_{i,2}} \tau_{i,\nu} d\nu}{N(F)} = \sum_{j=0}^M A_j^{AnthCor} \frac{\int_{v_{i,1}}^{v_{i,2}} \tau_{i,\nu} d\nu}{\sum_{i=0}^L \int_{v_{i,1}}^{v_{i,2}} \tau_{i,\nu} d\nu} \quad (1)$$

where $\tau_{i,\nu}$ is the optical depth of mode *i* in the Ar matrix at frequency ν (cm⁻¹); N(F) is the number of molecules (absorbers) present in the sample; A_j^{AnthCor} (cm molecule⁻¹) is the theoretical absolute intensity of vibrational mode *j* in the 1600 to 1000 cm⁻¹ range; *M* is the number of theoretical vibrational modes in the same region; *L* is the number of measured modes; $v_{i,1}$ and $v_{i,2}$ are, respectively, the lower and upper integration boundaries in cm⁻¹ for

absorption feature *i*. These spectral limits were chosen to exclude the contributions of far-IR bands ($< 500\text{ cm}^{-1}$), C-H stretching bands ($> 3000\text{ cm}^{-1}$)¹, potential contamination bands from matrix-isolated water ($1700 - 1580\text{ cm}^{-1}$; $6.33 - 5.88\text{ }\mu\text{m}$), and the overtone and combination bands ($2000 - 1667\text{ cm}^{-1}$; $6 - 5\text{ }\mu\text{m}$) that are present in the experimental data but are not included in the theoretical harmonic approximation. An advantage of this method is that even though there may be some band-to-band variability in the accuracy of the calculated intensity, the total intensity is generally accurate to within 10 – 20%, excluding the C-H stretching region around 3030 cm^{-1} ($3.3\text{ }\mu\text{m}$).

3.1.1- Neutral Anthracoronene Spectra in the MIR—This section focuses on the neutral MIR experimental data for band position and intensity, using the corresponding theory to assign the vibrational modes. The results of the mid-infrared spectroscopic investigation are summarized in Figures 3 and 4 and Tables 1 and 2. Figure 3 shows the comparison between the experimental and theoretical spectra for three distinct mid-infrared regions. The theoretical neutral spectrum (in red) and the normalized ($N = 1 \times 10^{16}$ molecules) experimental non-irradiated spectrum (in black) are shown for (a) 1650 to 1300 cm^{-1} ; (b) 1300 to 1000 cm^{-1} ; and (c) 1000 to 500 cm^{-1} . As is typical for a PAH, the majority of the neutral bands lie in the 1600 to 1000 cm^{-1} region, while the strongest bands fall in the C-H out-of-plane (CH_{oop}) bending region (900 to 700 cm^{-1}). The CH_{oop} bands can be identified as duo (two adjacent C-Hs) CH_{oop} bending modes at 850.7 cm^{-1} , quartet (four adjacent C-Hs) CH_{oop} bending modes at 736 cm^{-1} and solo (no-adjacent C-Hs) CH_{oop} bending modes at 895.1 cm^{-1} , followed by the less intense skeletal out-of-plane band at 575.9 cm^{-1} and 952.9 cm^{-1} (see Figure 3(c)).

A detailed comparison of the experimental and theoretical results is given in Table 1 from 400 to 1650 cm^{-1} and Table 2 for the C-H stretching mode. The strongest experimental combination and overtone bands with frequencies higher than 1650 cm^{-1} are also reported. As indicated in Mackie et al.²⁴ and Mattioda et al.²⁵, the C-H stretching region can be broken up into C-H stretches due to solo ($3040\text{--}3050\text{ cm}^{-1}$), duo ($3050\text{--}3060\text{ cm}^{-1}$), quartet ($3065\text{--}3080\text{ cm}^{-1}$), and bay (pairs of hydrogens on adjacent rings; $3090\text{--}3100\text{ cm}^{-1}$) hydrogens (see Figure 4). The AnthCor molecule inset shows the benzene rings with solo (1), duo (2), and quartet hydrogens (4) contributing to the C-H stretching region. Seven Gaussian functions were chosen to fit the experimental spectrum in the C-H stretching region between $3150 - 2950\text{ cm}^{-1}$ based on the six strongest theoretical C-H stretching bands. Table 2 summarizes the band positions and intensities derived from the fit for neutral AnthCor. The strongest bands are around 3063.2 cm^{-1} and a 3073.6 cm^{-1} , with A-values $> 50\text{ km mol}^{-1}$.

The experimental data are in very good agreement with theory for the $1000\text{--}500$ and $1300\text{--}1000\text{ cm}^{-1}$ regions. Most of the experimental band positions are within a 5 cm^{-1} range of the theoretical band positions, and all fall within 10 cm^{-1} of the theory. Similarly, the relative band strengths are in good agreement with the theoretical absolute intensities, having differences of 6 km mol^{-1} or less for weak and moderate intensities, and 27 km mol^{-1} or less for the stronger bands.

¹The bands in this region are often overestimated by quantum calculations

The agreement between theory and experiment is only qualitative in the 1650-1300 cm^{-1} region with the computed intensities of the bands at 1430 and 1510 cm^{-1} being considerably larger than experiment.

3.1.2- Anthracoronene compared with Coronene and Anthracene—Anthracoronene can be considered as a combination of the coronene and anthracene molecules. It is therefore interesting to compare the results obtained in our experiment with the data of the two ‘parent’ molecules. Anthracoronene has four solo, five duo and one quartet C-H groups, while coronene has a highly symmetric disk-like structure with only duo C-H groups and anthracoronene contains both solo and quartet C-H groups. A comparison of the experimental infrared data for AnthCor with those for coronene^{14,26} and anthracene^{25,27,28,30} (all in argon) in the MIR region is presented in Table 3 for the skeletal out-of-plane, C-H out-of-plane and C-H in-plane bending regions, and in Table 4 for the C-C and C-H stretching regions. It is important to note that for the Szczepanski et al.²⁹ paper, the A-values used are theoretical.

For the skeletal out-of-plane region from 450 to 1000 cm^{-1} , of the five AnthCor bands in this region, three bands can be aligned with the coronene and anthracene bands. The skeletal mode for AnthCor at 468.1 cm^{-1} is also seen for anthracene, but the A-value obtained for AnthCor is lower than for anthracene. The same trend can be seen for the 575.9 cm^{-1} band, which aligns with the 550.5 cm^{-1} band of coronene and 602.9 cm^{-1} of anthracene, and the 952.9 cm^{-1} band, which aligns with the 954.9 cm^{-1} band of anthracene.

The three strongest bands in the C-H out-of-plane region (CH_{oop}) are due to what are traditionally identified as the solo, duo, and quartet C-H groups. The AnthCor PAH exhibits a quartet mode around 736.5 cm^{-1} that can be related to the anthracene quartet mode at around 729 cm^{-1} . The duo AnthCor mode at 850.7 cm^{-1} is related to the coronene duo 857.0 cm^{-1} . The AnthCor solo mode around 895.1 cm^{-1} is related to the anthracene solo mode at 878.5 cm^{-1} . Combining anthracene and coronene to create AnthCor shifts the quartet CH_{oop} mode of anthracene by $\sim 7 \text{ cm}^{-1}$ to the blue, with a decrease in intensity due to only one set of quartet hydrogens. The duo hydrogens in coronene shift by $\sim 7 \text{ cm}^{-1}$ to the red and decrease in intensity as well for AnthCor. However, the solo hydrogen modes in anthracene shift over by 15 cm^{-1} to the blue for AnthCor.

In the C-C and C-H in-plane region, from 1000 to 1500 cm^{-1} , twelve AnthCor bands are observed. Comparing the AnthCor C-C, C-H in plane region to the parent PAHs several things can be noted (see Tables 3 and 4). First, AnthCor bands at 1319.3, 1341.7, 1420.9, 1439.9, 1484.9 and 1612.3 cm^{-1} , line up with anthracene, while those at 1134.1, 1220.3, 1319.3, 1495.3, 1515.6 and 1529.7 cm^{-1} line up with coronene. Second, it is interesting to note that the bands at 1134.1, 1319.3 and 1623.9 cm^{-1} appear to be common among all three PAH structures. These vibrational modes are due to C-H and C-C in-plane modes. Finally, bands at 1261.8 and 1296.9 cm^{-1} appear to be unique to AnthCor. These additional bands are possibly due to the lower symmetry of AnthCor (C_{2v}) compared to that of coronene (D_{6h}) and anthracene (D_{2h}).

The C-H stretching region for AnthCor extends from 3000 to 3100 cm^{-1} , and seven AnthCor bands can be fitted in this region (see Figure 4). The fitted C-H stretching bands of AnthCor tend to fall within $\pm 5 \text{ cm}^{-1}$ of those in coronene and anthracene. From the seven AnthCor bands fitted in this region, two (at 3030.5, and 3035.1 cm^{-1}) match the coronene positions within 1 cm^{-1} , one (at 3063.2 cm^{-1}) matches within 3 cm^{-1} , and one (at 3073.6 cm^{-1}) matches within 4 cm^{-1} . Similarly, two AnthCor bands at 3056.0 and 3063.2 cm^{-1} are less than 2 cm^{-1} from the measured anthracene bands. Bands at 3030.5 and 3063.2 cm^{-1} appear to be common among all three PAH structures.

The band at 3096 cm^{-1} in AnthCor is shifted to higher frequency due to steric repulsion as previously reported by Mattioda et al.²⁵.

3.2- Irradiated Anthracoronene

3.2.1- Spectra of ionized AnthCor in the MIR region—The new bands from AnthCor ions were identified by comparing the non-irradiated spectra (Figure 5(b)) with the spectra taken after 32 minutes of UV irradiation (Figure 5(a)). As with earlier PAH studies^{27–30,32}, the strongest of the ionized bands lie in the 1600 to 1000 cm^{-1} region, with the most intense cation and anion bands appearing at 1330 and 1315 cm^{-1} , respectively. It is interesting to note that, unlike earlier studies, some ion bands are clearly visible in the 500 to 1000 cm^{-1} region.

3.2.2- Identification of the Anthracoronene Ionic Modes—Comparison of the pre-photolysis neutral spectrum to spectra measured after photolysis permits identification of PAH ion features. By subtracting the neutral (non-irradiated) AnthCor spectrum from the 32 min. UV-irradiated spectrum, the resulting spectrum (Figure 6) reveals the photoproduct bands, such as anions and cations present, and directly reflects the amount of neutral AnthCor converted during photolysis.

In order to differentiate between AnthCor ion bands and spurious photo-products, the integrated areas of the bands present in the post-subtraction spectrum (i.e. $\text{AnthCor}_{UV} - \text{AnthCor}_{neutral}$) are plotted against UV photolysis time and are shown in Figure 7. The intensities of AnthCor ion bands peak after 8 – 10 minutes of photolysis and then slightly drop off or remain constant as photolysis continues, which is consistent with previous studies^{10,28,33,34}. Using this method, Figure 7(a) shows the graphs of the integrated band areas versus UV photolysis time for the AnthCor cation and Figure 7(b) shows those for the AnthCor anions. We identified 17 cations bands and 13 anions bands in the region from 500 to 1650 cm^{-1} .

Figure 6 compares the calculated cation spectrum (in red), anion (in blue) and the experimental normalized and subtracted irradiated MIR spectrum (in black) of the MIR spectrum of AnthCor isolated in an argon matrix at 18 K. The spectra have been normalized using the respective N values to display the intensity of the same number of molecules (1×10^{16} molecules) and have been baseline-corrected.

The cations and anions band positions observed in Fig.6(a) from 1650 to 1300 cm^{-1} ; Fig. 6(b) from 1300 to 1000 cm^{-1} ; and Fig.6(c) from 1000 to 700 cm^{-1} are provided in Tables 5 and 6.

3.2.3- A-values of the Anthracoronene Ions—Assuming that all neutral AnthCor molecules are converted into ions², an upper limit to the ionization efficiency can be derived by measuring the percent decrease (d) in the integrated areas of the neutral bands that accompany photolysis. This percent decrease can then be utilized in conjunction with the number of neutral PAH molecules (N^{neutral}) in the samples (determined in Section 3.1 to calculate the number of ions generated ($N^{\text{ion}} = d \times N^{\text{neutral}}$). The number of ions (N^{ions}) can be used in conjunction with the integrated ion band areas to calculate the A-values for the cation and anion bands via Equation (1), (for more details see Mattioda et al.⁹ and de Barros et al.¹⁴). The A-values for the AnthCor cations and anions are provided in Tables 5 and 6 respectively.

3.2.4- Separation of the Anion and Cation Vibrational Modes—The identities of the AnthCor cation photoproducts were separated from the anions bands by repeating the photolysis experiment in an argon matrix doped with an electron acceptor (NO_2) at a concentration of approximately 1 part in 1200. When the AnthCor sample is irradiated, the presence of NO_2 attracts the freed electrons, thereby inhibiting the formation of AnthCor anions and enhancing the production of cations. For a particular UV photoproduct band to be positively identified as a cation, it must grow in the presence of an electron acceptor (e.g. NO_2) and do so in fixed proportion to the other cation bands.

Figure 8 shows the MIR normalized ($N = 1 \times 10^{16}$ molecules) and subtracted spectra after 32 minutes of UV photolysis for AnthCor in argon. Ions bands, which appeared in Ar but don't appear in the Ar/ NO_2 spectrum, are identified as anions, as indicated by a blue cross, while the cation bands are identified by red stars. Some cation and anion bands overlap in frequency and are identified in Figure 8 with both a red star and a blue cross. All ions bands in the 500 to 1650 cm^{-1} are reported in Tables 5 and 6, with their respectable A-values (in km mol^{-1}) and are compared with the determined theoretical positions and absolute intensities (in km mol^{-1}). The symmetry of each vibrational mode is also reported along with the band assignments.

3.2.5- Anthracoronene Cations and Anions—As shown in Table 5, peak positions and relative band intensities for most of the medium and strong cation bands match well the theoretical values. For the most part, theoretical cation band positions are within 9 cm^{-1} of the experimental values, with the exception of three bands at 1040.9, 1402.1, and 1413 cm^{-1} that are ~ 30 , ~ 12 cm^{-1} , and 18 cm^{-1} off the theoretical values, respectively; however, their intensities are in good agreement. The strongest cation band from the experimental spectrum appears at 1330.9 cm^{-1} very close to the predicted theoretical value. The experimental intensities (A values) generally fall within a factor of 2 of the theoretical values. Of the

²Indicated by the consistent decrease in the intensity of neutral modes as irradiation progresses.

eleven strong cation bands observed (100 km mol^{-1}), five coincide with C-C stretching and six C-H coincide with in-plane bending modes, the weakest cation band is at 970.8 cm^{-1} .

The experimental AnthCor anion data is compared to the theoretical band positions and absolute intensities in Table 6. Experimental anion band positions are mostly within 4 cm^{-1} of the theory, while all anion bands fall within 8 cm^{-1} from the predicted theoretical band positions. Most of experimental intensities of the AnthCor anion are within a factor of 2–3 of the theory, except the 1545.0 cm^{-1} band, which is a shoulder of the cation band at 1554.9 cm^{-1} . The moderately strong bands are the most similar in intensity between the experimental and theoretical data. The six strongest anion bands, with A-values $> 100 \text{ km mol}^{-1}$, consist of four at C-C stretching and two C-H in-plane bending modes. The strongest bands at 1245.2 and 1318.8 cm^{-1} , consist of a mixture cation and anion modes.

The strongest theoretical anion band is positioned at 1315.60 cm^{-1} with an absolute intensities of $1408.8 \text{ km mol}^{-1}$, matches with the experimental anion band at 1318.8 cm^{-1} within an intensity of $1477.8 \text{ km mol}^{-1}$.

It is interesting to note that the intensities of the anthracoronene cation bands at 1252.3 cm^{-1} ($1163.5 \text{ km mol}^{-1}$) and 1330.9 cm^{-1} ($1270.3 \text{ km mol}^{-1}$) are close to the average overall intensity of PAH cation bands in the 1000 to 1600 cm^{-1} region which was reported by Weisman et al.¹⁶ to be 2298 km mol^{-1} . Weisman et al.¹⁶ reports the overall average PAH anion intensity for the 1000 – 1600 cm^{-1} range to be 5157 km mol^{-1} . The 1318.8 cm^{-1} anion band, with a strength of $1477.9 \text{ km mol}^{-1}$, represents a significant fraction of this amount.

3.2.6- Anthracoronene Ions Compared to Coronene and Anthracene Ions in the MIR—A comparison of the ionized species of AnthCor to those of coronene and anthracene is presented in Table 7 and Figure 9 for the skeletal out-of-plane, C-H out-of-plane, C-C and C-H in-plane, and the C-C stretching bands. The AnthCor results were compared with the work of Hudgins & Sandford²⁶, Szczepanski et al.²⁷, Hudgins & Allamandola²⁸, Szczepanski et al.²⁹ and Langhoff³⁰ for anthracene and coronene.

Three strong bands at 1418.4 , 1341 , and 1188.6 cm^{-1} dominate in the mid-infrared spectrum of the anthracene cation as observed by Hudgins & Allamandola³⁴. The first has been assigned to a C-C stretch, while the latter two have been attributed to in-plane C-H bends by Szczepanski et al.²⁹. The band at 912.0 cm^{-1} is likely due to a C-H out-of-plane bend, which corresponds nicely to the C-H out-of-plane bending frequency predicted by Szczepanski et al.²⁹. Hudgins & Allamandola³⁵ showed that the anthracene ion band shifts from 878 (neutral) to 912 cm^{-1} .

Because of its high degree of symmetry (D_{6h}), coronene produces a relatively simple spectrum for such a large molecule Hudgins & Sandford²⁶ exhibiting only three visible cations bands, with no visible anions being observed. The largest experimentally observed cation bands, located at 875 cm^{-1} , can be assigned to the duo mode, followed by the 1579.0 cm^{-1} C-C/C-H, and the less intense band at 1369.9 cm^{-1} (Szczepanski et al.²⁹, Hudgins & Allamandola³⁴).

A cation band at 970.8 cm^{-1} is observed in the skeletal in-plane region for AnthCor and is not observed for either coronene or anthracene. The stronger AnthCor cation band at 862.6 cm^{-1} is observed close to the coronene cation band (875 cm^{-1}) and anthracene cation band (876 cm^{-1}). It should be noted that the 875 cm^{-1} coronene cation band is due to the duo CH_{oop} mode, while the 876 cm^{-1} anthracene cation band is due to the solo CH_{oop} mode.

In the C-C and C-H in-plane region, from 1000 to 1500 cm^{-1} , fourteen ionized AnthCor bands are observed. Comparing the C-C, C-H in plane region of AnthCor we observed that the majority of bands of AnthCor can be related to anthracene, possibly due to the lower symmetry of both molecules when compared to coronene. The band at 1388.8 cm^{-1} can be related to the coronene mode at 1378.6 cm^{-1} . The band at 1371.4 cm^{-1} appears to be common among all three PAH structures. The two bands at 1147.9 and 1252 cm^{-1} appear to be unique to AnthCor in this region, similar to what was observed for neutral AnthCor.

In the C-C stretching region ($1500 - 1650\text{ cm}^{-1}$) three ionized AnthCor bands are observed, two anthracene bands were observed 1540 and 1586.4 cm^{-1} , and one coronene band was observed at 1579.0 cm^{-1} . The 1589.6 cm^{-1} band appears to be common among all three PAH structures, while the 1601 cm^{-1} band appears to be unique to AnthCor.

3.3- NIR and OVR for Ionized Anthracoronene

3.3.1- Spectra of NIR and OVR region—The NIR through OVR spectrum of AnthCor after 32 minutes of UV photolysis, in argon is shown in Figure 10. The spectrum has been normalized to 1×10^{16} ions. The bands observed in Figure 10 were fitted with Gaussian, as shown in Figure 11. In Figure 10, the cations are represented as red star, the anions as blue cross and mixtures of both by a red star and a blue cross. Identification of the cation/anion bands was confirmed by the NO_2 data and they are reported in Table 8 with their respective A-values.

Figure 11 shows the Gaussian fits to OVR and NIR spectra of ionized AnthCor in the following regions: (a) 14830 to 12100 cm^{-1} ; (b) 10590 to 10200 cm^{-1} ; (c) 9460 to 9240 cm^{-1} ; (d) 8900 to 5300 cm^{-1} . The fitted curves for the observed bands are in green, with the band centers, A values, and oscillator strengths presented in Table 8.

As can be seen in Figures 10 and 11, the spectrum in the NIR range tends to be dominated by a single strong band or a cluster of strong bands that fall between $14,000$ and $8,000\text{ cm}^{-1}$ (0.77 and $1.25\text{ }\mu\text{m}$). The band at 12526 cm^{-1} is the strongest observed band in this region (Fig.11(a)). Anion bands, when present, tend to be substantially weaker than the corresponding cation bands. However, in the case of AnthCor, we can see that some of the stronger bands in this range are a mixture of cations and anions transitions, such as the bands located at 6555.4 , 6811.2 , 7911.5 and 8017.2 cm^{-1} . The strongest cation band is observed in the OVR region, located at 6175.0 cm^{-1} followed by a cation/anion mixed band at 6555.4 cm^{-1} . The strongest anion band is located in the NIR region is the band at 14267.4 cm^{-1} and exhibit a cation shoulder.

3.3.2- Near-Infrared Band Intensities—Utilizing the band areas from the Gaussian fits, the integrated intensities for individual bands for the OVR and NIR region were determined

by the same way described in Section 3.1.2 for neutral AnthCor. The NIR-OVR integrated absorbance values in Table 8 have been reported in km mol^{-1} , for convenience when comparing them to MIR band strengths, and in oscillator strengths, which are more typical for electronic transitions. In order to convert the integrated absorbance values (km mol^{-1}) for each band to an oscillator strength, the values are multiplied by the total integrated absorbance, $1.87 \times 10^{-7} \text{ mol km}^{-1}$ (Kjaergaard et al.³⁶). Implicit in this conversion is the assumption that most of the strength of the bands corresponding to the electronic transition appears in the spectral regions studied.

3.2.3- Anthracoronene Compared to Coronene and Anthracene in the NIR and OVR—A comparison of the ionized species of AnthCor with coronene and anthracene in the NIR and OVR regions is presented in Table 8. The near-infrared spectrum of the anthracene cation ($\text{C}_{14}\text{H}_{10}^+$) is given in by Szczepanski et al.²⁹, Hudgins & Allamandola³², Andrews & Kelsall³⁷, Mattioda et al.³⁸. The strongest band is located at $\sim 14210.0 \text{ cm}^{-1}$ by Andrews & Kelsall³⁷ and by Hudgins & Allamandola³⁴ as 13832.0 cm^{-1} with an relative intensity of 1.0 (see middle spectrum in Figure 12). The coronene ($\text{C}_{24}\text{H}_{12}^+$) spectra is given by Mattioda et al.⁹. The strongest band is located at $\sim 10,410.0 \text{ cm}^{-1}$ with intensity of $12 \times 10^3 \text{ km mol}^{-1}$ (see top spectrum in Figure 12). In our experiment, we observed at least 26 bands for AnthCor in these regions with the strongest at 6175.0 cm^{-1} exhibiting an intensity of $33.7 \times 10^3 \text{ km mol}^{-1}$, followed by a band at 6555.4 cm^{-1} with intensity of $15.1 \times 10^3 \text{ km mol}^{-1}$. The intensity of the 6555 cm^{-1} and 6175 cm^{-1} bands is significantly greater than any neutral or ion vibrational feature in the MIR, precluding these bands from being an overtone or combination band of the lower frequency modes. Thus we assign the 6555 cm^{-1} and 6175 cm^{-1} bands to electronic transitions of the AnthrCor ions.

Figure 12 shows comparative spectra in the NIR (15000 to 10000 cm^{-1}) of AnthCor in argon at 32 minutes of UV photolysis (black), of 16 minutes UV anthracene in argon (red), and 32 minutes UV coronene in argon (blue). The AnthCor, anthracene and coronene spectra have been normalized to $N = 1 \times 10^{15}$ ions to facilitate comparison and account for differences in ion concentrations and photolysis times.. Given its strong electronic transition at $6,175 \text{ cm}^{-1}$, AnthraCor appears to exhibit the lowest energy electronic transition of any large PAH studied outdate, with the exception of the dibenzopolyacene family³⁹.

Conclusions

This study describes the MIR, NIR, and OVR-IR spectra for neutral and ionized AnthraCor ($\text{C}_{36}\text{H}_{18}$) in an Ar matrix. Band strengths (A-values) and positions are derived for neutral and ionized AnthCor isolated in Ar matrix at 18 K and compared to theory. Experimental band positions and band strengths of neutral and ionized AnthCor are reported in the MIR range of $1650 - 450 \text{ cm}^{-1}$ ($6.06 - 22.2 \mu\text{m}$), NIR range of $15000 - 9000 \text{ cm}^{-1}$ ($0.66 - 1.11 \mu\text{m}$), and the OVR range of 11000 and 6000 cm^{-1} ($0.91 - 1.67 \mu\text{m}$). The AnthCor results are compared with the parent molecules anthracene and coronene. This data will expand the experimental collection of IR spectra in the NASA Ames PAH IR Spectral database^{40,41}.

The VUV photolysis of the matrix-isolated neutral AnthCor induces the formation of cations and anions in contrast to the parent molecules which only formed cations Bouwman et al.¹¹,

Cook et al.¹³, de Barros et al.¹⁴, Hudgins & Allamandola^{28,34}. The cations bands are blueshifted and the anion bands are redshifted compared to the neutral bands the neutral bands as previously reported by Bauschlicher et al.¹⁵. The band positions and strengths of AnthCor cations and anions have been obtained for the majority of bands. The experimental and theoretical band positions generally agree within 0 – 10 cm⁻¹.

The four strongest mid-infrared absorption bands of neutral AnthCor between 1650 to 450 cm⁻¹ were observed to have A-values > 19 km mol⁻¹. The strongest bands fall in the C-H out-of-plane bending modes, as the duo 850.7 cm⁻¹, the quartet 736 cm⁻¹ and the solo 895.1 cm⁻¹ C-H out-of-plane hydrogen motions, followed by the less intense 575.9 cm⁻¹ skeletal out-of-plane band. For the C-H stretching region, two broad bands were observed experimentally, with the stronger band at 3063.2 cm⁻¹ and a weaker one at 3073.6 cm⁻¹. These two bands were deconvolved into six component features. For the ionized molecule, one new band is visible in the C-H out-of-plane region, a duo band at 862.6 cm⁻¹ with an intensity of 48 km mol⁻¹. As has been the case with previous PAH cations studied, no new features could be identified in the C-H stretch region between 3200 and 2900 cm⁻¹. Theory predicts these features to be weaker, implying that the C-H stretching modes of the cation are comparable to or weaker than for the neutral species Hudgins & Allamandola^{28,32,34}.

Comparison of neutral AnthCor IR spectra with those of anthracene and coronene shows that four bands are common among all three PAH structures, such as 575.9, 1134.1, 1319.3 and 1623.9 cm⁻¹ are common to all three PAH structures in the 500 to 1650 cm⁻¹ region as are four bands in the 3000 to 3100 cm⁻¹ region, namely 3030.5, 3035.1 3056.0 and 3063.2 cm⁻¹. However neutral AnthCor exhibits seven bands (456.6, 544.3, 761.5, 795.6, 823.9, 1261.8 and 1296.9 cm⁻¹), which are not seen in either parent PAH molecule, possibly a result of the reduced symmetry of AnthCor.

Of the seventeen bands observed, eight coincide with C-C stretching, seven C-H in-plane bending modes, one duo C-H out-of-plane and one weaker C-C skeletal in plane band. Of the thirteen anions observed, six coincide with the C-H in-plane bending modes, four with the C-C stretching, and three with C-C and C-H in-plane stretching. The weakest anion band is 1007.4 cm⁻¹ with 19.74 km mol⁻¹. AnthCor exhibits two intense ion features at 1245.2 cm⁻¹ (8.03 μm) and 1318.8 cm⁻¹ (7.58 μm) due to the cation and anion forms respectively. Three ionized AnthCor, coronene and anthracene bands are common among all three PAH structures located at 862.6, 1371.4 and 1589.8 cm⁻¹. The strongest common ionized band is at 1371.4 cm⁻¹ (7.3 μm) with 108.49 km mol⁻¹.

The AnthCor ion bands in the near-infrared (NIR) have been also reported. The oscillator strengths and integrated absorbance values have been determined for these electronic transitions. We observed that in this region, cation bands are more predominant than the anion bands. The two strongest electronic transition bands are observed at 6175.0 cm⁻¹ (1.62 μm) and 6555.4 cm⁻¹ (1.53 μm) with intensities > 15 × 10³ km mol⁻¹, placing them lower in energy than typically observed for PAH's.

AnthCor's strongest NIR/OVR ion band at 1.62 μm, is lower in energy than PAHs up to 50 carbon atoms (Mattioda et al.⁹ - NIR band), placing this PAH's NIR transitions, centered

around 1.25 μm , outside the 1 to 1.6 μm range typical of PAH's and PANH's (nitrogen containing PAH's) (Mattioda et al. ³⁸). The NIR/OVR spectrum of AnthCor is different than that of either coronene or anthracene. While Coronene exhibits its strongest electronic transition around 10,400 cm^{-1} (0.96 μm), anthracene's strongest transition is around 13,840 cm^{-1} (0.72 μm). AnthCor's NIR/OVR spectrum is much more complex than that of either anthracene or coronene, exhibiting very strong transitions around 6175, 6555, and 12,526 cm^{-1} (1.62, 1.53, and 0.79 μm), implying that the electronic structure of this PAH is different than either parent molecule.

Acknowledgments

This work was supported by National Aeronautics and the Brazilian Agency CAPES scholarship grant (BEX 5383/15-3), CNPq (301868/2017-4) and the Universities Space Research Association internship. This material is based upon work supported by the National Aeronautics and Space Administration through the NASA Astrobiology Institute under Cooperative Agreement Notice NNH13ZDA017C issued through the Science Mission Directorate. A. Ricca gratefully acknowledges support from NASA's Exobiology Program (NNX13AJ08G).

References

1. Haritash AK, Kaushik CP. Biodegradation Aspects of Polycyclic Aromatic Hydrocarbons (PAHs): A Review. *J Hazard Mater*. 2009; 169(1):1–15. [PubMed: 19442441]
2. Cerniglia CE. Biodegradation of Polycyclic Aromatic Hydrocarbons. *Biodegradation*. 1992; 3(2–3): 351–368.
3. Johnsen AR, Karlson U. Evaluation of Bacterial Strategies to Promote the Bioavailability of Polycyclic Aromatic Hydrocarbons. *Appl Microbiol Biotechnol*. 2004; 63(4):452–459. [PubMed: 14716468]
4. Verstraete L, Pech C, Moutou C, Sellgren K, Wright CM, Giard M, ... Drapatz S. The Aromatic Infrared Bands as Seen by ISO-SWS: Probing the PAH Model. *Astron Astrophys*. 2001; 372(3): 981–997.
5. Geers VC, Augereau JC, Pontoppidan KM, Dullemond CP, Visser R, Kessler-Silacci JE, ... Brown JM. C2D. Spitzer-IRS Spectra of Disks Around T Tauri Stars-II. PAH Emission Features. *Astron Astrophys*. 2006; 459(2):545–556.
6. Izawa MRM, Applin DM, Norman L, Cloutis EA. Reflectance Spectroscopy (350 – 2500nm) of Solid-State Polycyclic Aromatic Hydrocarbons (PAHs). *Icarus*. 2014; 237:159–181.
7. Plows FL, Elsila JE, Zare RN, Busec PR. Evidence That Polycyclic Aromatic Hydrocarbons in Two Carbonaceous Chondrites Predate Parent-Body Formation. *Geochim Cosmochim Acta*. 2003; 67(7): 1429–1436.
8. Sellgren K. The near-Infrared Continuum Emission of Visual Reflection Nebulae. *Astrophys J*. 1984; 277:623–633.
9. Mattioda AL, Hudgins DM, Allamandola LJ. Experimental near-Infrared Spectroscopy of Polycyclic Aromatic Hydrocarbons Between 0.7 and 2.5 μm . *Astrophys J*. 2005; 629(2):1188.
10. Hudgins DM, Sandford SA, Allamandola LJ. Infrared Spectroscopy of Polycyclic Aromatic Hydrocarbon Cations. 1. Matrix-Isolated Naphthalene and Perdeuterated Naphthalene. *J Phys Chem*. 1994; 98(16):4243–4253. [PubMed: 12269375]
11. Bouwman J, Mattioda AL, Linnartz H, Allamandola LJ. Photochemistry of Polycyclic Aromatic hydrocarbons in cosmic water ice-I. Mid-IR Spectroscopy and Photoproducts. *Astron Astrophys*. 2011; 525:A93.
12. Mattioda AL, Cook A, Ehrenfreund P, Quinn R, Ricco AJ, Squires D, ... Agasid E. The O/OREOS Mission: First Science Data from the Space Environment Viability of Organics (SEVO) Payload. *Astrobiology*. 2012; 12(9):841–853. [PubMed: 22984872]
13. Cook AM, Ricca A, Mattioda AL, Bouwman J, Roser J, Linnartz H, ... Allamandola LJ. Photochemistry of Polycyclic Aromatic Hydrocarbons in Cosmic Water Ice: The Role of PAH Ionization and Concentration. *Astrophys J*. 2015; 799(1):14.

14. de Barros ALF, Mattioda AL, Ricca A, Cruz-Diaz GA, Allamandola LJ. Photochemistry of Coronene in Cosmic Water Ice Analogs at Different Concentrations. *Astrophys J*. 2017; 848(2): 112. [PubMed: 29151610]
15. Bauschlicher CW Jr, Peeters E, Allamandola LJ. The Infrared Spectra of Very Large, Compact, Highly Symmetric, Polycyclic Aromatic Hydrocarbons (PAHs). *Astrophys J*. 2008; 678:316.
16. Weisman JL, Mattioda A, Lee TJ, Hudgins DM, Allamandola LJ, Bauschlicher CW Jr, Head-Gordon M. Electronic Transitions in the IR: Matrix Isolation Spectroscopy and Electronic Structure Theory Calculations on Polyacenes and Dibenzopolyacenes. *Phys Chem Chem Phys*. 2005; 7(1):109–118.
17. Becke AD. A New Mixing of Hartree-Fock and Local Density-Functional Theories. *J Chem Phys*. 1993; 98(2):1372–1377.
18. Stephens PJ, Devlin FJ, Chabalowski C, Frisch MJ. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J Chem Phys*. 1994; 98(45):11623–11627.
19. Dunning TH Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron Through Neon and Hydrogen. *J Chem Phys*. 1989; 90(2):1007–1023.
20. Frisch, MJ., Trucks, GW., Schlegel, HB., Scuseria, GE., Robb, MA., Cheeseman, JR., Scalmani, G., Barone, V., Mennucci, B., Petersson, GA., et al. Gaussian 09, Revision A.1. Gaussian, Inc; Wallingford, CT: 2009.
21. Pirali O, Vervloet M, Mulas G, Mallocci G, Joblin C. High-Resolution Infrared Absorption Spectroscopy of Thermally Excited Naphthalene. Measurements and Calculations of Anharmonic Parameters and Vibrational Interactions. *Phys Chem Chem Phys*. 2009; 11(18):3443–3454. [PubMed: 19421547]
22. Behlen FM, McDonald DB, Sethuraman V, Rice SA. Fluorescence Spectroscopy of Cold and Warm Naphthalene Molecules: Some New Vibrational Assignments. *J Chem Phys*. 1981; 75(12): 5685–5693.
23. Cané E, Palmieri P, Tarroni R, Trombetti A, Handy NC. The High-Resolution Infrared Spectra of Naphthalene-h8 and Naphthalene-d8: Comparison of Scaled SCF and Density Functional Force Fields. *Gazz Chim Ital*. 1996; 126(5):289–296.
24. Mackie CJ, Candian A, Huang X, Maltseva E, Pettrignani A, Oomens J, Tielens AG. The Anharmonic Quartic Force Field Infrared Spectra of Five Non-Linear Polycyclic Aromatic Hydrocarbons: Benz[a]anthracene, Chrysene, Phenanthrene, Pyrene, and Triphenylene. *J Chem Phys*. 2016; 145(8):084313. [PubMed: 27586928]
25. Mattioda AL, Bauschlicher CW, Ricca A, Bregman J, Hudgins DM, Allamandola LJ. Infrared Spectroscopy of Matrix-Isolated Neutral Polycyclic Aromatic 22 Nitrogen Heterocycles: The Acridine Series. *Spectrochim Acta Part A Mol Biomol Spectrosc*. 2017; 181:286–308.
26. Hudgins DM, Sandford SA. Infrared Spectroscopy of Matrix Isolated Polycyclic Aromatic Hydrocarbons. 1. PAHs Containing Two to Four Rings. *J Phys Chem A*. 1998; 102(2):329–343.
27. Szczepanski J, Vala M, Talbi D, Parisel O, Ellinger Y. Electronic and Vibrational Spectra of Matrix Isolated Anthracene Radical Cations: Experimental and Theoretical Aspects. *J Chem Phys*. 1993; 98(6):4494–4511.
28. Hudgins DM, Allamandola LJ. Infrared Spectroscopy of Matrix-Isolated Polycyclic Aromatic Hydrocarbon Cations. 2. The Members of the Thermodynamically Most Favorable Series Through Coronene. *J Phys Chem*. 1995; 99(10):3033–3046. [PubMed: 11538457]
29. Szczepanski J, Vala M. Infrared Frequencies and Intensities for Astrophysically Important Polycyclic Aromatic Hydrocarbon Cations. *Astrophys J*. 1993; 414:646–655.
30. Langhoff SR. Theoretical Infrared Spectra for Polycyclic Aromatic Hydrocarbon Neutrals, Cations, and Anions. *J Phys Chem*. 1996; 100(8):2819–2841.
31. Hudgins DM, Sandford SA. Infrared spectroscopy of matrix isolated polycyclic aromatic hydrocarbons. 2. PAHs containing five or more rings. *J Phys Chem A*. 1998; 102(2):344–352.
32. Hudgins DM, Allamandola LJ. The Spacing of the Interstellar 6.2 and 7.7 Micron Emission Features as an Indicator of Polycyclic Aromatic Hydrocarbon Size. *Astrophys J Lett*. 1999; 513(1):L69.

33. Hudgins DM, Allamandola LJ. Infrared Spectroscopy of Matrix-Isolated Polycyclic Aromatic Hydrocarbon Cations. 4. The Tetracyclic PAH Isomers Chrysene and 1, 2-Benzanthracene. *J Phys Chem A*. 1997; 101(19):3472–3477. [PubMed: 11541094]
34. Hudgins DM, Allamandola LJ. Infrared Spectroscopy of Matrix-Isolated Polycyclic Aromatic Hydrocarbon Cations. 3. The Polyacenes Anthracene, Tetracene, and Pentacene. *J Phys Chem*. 1995; 99(22):8978–8986. [PubMed: 11538316]
35. Hudgins DM, Allamandola LJ. Interstellar PAH Emission in the 11–14 Micron Region: New Insights from Laboratory Data and a Tracer of Ionized PAHs. *Astrophys J Lett*. 1999; 516(1):L41.
36. Kjaergaard HG, Robinson TW, Brooking KA. Calculated CH-Stretching Overtone Spectra of Naphthalene, Anthracene and Their Cations. *J Phys Chem A*. 2000; 104(48):11297–11303.
37. Andrews L, Friedman RS, Kelsall BJ. Vibronic Absorption Spectra of Condensed Ring Aromatic Cation Systems in Solid Argon. *J Phys Chem*. 1985; 89(19):4016–4020.
38. Mattioda AL, Rutter L, Parkhill J, Head-Gordon M, Lee TJ, Allamandola LJ. Near-Infrared Spectroscopy of Nitrogenated Polycyclic Aromatic Hydrocarbon Cations from 0.7 to 2.5 μm . *Astrophys J*. 2008; 680(2):1243.
39. Mattioda AL, Bauschlicher CW, Bregman JD, Hudgins DM, Allamandola LJ, Ricca A. Infrared Vibrational and Electronic Transitions in the Dibenzopolyacene Family. *Spectrochim Acta Part A: Mol and Biomol Spectrosc*. 2014; 130:639–652.
40. Bauschlicher CW Jr, Boersma C, Ricca A, Mattioda AL, Cami J, Peeters E, Allamandola LJ. The NASA Ames Polycyclic Aromatic Hydrocarbon Infrared Spectroscopic Database: the Computed Spectra. *Astrophys J Suppl Ser*. 2010; 189(2):341.
41. Boersma C, Bauschlicher CW Jr, Ricca A, Mattioda AL, Cami J, Peeters E, Allamandola LJ. The NASA AMES PAH IR Spectroscopic Database Version 2.00: Updated Content, Web Site, and on (off) Line Tools. *Astrophys J Suppl Ser*. 2014; 211(1):8.

Figure 1.
Structure of a) coronene - $C_{24}H_{12}$, b) anthracene - $C_{14}H_{10}$ and c) anthracoronene - $C_{36}H_{18}$ molecules, showing the benzene rings with solo (1), duo (2) and quartet (4) C-H groups.

Figure 2. Schematic of the experimental sample chamber. The inlets where the PAH sample tube connects and the matrix gas enters the chamber through copper tubing are marked. The H₂ lamp is also pictured. The CsI window rotates to permit deposition, data collection and UV photolysis.

Figure 3.

Comparison of the neutral theoretical spectrum (in red) and the experimental normalized non-irradiated spectrum (in black) for the Mid-infrared region of anthracoronene isolated in an argon matrix at 18 K. (a) from 1650 to 1300 cm^{-1} ; (b) from 1300 to 1000 cm^{-1} ; (c) from 1000 to 500 cm^{-1} . * denotes CO_2 from purged air and ** denotes H_2O in the argon matrix. The experimental spectrum has been normalized to $N = 1 \times 10^{16}$ molecules. The theoretical spectra were convolved using a Gaussian with a FWHM of 3 cm^{-1} for comparison purposes.

Figure 4.

The MIR spectrum (3150 to 2950 cm^{-1}) of the C-H stretching region for neutral anthracoronene isolated in an argon matrix at 18 K . The spectrum has been normalized to $N = 1 \times 10^{16}$ molecules. Seven Gaussian curves (green) have been fitted to this region based on theory. The fitting results of the C-H stretching region for the solo, duo, quartet and bay hydrogens between 3105 to 3000 cm^{-1} are presented in Table 2.

Figure 5. MIR spectra from 1650 to 450 cm^{-1} : (a) after 32 minutes of UV photolysis; (b) Non-irradiated in an argon matrix at 18 K. * denotes CO_2 from purged air and ** denotes H_2O in the argon matrix.

Figure 6.

Comparison of the theoretical cation spectrum (in red), theoretical anion spectrum (in blue) and the experimental photolyzed neutral-subtracted spectrum (in black) for the Mid-infrared spectrum of anthracoronene isolated in an argon matrix at 18 K. (a) from 1650 to 1300 cm⁻¹; (b) from 1300 to 1000 cm⁻¹; (c) from 1000 to 700 cm⁻¹. The experimental spectrum has been normalized to 1×10^{16} molecules.

Figure 7.
Growth of the anthracorone integrated band areas a function of UV photolysis time: (a) cations band and (b) anions bands.

Figure 8.

MIR spectra subtracted and normalized ($N = 1 \times 10^{16}$ molecules) after 32 minutes of UV irradiation for anthracorone from 1600 to 700 cm^{-1} . The bands identified with red stars are related to cations, while those identified by blue crosses are identified as anions. The two bands identified by both a star and a cross are related to cations and anions. Those values are presented in Tables 5 and 6.

Figure 9.

Comparative MIR spectra for UV-photolyzed spectra of anthracoronene (32 min)(black), anthracene (16 min)(red), and coronene (32 min)(blue) isolated in an argon matrix. Spectra were obtained from Hudgins & Allamandola²⁸ and de Barros et al.¹⁴ for anthracene and coronene, respectively. ** denotes H₂O in the argon matrix.

Figure 10.

AnthCor normalized spectrum in the NIR and OVR 15100 to 4500 cm^{-1} region obtained after 32 minutes of UV photolysis of anthracoronene in argon. The two insets show a zoom in the region from 10590 to 10200 cm^{-1} (green) and from 9460 to 9240 cm^{-1} region (red). The spectrum has been normalized to $N = 1 \times 10^{16}$ molecules. The cation and anion bands are marked using a red star and blue cross, respectively

Figure 11.

The OVR and NIR spectrum region of ionized anthracoronene in an argon matrix at 18 K: (a) 14830 to 12100 cm^{-1} ; (b) 10590 to 10200 cm^{-1} ; (c) 9460 to 9240 cm^{-1} and (d) 8900 to 5300 cm^{-1} . The spectra have been fitted using Gaussian functions, which are shown in green along with their peak positions. The fittings results are presented in Table 7.

Figure 12.

Comparative NIR spectra (15000 to 10000 cm^{-1}) after 32 minutes of UV irradiation of anthracoronene in argon (black), after 16 minutes of UV irradiation of anthracene in argon (red), and after 32 minutes of UV irradiation of coronene in argon (blue). The three PAH spectra were each normalized to $N = 1 \times 10^{15}$ ions to account to facilitate comparison and account for differences in ion concentrations and varying photolysis times. Spectra were obtained from Hudgins & Allamandola²⁸ and Mattioda et al.⁹ for anthracene and coronene, respectively.

Table 1

Summary of neutral anthracoronene ($C_{36}H_{18}^0$) band positions in an argon matrix for the MIR (450 to 2000 cm^{-1}) region (in cm^{-1} and μm), A-values (km mol^{-1}), theoretical band positions (cm^{-1}), absolute intensities (km mol^{-1}), and symmetry from theory, and assignments. Bands with A-values^a < 2 km mol^{-1} were not included in this table.

Wavenumber (cm^{-1})	Wavelength (μm)	A-value ^a (km mol^{-1})	Theoretical Position (cm^{-1})	Theoretical ^b Intensity (km mol^{-1})	Symmetry	Assignment/Comments
456.6	21.9	6.4	461.2	10.5	b_1	Skeletal out-of-plane
468.1	21.4	6.6	468.8	7.4	b_1	Skeletal out-of-plane
544.3	18.4	11.3	547.9	7.7	b_1	Skeletal out-of-plane
575.9	17.4	19.9	578.8	15.3	b_1	Skeletal out-of-plane
736.5	13.6	53.6	737.3	41.7	b_1	C-H quartet out-of-plane bending
761.5	13.2	3.1	752.1	3.6	a_1	Skeletal in-plane
777.8	12.9	10.9	773.6	13.3	a_1	Skeletal in-plane
795.6	12.6	2.9	788.7	4.6	b_1	C-H duo out-of-plane bending
823.9	12.1	9.6	820.5	7.7	b_1	C-H duo out-of-plane bending
850.7	11.8	92.2	851.8	81.8	b_1	C-H duo out-of-plane bending
895.1	11.2	58.1	897.7	67.7	b_1	C-H solo out-of-plane bending
952.9	10.5	3.2	954.3	3.9	b_1	C-H duo/duo out-of-plane bending
1134.1	8.8	10.3	1133.9	6.8	b_2	C-H in-plane bending
1220.3	8.2	4.2	1220.4	3.9	a_1	C-H in-plane bending
1261.8	7.9	6.8	1262.0	6.9	b_2	C-H in-plane bending
1282.8	7.8	5.7	1281.5	8.9	b_2	C-H in-plane bending
1296.9	7.7	4.3	1300.4	2.9	b_2	C-H in-plane bending
1319.3	7.6	7.4	1313.6	5.3	a_1	C-H in-plane bending
1341.7	7.5	6.7	1337.0	7.7	a_1	C-H in-plane bending
1420.9	7.0	3.5	1429.5	17.9	a_1	C-H in-plane bending
1439.9	6.9	5.3	1447.6	3.6	a_1	C-H in-plane bending
1484.9	6.7	3.6	1480.0	1.7	a_1	C-H in-plane bending
1495.3	6.7	5.4	1499.6	3.0	b_2	C-H in-plane bending
1515.6	6.6	7.8	1508.6	11.8	a_1	C-H in-plane bending

Wavenumber (cm ⁻¹)	Wavelength (μm)	A-value ^a (km mol ⁻¹)	Theoretical Position (cm ⁻¹)	Theoretical ^b Intensity (km mol ⁻¹)	Symmetry	Assignment/Comments
1529.7	6.5	3.4	1533.7	5.3	a ₁	C-C stretching
1608.3	6.2	3.3	-	-	a ₁	C-C stretching
1612.3	6.2	2.7	1612.6	2.4	a ₁	C-C stretching
1623.9 ^c	6.2	2.1	{1620.1 1625.2}	2.7	a ₁	C-C stretching
1661.1	6.0	11.9	-	-	b ₂	C-C stretching
1699.9	5.9	18.6	-	-	-	overtones and/or combinations modes
1783.7	5.6	26.2	-	-	-	overtones and/or combinations modes
1797.6	5.6	5.2	-	-	-	overtones and/or combinations modes
1893.2	5.3	6.9	-	-	-	overtones and/or combinations modes
1935.6	5.1	2.7	-	-	-	overtones and/or combinations modes

^b Theoretical value were determined for the gas phase with errors of ± 4.4 cm⁻¹ (average) and ± 11.7 cm⁻¹ (maximum),

^c possible water band.

Table 2

Summary of the neutral anthracenone ($C_{36}H_{18}^0$) band positions in an argon matrix for the C-H stretching region (cm^{-1} and μm) and A-values ($km\ mol^{-1}$), $-I$) obtained by fitting the experimental spectrum using seven Gaussian functions. Theoretical band positions (cm^{-1}), absolute intensities ($km\ mol^{-1}$), symmetry from theory, and assignments are also listed

Wavenumber ^a (cm^{-1})	Wavelength ^a (μm)	A-value ^a ($km\ mol^{-1}$)	Theoretical Position (cm^{-1})	Theoretical Intensity ($km\ mol^{-1}$)	Symmetry	Assignment/Comments
3017.2	3.31	1.9	-	-	-	-
3030.5	3.29	12.4	3041.8	10.0	b_2	C-H stretching
3035.1	3.29	7.8	3045.8	6.8	b_2	C-H stretching
3056.0	3.27	21.7	3052.4	18.0	b_2	C-H stretching
3063.2	3.26	60.3	3064.6	68.9	a_1	C-H stretching
3073.6	3.25	49.0	3074.4	46.8	a_1	C-H stretching
3096.1	3.22	22.1	3098.8	26.2	b_2	C-H stretching

^a Obtained by fitting the experimental data as shown in Fig. 4.

Table 3

Comparison of experimental band positions (in cm^{-1}) and A-values (in km mol^{-1}) for the skeletal out-of-plane, C-H out-of-plane, C-H in-plane bending and C-C stretching regions of neutral anthracoronene, coronene, and anthracene in argon.

AnthCor ^d (cm^{-1})	A-values ^d (km mol^{-1})	Coronene (cm^{-1})	A-values (km mol^{-1})	Anthracene (cm^{-1})	A-values (km mol^{-1})
Skeletal		out-of-plane			
456.6	6.4	-	-	-	-
468.1	6.6	-	-	468.0 ^{d,e,f} , 469.6 ^g	40.5 ^{d,f} , 17.3 ^e , 16.3 ^g
544.3	11.3	-	-	-	-
575.9	19.9	550.5 ^{b,c,d} , 550 ^f	27.9 ^b , 35.1 ^{d,f}	602.9 ^{d,e,f,g}	20 ^{d,f} , 7.5 ^e , 8.4 ^g
952.9	3.2	-	-	954.9 ^{d,e,f} , 957.2 ^g	10.1 ^{d,f} , 8.6 ^e , 6.4 ^g
-	-	-	-	1000.9 ^{d,e} , 1000.1 ^{f,g}	9.6 ^{d,f} , 3.2 ^e , 7.3 ^g
-	-	-	-	1125 ^d	1.0 ^d
C-H		out-of-plane			
736.5	53.6	-	-	729 ^d , 725.6 ^{d,e,g} , 729.6 ^{e,f}	139.9 ^{d,f} , 76.4 ^e , 68.1 ^g
761.5	3.1	-	-	-	-
777.8	10.9	771.6 ^{b,c} , 771 ^{d,f}	11.7 ^b , 21.6 ^{d,f}	-	-
795.6	2.9	-	-	-	-
823.9	9.6	-	-	-	-
850.7	92.2	857.0 ^{b,c,d,f}	175.8 ^b , 135.1 ^{d,f}	-	-
895.1	58.1	-	-	878.5 ^{d,e,f}	95.5 ^{d,f,g} , 63.9 ^e , 40.9 ^g
-	-	-	-	906.8 ^e , 908.5 ^{d,e,f}	3.2 ^{d,f} , 1.7 ^e
C-C + C-H		in-plane			
1134.1	10.3	1137.0 ^{b,c,d,f}	13 ^b , 12.2 ^{d,f}	1149.2 ^{d,e,f} , 1149.5 ^g	5.3 ^{d,f} , 4.7 ^{e,g}
-	-	-	-	1166.9 ^{d,e,f,g} , 1151 ^{d,f}	4.8 ^{d,f} , 1.0 ^e , 5.3 ^f , 4.4 ^g
1220.3	4.2	1214.6 ^b	2.0 ^b	-	-
1261.8	6.8	-	-	-	-

AnthCor ^a (cm ⁻¹)	A-values ^a (km mol ⁻¹)	Coronene (cm ⁻¹)	A-values (km mol ⁻¹)	Anthracene (cm ⁻¹)	A-values (km mol ⁻¹)
1282.8	5.7	-	-	1272.5 ^{d,e,f,g}	6.9 ^{d,f} , 10.2 ^e , 3.4 ^g
1296.9	4.3	-	-	-	-
1319.3	7.4	1317.4 ^{b,c,d,f}	48.1 ^{b,c} , 44.6 ^{d,f}	1318.1 ^{d,e,f,g}	17 ^{d,f} , 2.0 ^e , 7.6 ^g
1341.7	6.7	-	-	1345.6 ^{e,f,g}	4.2 ^e , 2.0 ^f , 1.7 ^g
1420.9	3.5	-	-	1400 ^d	2.7 ^d
1439.9	5.3	-	-	1450.5 ^{d,e,f} , 1449.8 ^g	6.4 ^{d,f} , 3.6 ^e , 3.2 ^g
1484.9	3.6	-	-	1460 ^{d,e,f,g}	5.3 ^{d,f} , 2.1 ^e , 1.4 ^g
1495.3	5.4	1497.9 ^{b,c}	2.7 ^b	-	-
1515.6	7.8	1505.3 ^b , 1505 ^{d,f}	2.7 ^b , 4.1 ^{d,f}	-	-
C-C stretch					
1529.7	3.4	1530.4 ^{b,c}	3.6 ^b	-	-
-	-	-	-	1542 ^{d,e,f,g}	5.3 ^{d,f} , 5.0 ^e , 6.7 ^g
1608.3	3.3	1579.2 ^b	1.75 ^b	-	-
1612.3	2.7	-	-	1610.5 ^e	7.9 ^e
1623.9	2.1	1620.7 ^{b,c,d,f}	26.3 ^b , 9.5 ^{d,f}	1627.8 ^{d,e,f,g}	16.3 ^{d,f} , 4.2 ^g

^aThis work,^bHudgins & Sandford ²⁶ Table 5 (A-values from theory),^cde Barros et al. ¹⁴,^dSzczepanski et al. ²⁹ Tables 2 and 5,^eHudgins & Sandford ³¹ Table 2 (A-values from theory),^fLanghoff³⁰,^gMattioda et al. ²⁵.

Comparison of experimental band positions (in cm^{-1}) and A-values (in km mol^{-1}) for the C-H stretching regions of neutral anthracoronene, coronene, and anthracene in argon.

Table 4

AnthCor ^d	A-values ^d (km mol^{-1})	Coronene (cm^{-1})	A-values (km mol^{-1})	Anthracene (cm^{-1})	A-values (km mol^{-1})
C-H stretch					
3017.2	1.9	-	-	3017 ^{d,f} , 3021.6 ^{d,e,f}	8.2 ^{d,f} , 10.7 ^e
3030.5	12.4	3029.2 ^b	-	3032 ^{d,e}	7.3 ^d , 18.7 ^e
3035.1	7.7	3034.3 ^{b,d}	13 ^d	3035 ^g	98.8 ^{g,*}
-	-	3044.4 ^b	15.6 ^b	-	-
3056.0	21.4	3051.4 ^b	279.8 ^b	3055 ^{d,f}	13.2 ^d , 35.2 ^f
3063.2	60.3	3066.8 ^b , 3068 ^{b,d}	20.3 ^d	3062 ^{d,f} , 3064.6 ^e	22.18 ^d , 81.3 ^e , 35.2 ^f
3073.6	49.0	3077.2 ^{b,d,f}	17.6 ^d , 53.6 ^f	-	-
3096.1	22.1	3099.0 ^b	-	-	-

^aThis work.

^bHudgins & Sandford ²⁶ Table 5 (A-values from theory).

^cde Barros et al. ¹⁴,

^dSzczepanski et al. ²⁹ Tables 2 and 5,

^eHudgins & Sandford ³¹ Table 2 (A-values from theory),

^fLanghoff³⁰,

^gMattioda et al. ²⁵,

^{*}Intensity corresponding to 5 bands.

Table 5

Summary of AnthCor cation ($C_{36}H_{18}^{+}$) band positions in an argon matrix for the MIR region (cm^{-1} and μm), A-values ($km\ mol^{-1}$), theoretical band positions (cm^{-1}), absolute intensities ($km\ mol^{-1}$), symmetry from theory, and assignments.

Wavenumber (cm^{-1})	Wavelength (μm)	A-value ($km\ mol^{-1}$)	Theoretical Position (cm^{-1})	Theoretical Intensity ($km\ mol^{-1}$)	Symmetry	Assignment/Comments
862.6	11.6	58.9	866.9	83.7	b_1	C-H duo out-of-plane bending
970.8	10.3	19.2	963.6	18.3	a_1	C-C skeletal in-plane
1040.9	9.6	26.8	1071.9	30.8	a_1	C-H in-plane bending
1147.9	8.7	229.5	1154.1	104.4	a_1	C-H in-plane bending
1182.3	8.5	110.4	1183.3	87.5	a_1	C-H in-plane bending
1245.2 ^{†,‡}	8.0	639.0	1243.1	566.6	a_1	C-H in-plane bending
1252.3	7.9	1163.5	1248.9	906.2	a_1	C-H in-plane bending
1318.8 ^{†,‡}	7.6	210.6	1317.8	294.9	a_1	C-H in-plane bending
1330.9	7.5	1270.3	1331.4	1090.4	a_1	C-C stretching + C-H in-plane bending
1388.8	7.2	159.3	1372.0	277.0	b_2	C-C stretching
1402.1	7.1	77.8	1389.7	67.3	a_1	C-C stretching + C-H in-plane bending
1413.1	7.1	76.9	1395.3	174.8	a_1	C-C stretching + C-H in-plane bending
1441.4	6.9	202.5	1438.3	214.8	a_1	C-C stretching + C-H in-plane bending
1470.9	6.8	125.4	1474.1	95.9	a_1	C-H in-plane bending
1554.9	6.4	568.7	1545.6	716.4	a_1	C-C stretching
1589.8	6.3	76.9	1590.9	38.2	b_2	C-C stretching
1601.6	6.2	243.8	1599.7	345.4	a_1	C-C stretching

[†]Mixture of cation and anion bands,

[‡]Integrated area corresponding only to cation.

Table 6

Summary of AnthCor anions ($C_{36}H_{18}^-$) position bands in an argon matrix in the MIR region (cm^{-1} and μm), A-values ($km\ mol^{-1}$), theoretical band positions (cm^{-1}), absolute intensities ($km\ mol^{-1}$), symmetry from theory, and assignments.

Wavenumber (cm^{-1})	Wavelength (μm)	A-value ($km\ mol^{-1}$)	Theoretical Position (cm^{-1})	Theoretical Intensity ($km\ mol^{-1}$)	Symmetry	Assignment/Comments
1007.4	9.9	19.7	833.4	140.8	b_1	C-H out-of-plane bending
1076.5	9.3	70.1	1013.1	10.5	a_1	C-H in-plane bending
1135.0	8.8	190.3	1071.9	30.8	a_1	C-H in-plane bending
1212.0	8.3	72.0	1139.8	189.6	b_2	C-H in-plane bending
1221.2	8.2	20.3	1209.1	27.5	a_1	C-H in-plane bending
1245.2 ^{†,‡}	8.0	701.8	1214.9	13.8	a_1	C-H in-plane bending
1314.1	7.6	398.4	1243.1	566.6	a_1	C-H in-plane bending
1318.8 ^{†,‡}	7.6	1477.9	1306.9	522.1	b_2	C-C stretching + C-H in-plane bending
1344.9	7.4	104.1	1315.6	1408.8	a_1	C-C stretching + C-H in-plane bending
1350.4	7.4	179.2	1338.7	43.7	a_1	C-C stretching
1371.4	7.3	108.5	1353.4	494.5	a_1	C-C stretching
1422.2	7.0	86.1	1375.9	38.5	a_1	C-C stretching
1545.0	6.5	181.8	1429.1	215.9	a_1	C-C stretching + C-H in-plane bending
			1537.2	517.8	a_1	C-C stretching

[†]Mixture of cation and anion bands,

[‡]Integrated area corresponding only to anion.

Table 7

Comparison of experimental C-C and C-H stretching bands position assignments for ionized anthracoronene, coronene, and anthracene in argon (in cm⁻¹), and their respectively A-values (in km mol⁻¹).

AnthCor ^d (cm ⁻¹)	A-values ^a (km mol ⁻¹)	Coronen ^{b,c} (cm ⁻¹)	A-values ^{b,c} (km mol ⁻¹)	Anthracene (cm ⁻¹)	A-values (km mol ⁻¹)
862.6	58.9	875 ^{b,c} , 874.5 ^{c,e,f}	71 ^{b,c} , 179 ^{c,f}	876 ^b	147 ^b
-	-	-	-	912 ^{b,c,d,e,f}	41 ^{b,d} , 27.3 ^d , 38.3 ^e
970.8	19.2	-	-	-	-
1040.9	26.8	-	-	1034 ^{c,d,f}	36.4 ^d
1147.9	229.5	-	-	-	-
1182.3	110.3	-	-	1188 ^{c,d,f} , 1188.6 ^e	178.6 ^d
1252.3	1390.1	-	-	-	-
1314.1	398.4	-	-	1291 ^{c,d,f} , 1290.4 ^e	834 ^b , 12.8 ^d
1318.8	1477.8	-	-	1314.6 ^e	9.03 ^g
1330.9	1270.3	-	-	1341 ^{c,d,e}	357.4 ^c , 182.3 ^d
1350.4	179.2	-	-	1352.6 ^e	48.16 ^g
1371.4	108.5	1369.9 ^{b,d} , 1379 ^c	24.1 ^{c,d}	1364.4 ^e	-
1388.8	159.3	1378.6 ^{c,e,f}	31.1 ^{c,f}	-	-
1413.1	98.4	-	-	1410 ^{c,d,f} , 1406.1 ^e	16.4 ^{c,d}
1422.2	86.1	-	-	1418 ^{c,d,f} , 1409.5 ^e	176.8 ^d
1431.3	76.9	-	-	1430.2 ^e	2.28 ^g
1441.4	202.5	-	-	1456.5 ^{c,d,e} , 1457.0 ^{d,f}	9.1 ^d , 57.6 ^d
1470.9	125.4	-	-	1485 ^b	56 ^b
1545.0	70.6	-	-	1540 ^{b,c,d,e,f}	55 ^b , 7.3 ^{c,d}
1589.8	76.9	1579.0 ^{c,f,e}	148 ^{c,f}	1586.4 ^e	21.67 ^g
1601.6	243.8	-	-	-	-

^aThis work.

^bHudgins & Allamandola ³²,

NASA Author Manuscript

NASA Author Manuscript

NASA Author Manuscript

^c Szczepanski et al. 27 Tables 2 and 5,^d Szczepanski et al. 29 experimental cations (Table VI) and theoretical values in (km mol^{-1}),^e Hudgins & Allamandola 28,^f Langhoff³⁰,^g Boersma et al. 41.

Table 8

Comparison of experimental electronic transitions for cations and anions of anthracenone, coronene, and anthracene in the OVR and NIR region (in cm⁻¹), and their respective A-values (in 10³ km mol⁻¹).

AnthCor ^d cm ⁻¹	AnthCor ^d (μm)	A-values ^d (10 ³) (km mol ⁻¹)	Oscillator Strength (10 ⁻³)	Coronene cm ⁻¹	A-values (10 ³) (km mol ⁻¹)	Anthracene cm ⁻¹	A-values (10 ³) (km mol ⁻¹)
6175 [*]	1.62	33.7	6.3	-	-	-	-
6555 [†]	1.53	15.1	2.8	-	-	-	-
6811 [†]	1.47	4.4	0.8	-	-	-	-
7012 [†]	1.43	6.9	1.3	-	-	-	-
7304 ^{**}	1.37	1.2	0.2	-	-	-	-
7515 [*]	1.33	1.9	0.4	-	-	-	-
7699 [*]	1.29	6.5	1.2	-	-	-	-
7912 [†]	1.26	8.5	1.6	-	-	-	-
8017 [†]	1.25	3.7	0.7	-	-	-	-
8380 [*]	1.19	2.1	0.4	-	-	-	-
9310 ^{**}	1.07	1.1	0.2	-	-	-	-
9340 [*]	1.07	vw	-	-	-	-	-
9388 ^{**}	1.06	vw	-	-	-	-	-
9408 ^{**}	1.06	1.2	0.2	9430 ^b	vw ^b	-	-
10237 ^{**}	0.98	vw	-	9990 ^b	vw ^b	-	-
103286 ^{**}	0.97	1.1	0.2	-	-	-	-
10414 [*]	0.96	1.5	0.3	10410 ^b , 10409 ^c	12 ^{b,c}	-	-
10505 ^{**}	0.95	1.3	0.2	10680 ^b , 10677 ^c	2.03 ^b	-	-
12526 [*]	0.79	9.2	1.7	12480 ^b , 12471 ^c	1.9 ^b	-	-
13004 [*]	0.77	1.1	0.2	-	-	-	-
13496 [*]	0.74	1.3	0.2	-	-	-	-
13701 [*]	0.73	vw	-	-	-	13839 ^c , 13850.0 ^d , 13835 ^e	48.2 ^e

AnthCor ^d cm ⁻¹	AnthCor ^d (μm)	A-values ^d (10 ³) (km mol ⁻¹)	Oscillator Strength (10 ⁻³)	Coronene cm ⁻¹	A-values (10 ³) (km mol ⁻¹)	Anthracene cm ⁻¹	A-values (10 ³) (km mol ⁻¹)
14193 [*]	0.70	1.0	0.2	-	-	13832 ^c , 13850.0 ^d	-
14267 ^{**}	0.70	2.7	0.5	-	-	14210.0 ^d	-
14644 ^{**}	0.68	1.8	0.3	-	-	14560.0 ^d	-
14977 [*]	0.66	1.1	0.2	-	-	-	-

^aThis work.

^bMattioda et al. 9 Table 4,

^cHudgins & Allamandola 28 Table 2 and 3,

^dAndrews & Kelsall 37 Table I,

^eMattioda et al. 38,

^{*} cation,

^{**} anion,

[†] cation/anion.