Published in final edited form as:

Astrophys J. 2017 October 20; 848(No 2): . doi:10.3847/1538-4357/aa8c71.

Photochemistry of coronene in cosmic water ice analogs at different concentrations

A. L. F. de Barros,

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

A. L. Mattioda,

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

A. Ricca,

Carl Sagan Center, SETI Institute, 189 Bernardo Ave., Mountain View, CA 94043, USA

G. Cruz, and

Bay Area Environmental Institute, 625 2nd St., Suite 209, Petaluma, CA, 94952, USA

L. J. Allamandola

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

Abstract

This work presents the photochemistry of ultraviolet (UV) irradiated coronene in water ices at 15 K, studied using mid-infrared Fourier transform (FTIR) spectroscopy for $C_{24}H_{12}:H_2O$ at concentrations of (1:50), (1:150), (1:200), (1:300) and (1:400). Previous UV irradiation studies of anthracene: H_2O , pyrene: H_2O and benzo[ghi]perylene: H_2O ices at 15 K have shown that aromatic alcohols and ketones, as well as CO_2 and H_2CO are formed at very low temperatures. Like-wise, here, in addition to the coronene cation, hydroxy-, keto-, and protonated coronene (coronene- H^+) are formed. The rate constants for the decay of neutral coronene and for the formation of photoproducts have been derived. It is shown that PAHs and their UV-induced PAH: H_2O photoproducts have mid-infrared spectroscopic signatures in the 5–8 μm region that can contribute to the interstellar ice components described by Boogert et al. (2008) as C1–C5. Our results suggest that oxygenated and hydrogenated PAHs could be in UV-irradiated regions of the ISM where water-rich ices are important.

Subject headings

Astrobiology; Astrochemistry; ISM: molecules; meteorites: organics; ultraviolet photolysis: ISM

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are one of the most abundant carbon containing molecules in the Interstellar Medium (ISM). Additionally, both direct and implied evidence

for their existence in the Solar System has been reported in comet nuclei, icy satellites, and in outer planet rings ((Izawa et al. 2014) and references therein). Numerous observations show that infrared (IR) emission from PAH molecules is found in all phases of the ISM, in our own and other galaxies (e.g., Draine & Li (2007); Geers et al. (2006); Verstraete et al. (2001)). The ubiquity of PAH IR emission features in such diverse environments implies the existence of the same molecules in dense clouds. In these dense clouds the PAH molecules would condense out into the solid phase or be incorporated in ice grain mantles as “guest molecules” as is the case for other interstellar molecules (e.g. Schutte et al. (1993); Bouwman et al. (2011a)). PAHs in dense clouds would be detected by their absorption features as is the case for other ice mantle molecular bands. In fact, the aromatic C-H stretching modes around $3.25\ \mu\text{m}$ have been detected, in IR absorption, for several lines of sight (Smith & Tokunaga 1989; Sellgren et al. 1995; Brooke et al. 1999). Furthermore, PAHs are thought to contribute to the blended absorption features in the 5 to $8\ \mu\text{m}$ region in the spectra of Young Stellar Objects (YSOs) (Keane et al. 2001; Boogert et al. 2008; Hardegree et al. 2014; Cook et al. 2014).

Laboratory work by Bernstein et al. (2002) showed that the vacuum UV (VUV) irradiation of naphthalene and water ice layers, typically naphthalene/ H_2O ratios of 1/100 at 15 K under astrophysical conditions, followed by a warm up of the ices to room temperature, produced 1-naphthol, 2-naphthol, and 1,4-naphthoquinone. The naphthalene cation is readily produced by in-situ UV photolysis of the molecule in H_2O ice at 15 K (Gudipati & Allamandola 2003; Gudipati 2004) suggesting that PAH cations are involved in the formation of alcohols and quinones when PAHs are photolyzed in water ice. The naphthalene cation is stable below 50 K implying that electron-PAH ion recombination rates are low and that there must be sites or species within the ice that trap the electrons, since solvated electrons are very short lived (Johnson & Quickenden 1997). The commonly accepted photochemical mechanism involves (i) PAH^+ cation formation, (ii) photodissociation of H_2O into the radicals H and OH, and (iii) subsequent reactions between photoproducts (Gudipati & Allamandola 2003; Bouwman et al. 2011a).

Subsequent studies of pyrene: H_2O ices (Bouwman et al. 2009, 2010; Guennoun et al. 2011a) at low temperature have shown that upon VUV photolysis, hydroxylated pyrene products form without the need of ice warm up, suggesting that oxygenated PAHs may well be present in cosmic ices. Additional studies of anthracene: H_2O , pyrene: H_2O and benzo[ghi]perylene: H_2O ices at 14 K have shown that aromatic alcohols and ketones, as well as CO_2 and H_2CO , form at 10–15 K for PAH: H_2O ratios ranging from (1:20) to (1:770), depending on the PAH (Bouwman et al. 2011a; Cook et al. 2015).

Guennoun et al. (2011a) were the first to tentatively identify oxygen containing coronene photoproducts in coronene:water experiments in a mid-infrared (MIR) ($4000 - 600\ \text{cm}^{-1}$) study. They followed the photoreactivity of coronene trapped with water in an argon matrix, $\text{Cor}:\text{H}_2\text{O}:\text{Ar}$ (1:10:500). A recent photochemical study of coronene:water complexes isolated in an argon matrix utilizing FTIR spectroscopy showed that coronene reacts with water, upon irradiation, producing oxygenated coronene photoproducts (Noble et al. 2016).

Recently, UV-Visible spectroscopic studies of coronene in water ice by Cuylle et al. (2014) have shown that coronene's ionization efficiency is concentration dependent. Ionization efficiencies are over 60% at low coronene concentration (Cor:H₂O(1:10,000)) dropping to about 15% at higher coronene concentration (Cor:H₂O(1:1000)).

In this work, we extend the mid-infrared (MIR) (6500 - 450 cm⁻¹) studies of UV irradiated coronene (C₂₄H₁₂) in water (H₂O) ices at 15 K following the same approach as in Cook et al. (2015) and Bouwman et al. (2010). Here, we characterize the effect of PAH concentration on band strengths, follow the evolution of the IR bands of identified photoproducts as a function of irradiation time and determine the rate constants for the formation, as well as the degradation rate of the coronene molecule. Theoretical data are used to interpret laboratory spectra and help identify the photoproduct bands. Finally we discuss the possible contribution of PAH and PAH-related photoproducts to the spectra of dense clouds.

2. Experimental and Theoretical Methodologies

2.1. Laboratory Methods

The UV irradiation techniques used in this study have been well described (Hudgins et al. 1994; Bouwman et al. 2011b; Mattioda et al. 2012; Cook et al. 2015), therefore we will only briefly summarize the procedure, focusing on the important details relevant to this particular work. The ices were prepared by vapor co-deposition of coronene with H₂O onto a CsI window cooled to 15 K and suspended in a high vacuum chamber ($P \sim 10^{-8}$ Torr).

Coronene (C₂₄H₁₂, Aldrich, 99%) was used without further purification and deposited for study by heating in pyrex tubes. Milli-Q grade water vapor, further purified by three freeze-pump-thaw cycles, was admitted through an adjacent deposition tube, coalescing with the PAH vapor onto the CsI window. To prepare the different concentrations of C₂₄H₁₂:H₂O (Cor:H₂O) ices the coronene deposition temperature was maintained constant from one experiment to the other, at around 186°C, while varying the water vapor flow.

The deposited C₂₄H₁₂:H₂O mixture was irradiated by UV photons using a flowing-H₂, microwave discharge lamp with H₂ gas at a dynamic pressure of 150 mTorr. The spectrum from such a 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 MgF₂ window. Actinometry measurements method were used to calculate the UV photon flux for the lamp. A polyethylene film with a thickness of 15 μ m was placed on top of the deposition window facing the UV lamp. Irradiation took place under 10⁻⁸ Torr at room temperature, the film was irradiated for 240 min with intervals of 20 min, taking an IR spectrum at the end of every irradiation period. Polyethylene was chosen because it is well studied under this condition, (see Truica-Marasescu & Wertheimer 2005; Alata et al. 2014). Irradiation of this material produces a band at 965 cm⁻¹, assigned to the trans-vinylene group, which gives access to the time-dependent dose at the sample position. Scaling the UV dose dependence of this band to the calibrated measurement in Truica-Marasescu & Wertheimer (2005), we obtained a photon flux of $(2 \pm 0.5) \times 10^{14}$ photon/(cm² s) for our lamp. Uncertainty was based on performing several experiments.

The FTIR spectra from 6500 to 450 cm^{-1} were measured with a Biorad Excalibur FTS 4000 FTIR spectrometer equipped with a KBr beam splitter and a liquid N_2 -cooled MCT detector. A complete spectrum consists of a background spectrum (I_0), taken on the cold sample window (~ 15 K) before sample deposition, and the sample spectra (I) taken after deposition and again after VUV processing of the sample. Spectra were collected with resolution of 0.5 cm^{-1} and co-addition of 225 scans. VUV photolyzed spectra were collected after 2, 4, 8, 16, 32 and 60 minutes of VUV irradiation. Mid-IR spectra were taken after each photolysis event and compared to the unphotolyzed spectra identify changes. Data were purge-subtracted, filtered and baseline-corrected for presentation purposes only.

Baseline corrections, spectral subtraction and filtering were performed using the Agilent Resolutions Pro software version 4.0. Spectral subtractions were performed by subtracting a fraction (Y) of the neutral or non-irradiated spectrum from the irradiated sample. The subtraction factor Y represents the fraction of neutral sample remaining in the irradiated sample, thus $(1 - Y)$ is the fraction of the original sample that has been converted. The resulting subtraction spectrum reveals only the photoproduct bands and the subtraction factor, Y ($0 < Y < 1$), directly reflects the amount of neutral coronene (N_0) converted to photoproducts during photolysis:

$$N_0(1-Y) = N_{\text{products}} \quad (1)$$

The factor Y is derived by determining the fraction of neutral necessary so that all neutral species are completely removed from the irradiation spectrum. For the coronene, in an argon matrix after 16 min of UV photolysis, the obtained factor value was $Y = 0.65$, implying that 1-0.65 or 0.35 of the neutral was converted to ions. However, for the case of water mixtures, this fine-tuning can result in a difficult comparison of the spectra, making it unclear whether weakly observed features (particularly those that appear near strong neutral bands) are the result of varying subtraction factors, or whether they are real photoproduct bands. Therefore, to remove this confusion, the subtraction factor $Y = 1.0$ was used for all of our neutral-subtracted spectra for Cor:H₂O experiments.

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 (Becke 1993; Stephens et al. 1994) in conjunction with the cc-pVTZ basis set (Dunning 1989) using the Gaussian09 suite of programs (Frisch et al. 2009). The computed harmonic frequencies were scaled to lower frequencies using three scale 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 scale factors were obtained by fitting to 25 bands obtained from gas phase experiments, namely to the 17 infrared allowed bands determined by Pirali et al. (2009) (the 16 bands in Table 1 and the band at 1601 cm^{-1} shown in Figure 2 of Pirali et al. (2009)), the four A_g and the two B_{2g} bands summarized by Behlen et al. (1981) and the one A_u and one B_{1g} bands summarized by Cané et al. (1996). A full-width at half-maximum (FWHM) of 5 cm^{-1} was used to broaden the computed spectra.

3. Results and Discussion

3.1. Non-irradiated neutral coronene in argon and water ices

In our non-irradiated Cor:H₂O (1:300) ice experiment we observed small shifts of the neutral coronene band positions, in particular for the C-H out-of-plane bands compared with those of coronene in an argon matrix (Hudgins & Sandford 1998). A summary of the IR data for unphotolyzed neutral coronene (C₂₄H₁₂) in argon and in the water ice mixture is presented in Table 1. The relative strengths of the measured coronene bands were normalized to the most intense band at 857.0 cm⁻¹ for argon and 858.1 cm⁻¹ for H₂O. A comparison of our results for Cor:H₂O (1:150) with those of Bernstein et al. (2005) for Cor:H₂O (1:160) shows that the band positions and the relative intensities are in very good agreement, with differences of 1 cm⁻¹ or less, except for the 858.1 cm⁻¹ band which is affected by the H₂O librational mode (see Figure 1). There is also a wide range in the variability of the relative intensities for the 550 cm⁻¹ band, which is on the edge of the H₂O librational band.

Comparison of coronene band positions in H₂O ice to those in the argon matrix reveals differences in band positions between 1 and 6 cm⁻¹, with the largest differences occurring in the C-C in plane region. Figure 1 presents the 4000 - 450 cm⁻¹ spectrum of non-irradiated Cor:H₂O (15 K) at a concentration of (1:50). It clearly shows that the H₂O ice bands dominate the spectrum even at this lower water concentration. Comparing this work with that of Sandford et al. (2004) and Bernstein et al. (2005), who reported coronene spectra at concentrations of a few percent in H₂O ice, reveals that their observed CH-stretching bands near 3030 cm⁻¹ (3.3 μm) are imperceptible in our sample. The strong C-H out-of plane bending bands between 900–500 cm⁻¹ (11–20 μm) suffer from severe blending with the H₂O ice libration mode. This makes the PAH IR bands between 1650-1000 cm⁻¹ (~6.06–10 μm) the most promising for studying PAH:H₂O photochemistry, as well as in identifying astronomical PAHs and PAH related photoproduct species in interstellar ices (e.g, Sandford et al. (2004)).

Bouwman et al. (2011b) using a near-UV/VIS absorption spectra and Hardegree et al. (2014) using FTIR and UV-Vis spectrometers, reported a change in PAH band strengths between the argon matrix and H₂O ice. Based on this apparent discrepancy we calculated the A-values (integrated band strengths) for coronene in H₂O ice using the theoretical absolute band intensities for coronene. The total theoretically calculated absolute intensity in the region of these observed bands is proportionally divided over the experimentally measured PAH band areas in this frequency range, utilizing the relative intensities of the band areas, as shown in equation (2), as:

$$A_i^{exp} = \frac{\int_{v_{i,1}}^{v_{i,2}} \tau_{i,v} dv}{N(F)} = 2.303 \frac{\int_{v_{i,1}}^{v_{i,2}} A_{i,v} dv}{N(F)} = \sum_{j=0}^M A_j^{Cor} \frac{\int_{v_{i,1}}^{v_{i,2}} \tau_{i,v} dv}{\sum_{i=0}^L \int_{v_{i,1}}^{v_{i,2}} \tau_{i,v} dv} \quad (2)$$

where A_i^{exp} is the experimentally measured integrated band strength of coronene mode i in H₂O ice in cm molecule⁻¹, $\tau_{i,v}$ is the optical depth of mode i in H₂O ice at frequency v

(cm^{-1}), $N(F)$ is the number of molecules (absorbers), $A_{i,v}$ is the absorption coefficient of mode i in H_2O ice at frequency v (cm^{-1}), A_j^{Cor} is the theoretically calculated absolute intensity of vibrational mode j in the 1600 to 1000 cm^{-1} range, in cm molecule^{-1} , M is the number of theoretically calculated modes in the respective region, L is the number of measured modes, and $v_{i,1}$ and $v_{i,2}$ are the lower and upper integration boundaries in cm^{-1} , respectively, for absorption feature i . The A-values units are typically present in km/mol , which can be converted to cm molecules^{-1} by dividing by 6.02×10^{18} .

Once the A-values are determined, the number of absorbers molecules, $N(F)$, can be obtained by using equation (3) given by:

$$N(F) = \frac{\int_{v_{i,1}}^{v_{i,2}} \tau_{i,1} dv_{i,1}}{A_{value}(v_{i,1})} \quad (3)$$

The knowledge of the band strength is required to obtain the column densities from both astronomical and laboratory spectra, and allows one to obtain the PAH abundances in the outer solar system and in the ISM (Hudson et al. 2014). The A-values of the ten coronene bands (1621.5, 1590.0, 1532.4, 1498.9, 1317.3, 1212.6, 1137.3, 858.1, 769.1 and 549.5 cm^{-1}) of neutral coronene in water ice were determined following the above procedure and are compared with those obtained for argon matrices in Table 1 and Figure 2.

Figure 2(a) shows the band strengths for the lower water concentration, Cor: H_2O (1:50), in Figure 2(b) shows the band strengths for the higher water concentration, Cor: H_2O (1:400), and Figure 2(c) shows the band strengths for all water concentrations. While the positions of the features measured in argon and in water matrices are essentially identical, the band strengths for coronene H_2O ices are slightly lower than those in argon, varying between 0.81 for 1:50 ratio and 0.89 for the 1:400 ratio.

Bossa et al. (2015), used mid-infrared optical constants to determine the porosity and the band strengths of composite ices. They noticed that the presence of pores has only a small effect on the overall band strengths (for the $\text{H}_2\text{O}:\text{CH}_4$ ices), whereas a water dilution can considerably alter them. They have shown that the A-values related to the C-H stretching and CH_4 bending modes undergo considerable attenuations with water dilution. This effect was also observed by Hudgins et al. (1993). Our data shows a slight decrease ($\sim 15\%$, see Figure 2(c)) in the band strength of coronene in water ices compared to argon. However Hardegree et al. (2014) reported a 50% increase over the argon values for the A-values of the PAH pyrene in water ice. The disagreement regarding the influence of the water ice environment on A-values may be simply due to the fact that Hardegree et al. (2014) utilize UV-Vis absorptions measurements in their determination of the A-values for the Mid-IR. While H_2O does not obscure the electronic transitions visible in the UV-V is region, these transitions are highly influenced by their environments, much more so than the vibrational transitions measured in the mid-infrared (see Mattioda et al. (2012)).

3.2. Photochemistry of coronene in water ices

3.2.1. Decay of Coronene—The Cor:H₂O photolysis experiments were performed for Cor:H₂O ratios of 1:50, 1:150, 1:200, 1:300 and 1:400. Integrated band areas for neutral coronene bands, namely 858.1 cm⁻¹, 1137.3 cm⁻¹, 1317.3 cm⁻¹ and 1603.0 cm⁻¹, were utilized in conjunction with their corresponding A-values from Table 1, to determine the average neutral coronene concentrations remaining after photolysis (see Figure 3). As clearly shown in Figure 3, coronene loss is far more efficient at lower coronene concentrations.

At the highest coronene concentration (Cor:H₂O = 1:50) only about ~ 20% of the neutral coronene is depleted at 30 minutes whereas at lower concentration (Cor:H₂O = 1:400), almost 60% the neutral coronene is gone for the same photolysis time.

Bouwman et al. (2009) and Gudipati & Allamandola (2003) proposed that the processes for the PAH decay may be governed by recombination with trapped electrons, a process that will be temperature dependent. Figure 3 shows that the neutral coronene decay for all concentrations can be fitted with a single exponential decay:

$$\Lambda(t) = \Lambda_0 \exp - \frac{t}{\tau} \quad (4)$$

where Λ_0 is the initial value and τ the time of decay, as revealed by the red fittings curves in Figure 3. Table 2 displays the results for all the Cor:H₂O concentrations. These parameters are used in the rate constant calculations in Subsection 4.1.

Figure 4 shows that the efficiency of coronene loss depends on both the photolysis time and concentration. This figure shows that there are two distinct regimes visible. For the first few minutes the concentration effect seems minimal, however after 4 minutes a high and low concentration regime become evident. At 60 minutes the concentration effect seems to disappear, possibly due to a depletion of adjacent H₂O molecules.

3.2.2. Formation of the photoproducts—To characterize the PAH photoproducts produced in our experiments we computed the IR spectra of all possible isomers of hydroxy-, keto- and protonated coronene, and of the coronene cation and anion. The best fits between our computed spectra and the experimental ones were obtained for the molecules shown in Figure 5. Our comparison between the experimental and theoretical spectra focused on the 1650 to 1000 cm⁻¹ spectral regions, since this region does not suffer from overlap with the broad H₂O bands.

Figure 6 shows the spectra of Cor:H₂O (1:200) during UV irradiation. Previous studies showed that PAH cations have much stronger bands in the 1650-1000 cm⁻¹ range than their neutral counterparts in an argon matrix (e.g. Szczepanski & Martin (1993)). This is demonstrated by the mid-infrared absorption bands shown in Fig.6 (Cor:H₂O at 1:200), where the coronene cation's C-C stretching and C-H in-plane bending modes centered at 1580.1 and 1387.9 cm⁻¹ in the C-C stretching and C-H in plane bending modes are clearly visible. despite a conversion of only 40% of the neutral coronene to all the photoproducts

(e.g. compare the strength of the *a* bands to *b* bands in Fig. 6). Three cations bands have been reported for coronene (Hudgins & Allamandola 1995a,b), namely the 876.6, 1387.9 and 1580.1 cm^{-1} .

The identified bands are summarized in Table 3, with the structures of the photoproducts shown in Figure 5. Upon increasing photolysis time, the photoproducts bands begin to overlap making it difficult to trace the precise photochemistry at the longer photolysis time (e.g. compare *a* and *c* around 1500 cm^{-1} and at *a* and *d*₁ around 1130 cm^{-1} in Figure 5). The analysis for the photoproducts in the 1650 to 1000 cm^{-1} region was performed by subtracting the spectra of neutral species from the photolyzed spectrum using a subtraction factor of 1 for all of our neutral-subtracted spectra (see Eq.(3) and Figure 7).

The neutral, photolyzed and subtracted spectra were compared to avoid identifying subtraction artifacts as new photoproducts. Figure 7 shows the spectra of the photoproducts obtained after 32 minutes of UV irradiation for all concentrations studied. As the H₂O concentration increases the new bands, not seen in the lower concentration, become visible in the spectra. The negative peaks are due to the subtraction of neutral coronene.

3.2.3. Cor:H₂O concentration effects

3.2.3.1. Coronene Cations: The H and OH radicals, produced by the H₂O photodissociation, react with coronene to form the photoproducts shown in Figure 5. Table 3 contains the band positions, intensities and assignments of bands detected at lower and higher concentrations. Due to the multiple photoproducts and overlapping bands, the positions given in H₂O indicate the most predominant peaks.

The Cor:H₂O photoproduct absorption bands were decomposed by Gaussian fits and the peak positions of these band strengths were measured in water at different concentrations. The photoproducts species were identified by finding the best fit between all the computed and experimental bands of each molecule. The corresponding correlation plots utilize bands with stronger intensities whose positions are linked to the specific functional group (e.g. -OH and -CO) of the photoproducts and are also dependent on the given structure of the molecule.

Figure 8(a) shows the growth of the 1580.1 cm^{-1} coronene cation band with photolysis time (VUV fluence) for the Cor:H₂O (1:50), (1:150), (1:200), (1:300) and (1:400) mixtures. As one can see, from (1:50) to (1:200) concentrations the cation growth rate increases very slowly with an inflection point in cation production at the 1:300 Cor:H₂O ratio. This behavior is similar to what was observed by Cook et al. (2015) and Bouwman et al. (2011a). Figure 8(b) shows the UV correlation plots for the growth of the three bands attributed to the coronene cation, namely 876.6, 1376.9 and 1580.1 cm^{-1} for the Cor:H₂O (1:300) concentration. Multiplicative factors are used for some bands to highlight the similarities in growth patterns (e.g. 1376.9 and 1580.1 cm^{-1}). Figure 8(b) demonstrates how the correlation plots were utilized in identifying bands belonging to a single photoproduct, in that all the bands attributed to the coronene cations grew in at the same rate. Figure 8(c) and (d) show the integrated band areas of 876.6 cm^{-1} plotted versus the integrated band areas of 1376.9 and 1580.1 cm^{-1} respectively. The data were fitted as a straight line which reflects the

correlation between the two bands. The R^2 and Pearson's r values were calculated (inset in the figure). In both instances the R^2 and Pearson's r are almost 1, indicating a very strong correlation.

3.2.3.2. Oxygenated and protonated photoproducts: Figure 9(a) and 9(b) compares the most intense bands for 1,6 and 1,7-dihydroxycoronene, namely the 1148 and 1218 cm^{-1} bands respectively. It is easily observed in Figure 9(a) and 9(b) that the production of 1,6- and 1,7-dihydroxycoronene increases with the decreasing coronene concentration with a marked increase occurring at Cor:H₂O concentration of 1:300. Previous work has shown that H₂O ice chemistry is dominated by reactions that primarily involve the water photodissociation into the radicals OH and H (Gudipati & Allamandola (2006); Cuylle et al. (2014); Woon & Park (2004) and references therein). This behavior was also observed by Cook et al. (2015) for the formation of CO₂ and H₂CO during the irradiation of PAH:water ice mixtures. As seen in the cation plot of 1580.1 cm^{-1} (Fig. 8(a)), the 1,7-dihydroxycoronene band at 1218.0 cm^{-1} (Fig. 9(b)) also exhibits a sharp increase in formation starting at the 1:300 concentration.

Two very small bands were observed at 1281.2 and 1248.0 cm^{-1} that we identify as 1,6- and 1,7-coroquinone, respectively through comparison with theory. Figure 9(c) and (d) shows the behavior of these small bands with varying concentrations. It is interesting to note that the band at 1281.2 cm^{-1} of 1,6-coroquinone was not observed in the Cor:50 concentration. As can be seen in Fig. 9(c), the band areas for 1,6-coroquinone are 5 times smaller than for 1,7-coroquinone (Fig. 9(d)). Overall these areas for the corokinones are 30 times smaller than those for the dihydroxycoronenes. While these photoproducts bands have very small areas, they exhibit increases, with increasing water concentration, as would be expected for a photoproduct. However, the Cor:H₂O (1:300) inflection point is not clearly defined for these species, we believe this is simply due to the small band areas of the vibrational bands.

Figure 10 shows the correlation for the growth of the two bands of 1,6-dihydroxycoronene, namely 1148.5 and 1076.2 cm^{-1} , at UV photolysis times of 0 through 60 minutes (closed black data points). Both of these bands appear to reach their maximum strength around 60 minutes of photolysis time. The same procedure was followed for the two bands of 1,7-dihydroxycoronene, namely 1027.6 and 1357.8 cm^{-1} (open blue data points).

Figure 11(a) shows the growth of the protonated coronene ($\text{C}_{24}\text{H}_{13}^+$, structure *c* in Figure 5) with the photolysis time (VUV fluence) for Cor:H₂O concentrations (1:50), (1:150), (1:200), (1:300) and (1:400) mixtures. Figure 11(b) shows the UV Correlation plots for the growth of the three bands attributed to protonated coronene, namely 1606.1, 1342.4 and 1545.5 cm^{-1} for Cor:H₂O (1:300) concentration. Multiplicative factors were used to scale for comparison in showing the similarities in growth patterns (e.g. 1342.4 and 1545.5 cm^{-1}). Figure 11(c) and (d) show the integrated band areas of 1606.1 cm^{-1} versus the integrated band areas of 1342.4 and 1545.5 cm^{-1} respectively. As previously discussed for the cations, the data were fitted as a straight lines obtaining the correlation between the bands as well as the R^2 and Pearson's r values, which are close to 1.

For the coronene cation ($C_{24}H_{12}^+$), all the positions for H atom addition are equivalent, yielding only one chemically unique protonated cation structure ($C_{24}H_{13}^+$) shown as the structure *c* in Figure 5(c). Hudgins et al. (2001) and Weilmünster et al. (1998) reported that PAH cations containing an even number of carbon atoms were found to exist predominantly in the protonated form. Together, these experiments indicate that PAH radical cations readily add an H atom while closed-shell ion structures do not. Since the resultant protonated cation already has the preferred closed-shell electronic structure they are far less reactive with H atoms because the addition of another H atom would disrupt this favorable configuration.

The bands positions of $C_{24}H_{13}^+$, their assignments and their intensities are given in Table 3. Of the eight bands which can only be attributed to $C_{24}H_{13}^+$, four of these bands are in good agreement (± 6 cm $^{-1}$) with those identified in the gas phase by Knorke et al. (2009) at 1002, 1356, 1509, and 1600 cm $^{-1}$, with a fifth band at 1545.5 cm $^{-1}$ differing by 9 cm $^{-1}$ from Knorke et al.'s value of 1537 cm $^{-1}$. The three remaining $C_{24}H_{13}^+$ bands at 1345.3, 1572.7 and 1590.4 cm $^{-1}$, which were not identified in Knorke et al. (2009), could easily have been obscured by the breath of the gas phase bands in the Knorke et al. (2009) study. The absorption bands for the coronene cation and for the protonated coronene were decomposed using Gaussian functions for the different Cor:H₂O concentrations. Both band areas increased with the water concentration and with UV photolysis time.

Interestingly, coronene protonated band areas sharply increase for the (1:200) and (1:300) ratios (Figure 11(a)) implying that additional water molecules contribute to the stabilization of electrons and of the coronene protonated cation, as discussed by Gudipati & Allamandola (2006) and Allamandola et al. (1999).

3.3. Column density evolution of coronene and the observed photoproducts

Utilizing the same method and neutral coronene bands discussed in Section 3.2, the coronene column densities were determined for each concentration. To determine the water column densities we adopted the band strength values (A-values): 2×10^{-16} , 1.2×10^{-17} and 3.1×10^{-17} cm molecule $^{-1}$ for the stretching, bending and libration mode, respectively (Hudgins & Sandford 1998). The H₂O column density was determined by taking the average of at least two of the H₂O bands, ~ 3300 cm $^{-1}$ and ~ 1660 cm $^{-1}$, the reason for this being that the H₂O libration modes (~ 833 cm $^{-1}$) could not accurately be integrated due to the spectrometer cutoff.

Since no information is available on experimental A-values (integrated band strengths) of UV photoproducts of coronene in H₂O, we used the theoretical molar absorbances to calculate the column densities of the photoproducts, applying the same procedure used for neutral coronene (Eqs (1) – (3)), details in Section 3.1.

In this manner, it was also possible to derive the first order estimate of the fraction of neutral coronene that is converted into photoproducts species. The amount of deposited neutral, N_0 , is known from concentration measurements Eqs. (1) and (2) and the amount of consumed neutral is given by Eq. (3). The photoproducts were treated individually. Using their

corresponding integrated band areas, we were able to determine the number of molecules for each species produced during irradiation.

Figure 12 shows the time evolution of the relative amount of neutral $C_{24}H_{12}$ converted or destroyed during irradiation along with the corresponding increase of the photoproducts for all concentrations of the Cor:H₂O ice sample. Using the theoretical A-value the column density was determined by taking the average N values determined from all the observed bands of the species.

Just as earlier discussions, there is an increase $\sim 20\%$ in the loss of coronene between Cor:200 and Cor:300. This corresponds to a 11% increase of cation, 10% increase in 1,6- $C_{24}H_{12}O_2$, 9% increase in 1,7- $C_{24}H_{12}O_2$, 3% increase in $C_{24}H_{13}^+$ and $\sim 1.5\%$ for 1,6- and 1,7- $C_{24}H_{10}O_2$. Interestingly, there did not seem to be a corresponding increase over the 1,6- and 1,7- $C_{24}H_{10}O_2$ produced, indicating these products are not dependent on the initial Cor:H₂O concentrations. A possibility is those photoproducts are not directly related to neutral coronene but they can be formed from the 1,6- and 1,7-dihydroxycoronene.

At the Cor:H₂O (1:400) concentration and 60 minutes UV photolysis time, we estimate that $\sim 86\%$ of the neutral coronene is converted into photoproducts (see Figure 12). Of this 86% fraction, roughly 38% is converted into cations, 7% is converted to protonated coronene, 16% to 1,7-dihydroxycoronene, 13% to 1,6-dihydroxycoronene, 1.2% to 1,7- coroquinone, around 1% to 1,6-coroquinone, and $\sim 11\%$ into other species like CO₂, CO and H₂CO (not shown in Fig. 12).

CO was also observed for some Cor:H₂O concentrations, but CO₂ and H₂CO appear in all concentrations. Recent studies have shown the key importance of H₂O in the process of PAH loss and the growth of CO₂ and H₂CO (Cook et al. 2015). Radich et al. (2014) showed that continued UV irradiation of graphene (an extremely large PAH) in an aqueous media produces smaller PAH like molecules as well as CO₂. Mattioda et al. (2012) studied the PAH photochemistry of the PAH isoviolanthrene ($C_{32}H_{18}$) in different environments and showed that growth of CO₂ appears with the loss of the PAH isoviolanthrene, when water vapor is present. The O and OH formed from water dissociation erodes the PAH, leading to the formation of CO, CO₂ and H₂CO within the ice (Cook et al. 2015). The CO₂ band at 2341.5 cm^{-1} is a clear and unperturbed band in all of the photolysis spectra, and it possesses an extraordinarily large integrated band strength in water ice and other ices. The H₂CO ν_3 CH₂ scissor mode at 1718.5 cm^{-1} is clearly seen at all concentrations, although much smaller compared to the CO₂ band. The integrated band strengths for CO₂ ($A_{CO_2} = 2 \times 10^{-16}\text{ cm molecule}^{-1}$, e.g., Hudgins et al. (1993) and references therein) and H₂CO ($A_{H_2CO} = 9.6 \times 10^{-18}\text{ cm molecule}^{-1}$ (Schutte et al. 1993) were used to track the growth of CO₂ and H₂CO shown in

Figure 13. Figure 13(a) and (b) shows the growth of the integrated band area for the 2341.5 cm^{-1} band of CO₂ and 1718.5 cm^{-1} band of H₂CO, respectively, plotted versus photolysis time for the different Cor:H₂O concentrations studied. It is interesting to note that, although the concentration of CO₂ and, to a lesser extent, H₂CO increase with increasing UV photolysis time, these two molecules do not exhibit the same Cor:H₂O concentration

dependence as the coronene photoproducts (e.g. no abrupt increase at Cor:H₂O (1:300). The CO₂ data was corrected removing the CO₂ background growth due to processes such as UV photodesorption from the chamber walls.

4. Reaction Scheme

4.1. Determining the experimental rate constants

We can use the column densities of the photoproducts to obtain the reaction rates. It was shown in Figure 3 that the neutral coronene molecules undergo an exponential decay upon photon bombardment, similar to that observed for a radioactive decay, giving the following rate Eq. (5) that is the same form as Eq. (4). This equation can be used to fit the column density of the coronene molecule during the irradiation phase via Eq.(6). It is important to remember that all column densities for the observed species shown in Figures 5 and 7 and identified in Table 3, were determined by averaging the number of molecules (N) obtained for all the observed bands for each species, using the theoretical A values for each band. The process was repeated for all concentrations.

$$-\frac{d[C_{24}H_{12}]}{dt} = k_a [C_{24}H_{12}] \quad (5)$$

$$C_{24}H_{12}(t) = C_{24}H_{12}(t=0)e^{-k_a t} \quad (6)$$

For the photoproducts showed in Figure 12, the cation can be assumed to be produced via reaction of a first order growth using Eq. (7), where k_1 is the rate constant.

$$C_{24}H_{12}^+(t) = a[1 - e^{-k_1 t}] \quad (7)$$

Assuming that all the photoproducts are also formed via first order reactions, we used the Eq. (7) to fit the experimental data through 30 min irradiation for Cor:H₂O (1:50) and 60 min irradiation for (1:150), (1:200), (1:300), and (1:400) concentrations. The rate constants obtained from the individual fitting for each photoproduct species are shown in Table 4 with the degradation rate of coronene varying between 7.0×10^{-6} to $2.3 \times 10^{-5} \text{ sec}^{-1}$.

Bouwman et al. (2010) and Cook et al. (2015) found two distinct reaction pathways for the PAH's they studied. At low temperatures (< 50 K), the chemistry is largely governed by ion-molecule interactions and processes, and at higher temperatures (> 50 K), the reactions are dominated by diffusing radical species. They also discussed a dependency on the concentration. For example: low PAH concentrations, usually lower than PAH:H₂O < 1:300, favor PAH ion-driven and ion-dominated reaction networks and processes while PAH:H₂O > 1:300, favor reaction networks dominated by neutral species.

5. Astrophysical implications

5.1. Coronene behavior

This study shows that UV photolysis of coronene (a small condensed PAH) in water ice produces coronene cations, oxygenated photoproducts as well as CO, CO₂ and H₂CO. This work is the first detailed IR study of the effect of different concentrations of coronene on its ionization efficiency in H₂O ice, and all the photoproducts formed. There is a clear link between coronene concentration and photoproduct yield and thus, by implication, with the types of coronene photoproducts present in the ice that are available for subsequent reactions and processes.

The ionization behavior of coronene in H₂O ice falls in two distinct concentration regimes. At low coronene concentrations, ionization yield and stabilization is high, ranging from around 70% for Cor:H₂O (1:400), to about 40% for Cor:H₂O (1:200), and dropping to nearly 15% for Cor:H₂O (1:50) (Figure 3). The PAH concentrations with respect to H₂O in interstellar ices are estimated to be on the order of up to 2–3%. In this regime PAH ionization occurs, with conversion efficiency's on the order of 10–20% (e.g. Bouwman et al. (2011a) and references within).

Rapacioli et al. (2006) suggest that very small grains made up of PAHs or clusters of PAHs appear near the edge of a molecular cloud, where the interstellar radiation field is not completely attenuated, but where molecules such as water begin to form on grain surfaces. Gordon et al. (2008); Madden (2000) have reported that smaller gas phase PAHs will be destroyed by UV irradiation in regions of high photon flux. Likewise, the unattenuated intense radiation fields at the edges of dense clouds will also destroy the coronene molecules trapped in ices via the reaction networks described here.

In this work we observed that the photodriven oxygenation of the C-H groups at the edge of PAHs is possible in coronene:water ices, suggesting that it may be possible to detect oxygenated PAHs in regions containing irradiated ices such as at the edges of molecular clouds, in photon dominated regions, and planet forming disks. A few observational studies have provided evidence for the absorption features of PAHs in molecular clouds (e.g. Keane et al. (2001); Chiar et al. (2000)). While Hardegree et al. (2014) have postulated that in molecular clouds, such molecules (9% of the cosmic carbon budget) may survive in icy grain mantles where they are somewhat shielded from radiation. In the spectra of YSOs, up to 9% of the unidentified absorption in the 5–8 μ m range can be attributed to neutral PAHs frozen out in dust grain mantles (Boogert et al. 2008).

5.2. CO₂ production

Concerning CO₂ production, following the reaction scheme suggested in Cook et al. (2015) CO is ultimately produced from oxygen capture by coronene. Oxygen capture can initiate ring rupture and PAH erosion producing CO. This CO can again capture another oxygen from photodissociated water, forming CO₂.

Figure 14 shows the growth pattern of CO₂ compared to the loss of neutral coronene molecules. From these graphs, several interesting things are evident. First, the percentage

loss of coronene after 30 minutes of UV photolysis goes from only 20% for Cor:50 to nearly 60% loss for Cor:400. This rapid increase in degradation of coronene with dilution occurs around a concentration of Cor:300, the inflection point previously discussed in Subsection 3.2.3. While, in principle, in water rich ices exposed to long duration UV irradiation, the carbon inventory of PAHs may be completely converted to CO₂, that is not what we find here. Our results show that the production of CO₂ only goes from 1.24×10^{15} CO₂/cm² to 3.22×10^{15} CO₂/cm² for this concentration regime. While this represents a 3-fold increase (5% error bar) in the number of CO₂ molecules produced, as well as a 3-fold increase in the percent of coronene lost, the relationship is not 1 to 1. Remember, for each coronene molecule lost, 24 carbon atoms are potentially released. This implies CO₂ production is dependent on factors other than the coronene concentration alone. In other words, the carbon tied up in the coronene (PAH) lost is not directly converted into CO₂ during UV photolysis in H₂O ice. This is a sharp contrast to behavior found by Cook et al. (2015) for small, irregular PAHs.

5.3. Spectra of Dense Clouds

There is a vast literature on interstellar ice features (e.g. Keane et al. (2001); Gibb & Whittet (2002); Schutte et al. (2003); Boogert et al. (2008, 2015); van Dienenhoven et al. (2004); Öberg et al. (2011); Penteado et al. (2015) and references therein). Of particular interest here is the careful, detailed analysis of the Spitzer 5.3 to 7.7 μ m interstellar ice spectra associated with 41 low luminosity Young Stellar Objects (YSOs) carried out by Boogert et al. (2008). After correcting for the broad 6 μ m H₂O-ice feature, Boogert et al. (2008) showed that the residual absorption consists of at least 5 independent spectroscopic components. They also discuss and review the possible carriers of these components and conclude that ices in quiescent dense clouds and in regions associated with embedded young stars have much in common. The 5 spectroscopic components identified by Boogert et al. (2008), labelled C1 through C5, are shown in Figure 15. For comparison, the top panel is a composite made up of all the computed coronene's photoproduct bands between 6.1 and 7.8 μ m reported here, as well as the photoproduct bands reported by Cook et al. (2015) for anthracene, pyrene, and benzo(ghi)perylene. Likewise, since the interstellar residual spectra do not extend beyond 7.8 μ m due to the overlap with the interstellar silicate feature (Boogert et al. 2008), we do not show the computed features in this region.

Comparing the PAH photoproduct bands with the interstellar residual components shown in Figure 15 supports the suggestion that PAHs and their photoproducts trapped in interstellar ices should be considered as possible contributors to the components described by Boogert et al. (2008). The following discussion of Figure 15 is similar to that given in Cook et al. (2015). Throughout this discussion, keep in mind that *Spitzer's* spectral resolution, coupled with the band broadening and blending inherent in a mixture of PAHs and their photoproducts trapped in water-rich ices would produce very broad, slightly structured features.

The 5.5 to 6.5 μ m region of the residual spectrum of W33A is dominated by components C1, C2, and the strongest section of C5. As mentioned earlier, bands between roughly 5.8 and 5.3 μ m fall in the region characteristic of the very strong carbonyl (>C=O) stretch, with C1

reasonably well accounted for by overlapping $>\text{C}=\text{O}$ stretching bands of ice-bound HCOOH and H_2CO (see refs in Boogert et al. (2008, 2015)). The $>\text{C}=\text{O}$ stretch falls between roughly 5.5 and 6.25 μm (1740 and 1600 cm^{-1}) for these species and, as with most carbonyls, the $>\text{C}=\text{O}$ stretching bands are by far the strongest (see also Bellamy & Rogasch (1960) and Silverstein & Bassler (1961)). Thus, the suggestion that a mixture of aromatic ketones and quinones contribute to the dominant 5.5 to 6.5 μm portion of the C5 component seems reasonable.

It can be observed from Figure 15, the ketones ($\text{RC}(=\text{O})\text{R}'$) dominate the region between 5.8 to 6.2 μm corresponding to a C1 and C2 components. The cations (R^+ and R-H^+) are more abundant in the part of C2, C3 and C4 (6.2 to 7 μm) and the alcohols (R-OH) dominate the C2 (6 to 6.2 μm) component. Further perusal of Figure 15 shows that the C2 component, which extends from about 5.8 to 6.5 μm , corresponds to the region with the highest density of PAH photoproduct bands. These bands primarily originate in the aromatic CC stretch of the various PAHs. Since this density of bands is produced by only four PAHs and their photoproducts while interstellar ices likely contain far more than a handful of PAHs, it is reasonable to assign the C2 component to overlapping PAH bands. See Cook et al. (2015) for a detailed discussion of this band within the context of the PAH hypothesis/model.

In 2001, Keane et al. (2001) attributed excess absorption peaking near 6.3 μm (now known to be the C2 component from Boogert et al. (2008)) in their collection of dense cloud spectra to the aromatic CC stretch and consider several possible carriers including PAHs in the gas, PAHs condensed on grains, and carbonaceous dust. However, at that time, it was not known that charged PAHs could be present in ices. Attributing the 6.3 μm excess absorption to PAHs in the gas phase, Keane et al. (2001) estimated the amount of carbon tied up in PAHs. However, since the intrinsic strength of this band is very sensitive to the degree of ionization, they made two estimates, one based on the intrinsic strength of neutral PAHs, the other for PAH cations. Adopting the intrinsic strength for PAH cations, they calculated that the fraction of elemental carbon tied up in PAHs to be about 7% for NGC 7538:IRS9, an amount consistent with that determined from the PAH IR emission bands. However, assuming neutral PAHs produce the band requires 83% of the elemental carbon. Clearly, this supports the picture that ionized PAHs are components of interstellar ice.

Components C3, C4 and the moderately strong section of C5 span the 6.5 to 7.8 μm region. Summarizing the discussion in Cook et al. (2015), these components fall in the region of a few strong PAH cation bands, alcohols and weaker aromatic ketones bands. Keane et al. (2001) and Schutte et al. (2003) initially showed that the 6.8 μm feature is made up of at least two components, one centered near 6.75 μm , the other at 6.95 μm . These are components C3 and C4 identified by Boogert et al. in 2008. As shown in the top panel of Figure 15, although aromatic alcohols and aromatic ketones have bands that could contribute to C3, they are sparse and weak, roughly a quarter of the density of the bands near 6.3 μm , the peak position of C2. However, since this position corresponds to aliphatic CH deformation modes, and depending on the extent of hydrogenation, hydrogenated PAHs can have moderately strong bands here and these would contribute to C3 and C4.

Now consider the moderately strong, 6.5 to 7.8 μm section of C5. Discussions of the weak substructure evident on C5, and possible assignments, can be found in e.g. (Lacy et al. 1991; Schutte et al. 1996; Boogert et al. 2006, 1997; Schutte et al. 1999; Keane et al. 2001). Figure 15 also shows that a simple mixture of small, pure PAHs, PAH cations, PAH alcohols and PAH ketones can produce a rich, weakly structured spectrum between 6.5 and 7.8 μm that may contribute to C5. These bands are only moderately intense compared with the very strong CC PAH cation and $>\text{C}=\text{O}$ stretching bands that we suggest contribute to the 5.8 to 6.5 μm portion of C5.

6. Discussion

The manuscript describes mid-IR absorption spectroscopy of $\text{C}_{24}\text{H}_{12}:\text{H}_2\text{O}$ UV photoproducts. Band positions and relative intensities of neutral coronene in H_2O ice in the 1650–1000 cm^{-1} (6.1 – 10 μm) spectral window are compared to their argon matrix isolation data, noting a small decrease compared to argon matrix. Additionally, band strengths are derived for neutral coronene isolated in an astrophysically relevant H_2O ice at 15 K. The main conclusions of this manuscript are summarized below.

1. VUV photolysis of coronene containing H_2O ice causes the embedded coronene to ionize and react with H_2O photoproducts. The band positions of coronene cations trapped in H_2O ice are measured. Additionally, peak positions of $\text{C}_{24}\text{H}_{12}:\text{H}_2\text{O}$ photoproducts, other than the cation, are determined and tentatively assigned to $\text{C}_{24}\text{H}_{12}\text{-Xn}$ species, with X being O, H or OH.
2. The photochemistry is tracked as a function of $\text{C}_{24}\text{H}_{12}:\text{H}_2\text{O}$ ice concentration for Cor: H_2O ratios (1:50) to (1:400). The fraction of neutral molecules converted into the cation is found to be larger in ices of lower coronene concentration, consistent with previous work. The same way, the fraction of neutral coronene converted into photoproduct species other than the $\text{C}_{24}\text{H}_{12}^+$ is larger in ices of higher water concentration.
3. The $\text{C}_{24}\text{H}_{12}:\text{H}_2\text{O}$ ice photochemistry is tracked as a function of VUV fluence by monitoring the integrated absorbances of the parent coronene and coronene photoproduct bands periodically during photolysis time. In all cases, the photoproduct bands increase faster in the first 10 to 16 min before slowing and growing steadily until an hour of irradiation.
4. It was found that the corresponding increase, over the different water concentrations, the 1,6- and 1,7- $\text{C}_{24}\text{H}_{10}\text{O}_2$ photoproducts do not depend on the initial Cor: H_2O concentrations.
5. Another interesting result is that the photoproducts 1,6- and 1,7- $\text{C}_{24}\text{H}_{10}\text{O}_2$ do not depend on the initial Cor: H_2O concentrations, strongly suggesting that they can be formed from the 1,6- and 1,7-dihydroxycoronene.
6. A comparison of the growth pattern of CO_2 with the loss of neutral coronene molecules was made. We observed that after 30 minutes of UV photolysis, coronene loss increases from ~ 20% for Cor: H_2O (1:50) to ~ 60% loss for

Cor:H₂O (1:400). Therefore the production of CO₂ from coronene is only 2.5×10^{15} CO₂/cm² for this concentration regime, 0.01% of the carbon inventory.

Summarizing, in this study, we have show that neutral coronene is highly reactive with water ice, readily forming alcohols and ketone species. We investigated the possible destruction routes for these molecules, determining their rate constants. This area should be investigated in more detail to help to understand the low derived interstellar abundances of oxygenated PAHs. The impact of the work reported here is significant. Foremost among these results is that, typical interstellar ices should contain neutral and ionized PAHs, aromatic alcohols and ketones.

Acknowledgments

This work was supported by National Aeronautics and Space Administration and by the Brazilian agency under the scholarship CAPES (BEX 5383/15-3) grant. This material is based upon work supported by the National Aeronautics and Space Administration through the NASA Astrobiology Institute under Cooperative Agreement Notice NNN13ZDA017C issued through the Science Mission Directorate. L. Allamandola gratefully acknowledges support from NASA's ADAP programs (numbers NNX14AG80A and NNX17AG8A). A. Ricca gratefully acknowledges support from NASA's Exobiology Program (NNX13AJ08G).

References

- Allamandola LJ, Hudgins DM, Sandford SA. ApJ. 1999; 511:L115.
- Alata I, Cruz-Diaz GA, Muñoz Caro GM, Dartois E. A&A. 2014; 569:A119.
- Andersson S, van Dishoeck EF. A&A. 2008; 491:907.
- Bauschlicher CW Jr, Peeters E, Allamandola LJ. ApJ. 2008; 678:316.
- Becke AD. J Chem Phys. 1993; 98:5648.
- Bernstein MP, Dworkin JP, Sandford SA, Allamandola LJ. Adv Space Res. 2002; 30(6):1501–1508.
- Bernstein MP, Sandford SA, Allamandola LJ. ApJS. 2005; 161:53.
- Behlen FM, McDonald DB, Sethuraman V, Rice SA. J Chem Phys. 1981; 75:5685.
- Bellamy LJ, Rogasch PE. Spectrochimica Acta. 1960; 16(1–2):30–34.
- Boogert ACA, Pontoppidan KM, Knez C, et al. ApJ. 2008; 678:985B.
- Boogert ACA, Schutte WA, Helmich FP, et al. A&A. 1997; 317:929.
- Boogert ACA, Schutte WA, Tielens AGGM, et al. A&A. 1996; 315:L377.
- Boogert AA, Gerakines PA, Whittet DC. Annual Review of Astronomy and Astrophysics. 2015; 53:541–581.
- Bouwman J, Paardekooper DM, Cuppen HM, Linnartz H, Allamandola LJ. ApJ. 2009; 700:56.
- Bouwman J, Meeus G, de Koter A, Hony S, Dominik C, Waters LBFM. A&A. 2001; 375:950B.
- Bouwman J, Cuppen HM, Bakker A, Allamandola LJ, Linnartz H. A&A. 2010; 511:A33.
- Bouwman J, Cuppen HM, Steglich M, Allamandola LJ, Linnartz H. A&A. 2011a; 529:A426.
- Bouwman J, Mattioli AL, Linnartz H, Allamandola LJ. A&A. 2011b; 525:A93.
- Brooke TY, Sellgren K, Geballe TR. ApJ. 1999; 517:883.
- Brownlee, Robert G., Silverstein, Robert M. Analytical Chemistry. 1968; 40(13):2077–2079.
- Bossa JB, Maté B, Fransen C, Cazaux S, Pilling S, Rocha WRM, Ortigoso J, Linnartz H. The Astrophysical Journal. 2015; 814(1):47.
- Cané E, Palmieri P, Tarroni R, Trombetti A, Handy NC. Gazz Chim, Ital. 1996; 126:289.
- Chiar JE, Tielens AGGM, Whittet DCB, et al. ApJ. 2000; 537:749.
- Ciesla FJ, Sandford SA. Sci. 2012; 336:452.
- Cook AM, Mattioli AL, Quinn RC, et al. ApJS. 2014; 210:15.
- Cook AM, Ricca A, Mattioli AL, Bouwman J, et al. Astrophys J. 2015; 799(14):A93.
- Cuyllé SH, Allamandola LJ, Linnartz H. A&A. 2014; 562:A22.

- Draine BT, Li A. *ApJ*. 2007; 657:810.
- Dunning TH Jr. *J Chem Phys*. 1989; 90:1007.
- Frisch, MJ., et al. Gaussian 09, Revision D.01. Gaussian, Inc.; Wallingford CT: 2013.
- Geers VC, Augereau JC, Pontoppidan KM, Dullemond CP, Visser R, et al. *A&A*. 2006; 459:545.
- Gibb EL, Whittet DCB. *The Astrophysical Journal Letters*. 2002; 566(2):L113.
- Gordon KD, Engelbracht CW, Rieke GH, et al. *ApJ*. 2008; 682:336.
- Guenoun Z, Aupetit C, Mascetti J. *PCCP*. 2011a; 13:7340. [PubMed: 21431140]
- Guenoun Z, Aupetit C, Mascetti J. *J Phys Chem A*. 2011b; 115(10):18441852.
- Gudipati MS, Allamandola LJ. *ApJL*. 2003; 596:L195.
- Gudipati MS. *JPCA*. 2004; 108:4412.
- Gudipati MS, Allamandola LJ. *ApJ*. 2006; 638:286.
- Hardegree-Ullman EE, Gudipati MS, Boogert ACA, et al. *ApJ*. 2014; 784:172.
- Hudgins DM, Sandford SA, Allamandola LJ, Tielens AGGM. *ApJS*. 1993; 86:713.
- Hudgins DL, Sandford SA, Allamandola LJ. *J Phys Chem*. 1994; 98:4243. [PubMed: 12269375]
- Hudgins DM, Allamandola LJ. *J Phys Chem*. 1995a; 99:3033. [PubMed: 11538457]
- Hudgins DM, Allamandola LJ. *J Phys Chem*. 1995b; 99:8978. [PubMed: 11538316]
- Hudgins DL, Sandford SA. *Phys Chem A*. 1998; 102:344–352.
- Hudgins DM, Bauschlicher CW Jr, Allamandola, Louis J. *Spectrochimica Acta Part A*. 2001; 57:907, 930.
- Hudson RL, Gerakines PA, Moore MH. *Icar*. 2014; 243:148.
- Izawa MRM, Applin DM, Norman L, Cloutis EA. *Icarus*. 2014; 237:1591.
- Johnson RE, Quickenden TI. *JGR*. 1997; 102:10985J.
- Keane JV, Tielens AGGM, Boogert ACA, Schutte WA, Whittet DCB. *A&A*. 2001; 376:254.
- Knorke, Harald, Langer, Judith, Oomens, Jos, Dopfer, Otto. *ApJ*. 2009; 706L:66K.
- Lacy JH, Carr JS, Evans NJ II, et al. *ApJ*. 1991; 376:556.
- Madden SC. *New Astron Rev*. 2000; 44:249.
- Mattioda AL, Cook AM, Ehrenfreund P, et al. *AsBio*. 2012; 12:841.
- Noble JC, et al. 2016 *A&A* arXiv:1612.03008.
- Öberg, Karin I., et al. *The Astrophysical Journal*. 2011; 734(2):98.
- Peeters E, Hony S, van Kerckhoven C, et al. *A&A*. 2002; 390:1089.
- Penteado EM, Boogert ACA, Pontoppidan KM, et al. *MNRAS*. 2015; 454:531.
- Pirali O, Vervloet M, Mulas G, Mallocci G, Joblin C. *Phys Chem Chem Phys*. 2009; 11:3443. [PubMed: 19421547]
- Radich JG, Krenselewski A, Zhu J, Kamat PV. *Chem Mater*. 2014; 26:4662.
- Rapacioli M, Calvo F, Joblin C, et al. *A&A*. 2006; 460:519.
- Sandford SA, Bernstein MP, Allamandola LJ. *ApJ*. 2004; 607:346.
- Schutte WA, Allamandola LJ, Sandford SA. *Icar*. 1993; 104:118.
- Schutte WA, et al. *Astronomy and Astrophysics*. 1999; 343:966–976.
- Schutte WA, Tielens AGGM, Whittet DCB, et al. *A&A*. 1996; 315:L333.
- Schutte WA, Khanna RK. *A&A*. 2003; 398:1049–1062.
- Sellgren K, Smith RG, Brooke TY. *ApJ*. 1994; 433:179.
- Sellgren K, Brooke TY, Smith RG, Geballe TR. *ApJL*. 1995; 449:L69.
- Silverstein, Bassler, Bassler, G. Morril (1981). *Spectrometric identification of organic compounds*. 1961
- Smith RG, Sellgren K, Tokunaga AT. *ApJ*. 1989; 344:413.
- Szczepanski, Jan, Martin, Vala. *The Astrophysical Journal*. 1993; 414:646–655.
- Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ. *J Phys Chem*. 1994; 98:11623.
- Tielens AGGM. *ARA&A*. 2008; 46:289.
- Truica-Marasescu FE, Wertheimer MR. *Macromol Chem Phys*. 2005; 206:744.

- Weilmünster P, Keller A, Homann KH. Combustion and Flame. 1998; 116:62.
- Woon DE, Park JY. ApJ. 2004; 607:342.
- van Diedenhoven B, Peeters E, Van Kerckhoven C, Hony S, Hudgins DM, Allamandola LJ, Tielens AGGM. The Astrophysical Journal. 2004; 611:928939.
- Verstraete L, et al. A&A. 2001; 372:981.

Fig. 1.

Non-irradiated FTIR absorption spectra (4000 - 450 cm^{-1}) of Cor:H₂O (1:50) at 15 K. The inset shows the spectrum in the range 1650 - 1000 cm^{-1} . The modes attributed to water are labelled in the spectrum as H₂O stretch, libration and bend.

Fig. 2.

Band strength comparison between the average of several coronene bands in an argon matrix and coronene in a water ice at different concentrations. (a) Cor:H₂O (1:50), (b) Cor:H₂O (1:400) and (c) all concentrations. See Section 3.1 for details.

Fig. 3.

Average neutral coronene band decay as a function of photolysis time (VUV fluence) for Cor:H₂O concentrations of (1:50), (1:100), (1:200), (1:300) and (1:400) at 15 K.

Conservative errors are $\pm 3\%$ of the initial amount of deposited neutral species. Fits to the data based on a one exponential (red solid lines) are indicated as well. Λ_0 and τ values from the fits are provided in Table 3.

Fig. 4.
Coronene yield for Cor:H₂O different concentrations ranging from 1:50 to 1:400.

Fig. 5.
Structures of the species predicted to be present in the Cor:H₂O photolysis experiments.

Fig. 6. FTIR spectra 1620-1000 cm^{-1} for the UV irradiation of Cor:H₂O (1:200) as a function of irradiation time (0 – 1hr). Data have been baseline and filtered for presentation proposes. The letter (e.g. *a*, *b*, *c*, *d*₁ and *d*₂) refer to the molecules shown in Fig. 4.

Fig. 7.

Neutral-subtracted spectra for the region from 1625 to 1000 cm^{-1} showing only the photoproducts features appearing after 32 min of in situ VUV photolysis of Cor:H₂O at different concentrations. Data have been baseline corrected for presentation proposes. The indicated letter in the molecules are shown at Fig. 4.

Fig. 8.

(a) Growth rates for the coronene cation band 1580.1 cm^{-1} for $\text{Cor}:\text{H}_2\text{O}$ concentrations of (1:50), (1:150), (1:200), (1:300) and (1:400); (b) Correlation plots showing the nearly identical growth patterns for the 876.6, 1376.9 and 1580.1 cm^{-1} bands of the coronene cations; (c) and (d) the integrated band areas of 876.6 cm^{-1} versus the bands 1376.9 and 1580.1 cm^{-1} respectively. Inset the calculated values for the relative band strength, the Pearson's r value and adjusted R^2 . Slope of the fitting through (0,0)
The areas were taken using the results for the $\text{Cor}:\text{H}_2\text{O}$ (1:300) concentration.

Fig. 9. Growth of the (a) 1,6-dihydroxycoronene, (b) 1,7-dihydroxycoronene, (c) 1,7-coroquinone and (d) 1,6-coroquinone bands with photolysis time (VUV fluence) for Cor:H₂O concentration of (1:50), (1:150), (1:200), (1:300) and (1:400).

Fig. 10.

Correlations plots for 1,6- and 1,7-dihydroxycoronene. Black data points (and black axes) show similar growth patterns between the two identified 1,6-dihydroxycoronene bands. Blue data points (and blue axes) show a correlation in the growth of the two identified 1,7-dihydroxycoronene bands. The bands areas were taken from the Cor:H₂O (1:300) concentration.

Fig. 11.

(a) Growth rates for the protonated coronene band 1342.4 cm⁻¹ for Cor:H₂O concentration of (1:50), (1:150), (1:200), (1:300) and (1:400) mixtures; (b) Correlation plots for the three protonated bands 1606,1, 1342.4 and 1545.5 cm⁻¹; (c) and (d) the integrated band areas of 1606.1 cm⁻¹ versus the bands 1342.4 and 1545.5 cm⁻¹ respectively. Inset the calculated values for the relative band strength, the Pearson's r value and adjusted R^2 . The areas were taken using the results for the Cor:H₂O (1:300) concentration.

Fig. 12.

Evolution of $C_{24}H_{12}^0$, $C_{24}H_{12}^+$, $C_{24}H_{13}^+$, 1,6- and 1,7- $C_{24}H_{12}O_2$ and 1,6-, 1,7- $C_{24}H_{10}O_2$ photoproducts for all Cor:H₂O ice concentrations at 15 K as a function of photolysis time. The relative error of the bands was estimate to be $\pm 3\%$ of the deposited amount of neutral coronene and, thus, the shape of the time dependence curve is well defined.

Fig. 13.

Growth of the (a) CO_2 and (b) H_2CO band areas as a function of VUV irradiation time for the $\text{C}_{24}\text{H}_{12}:\text{H}_2\text{O}$ ices at different concentrations. Note how both CO_2 and H_2CO continue to increase with photolysis time.

Fig. 14.

Neutral coronene loss (red close circles) and CO_2 growth (black open squares) as a function of VUV irradiation time for the $\text{C}_{24}\text{H}_{12}:\text{H}_2\text{O}$ ices.

Fig. 15.

Top Panel: DFT computed band positions for the cation (R^+ , R-H^+), alcohol (R-OH) and ketone (RC(=O)R') forms of the PAHs considered here, namely: $\text{R} = \text{anthracene}$, $\text{R} = \text{pyrene}$, $\text{R} = \text{benzo[ghi]perylene}$, and $\text{R} = \text{coronene}$. Bands with predicted strengths greater than $\sim 30 \text{ km mol}^{-1}$ are shown. Lower Panels: The C1 through C5 components associated with ices in dense clouds and star forming regions described by Boogert et al. (2008). See discussion, Section 5.3.

Table 1

Summary of experimental band position assignments for neutral coronene in argon and water ice at different concentrations (in cm^{-1}), relative intensities, vibrational assignments A-values (in km/mol), theoretical band positions (in cm^{-1}) and intensities (in km/mol) of bands. The data for coronene in argon are from Hudgins & Sandford (1998) and those for Cor:H₂O (1:160) are from Bernstein et al. (2005).

Cor:Ar ^{a,b} Position (cm^{-1})	Relative ^{b,c} Intensity	Cor:H ₂ O ^b (Cor:150) (cm^{-1})	Relative ^{b,c} Intensity	Cor:H ₂ O ^d (Cor:160) (cm^{-1})	Relative ^d Intensity	Theoretical Bands Position ^e (cm^{-1})	Theoretical Absolute ^a Intensity (km/mol)	A-values Argon ^b (km/mol)	A-values H ₂ O ice ^b (km/mol)	Assignments / Comments
1620.7	0.17	1621.5	0.14	-	-	1618.9	-	7.22	5.84	C-C stretching
1599.2	0.04	1603.0	0.03	-	-	1602.7	26.3	27.45	24.68	C-C stretching
1530.4	0.02	1532.4	0.02	-	-	-	-	3.55	3.73	C-C stretching
1505.3	0.01	1498.9	0.009	-	-	1504.1	2.7	1.75	1.51	C-C stretching
1317.4	0.32	1317.3	0.27	1316.1	0.37	1314.5	48.1	49.97	46.01	C-H in plane bending
1214.6	0.005	1212.6	0.007	-	-	1213.9	2.0	0.90	1.14	C-H in plane bending
1137.0	0.11	1137.3	0.06	1138.3	0.08	1140.3	13.0	15.83	12.76	C-H in plane bending
857.0	1.00	858.1	1.00	865.2	1.00	858.2	175.8	174.58	165.55	C-H out-of-plane bending
771.6	0.11	769.1	0.08	770.0	0.07	768.4	11.7	16.97	13.66	C-C skeletal in plane
550.5	0.27	549.5	0.33	550.7	0.48	555.3	37.9	28.89	26.79	C-C skeletal out-of-plane

^aHudgins & Sandford (1998),

^bThis work. Only the Cor:H₂O (1:150) is reported, the bands positions at different concentrations varies by $\pm 3 \text{ cm}^{-1}$,

^cIntensities relative to the strongest band at 857.0 cm^{-1} for argon and 858.1 cm^{-1} for water,

^dBernstein et al. (2005),

^eTheoretical value were determined for the gas phase with errors of $\pm 4.4 \text{ cm}^{-1}$ (average) and $\pm 11.7 \text{ cm}^{-1}$ (maximum).

Table 2

Decay time of neutral coronene at various concentrations obtained using Eq. (4).

Concentration	Λ_0	τ (min)
Cor:50	0.28	32.3
Cor:150	0.39	25.1
Cor:200	0.49	23.2
Cor:300	0.62	18.9
Cor:400	0.79	16.2

Table 3

Coronene photoproducts bands.

Positions in $\text{H}_2\text{O}^a \pm 2.0$ cm^{-1}	Relative Intensity in H_2O	Theoretical ^b Band Positions ± 20.0 cm^{-1}	Theoretical ^b Absolute Intensities (km/mol)	Assigned photo products	Assignments/Comments
656.05	-	650 ^c	-	CO_2	ν_2 bend (only seen for Cor:H ₂ O ratios of 1:50 and 1:150)
876.6	-	880.7	144.7	$\text{C}_{24}\text{H}_{12}^+$	C-H out-of-plane bend (hard to see because of water band)
1006.8 ^d	0.22	1000.5	25.5	$\text{C}_{24}\text{H}_{13}^+$	CH ₂ wag and C-H in plane bend (seen for the Cor:H ₂ O ratios 1:50 and 1:150)
1027.6 ^{d,e}	0.72	1032.5	208.4	1,7- $\text{C}_{24}\text{H}_{12}\text{O}_2$	C-O stretch (Peaks at 1032, 1028)(seen for the Cor:H ₂ O ratios 1:50 and 1:150)
1148.5 ^e	0.38	1148.1	90.6	1,6- $\text{C}_{24}\text{H}_{12}\text{O}_2$	C-H scissor and O-H in plane bend - Stronger/well defined
1189.0	-	1163.2	66.6/46.1	1,6- $\text{C}_{24}\text{H}_{12}\text{O}_2$ /1,7-	C-H scissor/C-H bend (Peaks at 1192,1189,1183,1179,1176)
1207.8 ^{d,e}	-	1206.0	209.2/113.0	1,7- $\text{C}_{24}\text{H}_{12}\text{O}_2$ /1,6-	C-H rock and O-H in-plane bend (Broad peaks at 1208,1219)
1217.9 ^{d,e}	0.28	1213.7	95.1	1,7- $\text{C}_{24}\text{H}_{12}\text{O}_2$	C-H rock and O-H in-plane bend (Broad peaks at 1208,1219)
1234.1 ^d	0.34	1257.9	107.3	1,7- $\text{C}_{24}\text{H}_{10}\text{O}_2$	C-C stretch α to the carbonyl (Peaks at 1237,1234,1239)
1281.2	0.45	1272.6	136.9	1,6- $\text{C}_{24}\text{H}_{10}\text{O}_2$	C-C stretch α to the carbonyl (not seen for Cor:H ₂ O ratio of 1:50)
1345.3 ^e	0.55	1345.7	213.1	$\text{C}_{24}\text{H}_{13}^+$	CH ₂ scissor (Peaks at 1339,1342.5,1345.7)
1357.8 ^e	-	1356.5	146.0/869.0	1, 7- $\text{C}_{24}\text{H}_{12}\text{O}_2$ / $\text{C}_{24}\text{H}_{13}^+$	CH ₂ wag and C-H in-plane bend (Peaks at 1366,1357)
1376.9	0.56	1369.9	253.4	$\text{C}_{24}\text{H}_{12}^+$	C-C stretch (Broad peaks at 1360,1370,1377)
1387.7 ^e	0.19	1399.1	32.0	1,7- $\text{C}_{24}\text{H}_{12}\text{O}_2$	C-C stretch (Peaks at 1406,1388) (only seen for Cor:H ₂ O ratios of 1:300 and 1:400)
1436.7	0.12	1435.7	33.5	1,6- $\text{C}_{24}\text{H}_{12}\text{O}_2$	C-C Stretch (Broad peaks at 1436.8,1442.0) (not seen for Cor:H ₂ O ratio of 1:50)
1515.1	0.80	1516.9	137.5	$\text{C}_{24}\text{H}_{13}^+$	CH ₂ sym. stretch
1545.5	0.21	1553.1	60.7	$\text{C}_{24}\text{H}_{13}^+$	C-C stretch (Peaks at 1545 and 1539)
1572.7 ^d	0.55	1569.0	107.1	$\text{C}_{24}\text{H}_{13}^+$	C-C stretch (Broad peaks at 1576,1573,1570)

Positions in H ₂ O ^a ± 2.0 cm ⁻¹	Relative Intensity in H ₂ O	Theoretical ^b Band Positions ± 20.0 cm ⁻¹	Theoretical ^b Absolute Intensities (km/ mol)	Assigned photo products	Assignments/Comments
1580.1	0.74	1584.4	408.0	C ₂₄ H ₁₂ ⁺	C-C stretch
1590.4	0.24	1598.4	67.4	C ₂₄ H ₁₃ ⁺	C-C stretch (Peaks at 1590 and 1600)
1606.1 ^d	1	1607.3	106.4	C ₂₄ H ₁₃ ⁺	C-C stretch (a band at 1590,1588 was also seen)
1718.5	-	1723 ^c	-	H ₂ CO	ν ₃ ν ₂ C=O stretch
2136.9	-	2139 ^c	-	CO	¹² CO stretch (only seen for Cor:H ₂ O ratio of 1:50 and 1:150)
2341.5	-	2342 ^c	-	CO ₂	ν ₃ , asymmetric stretch
2856.8	-	2850 ^c	-	H ₂ CO	ν ₁ CH ₂ sym. stretch (only seen for Cor:H ₂ O ratio of 1:150)

Notes:

^a Only the photoproducts for the Cor:H₂O (1:400) concentration, the other band positions varies by ± 3.0 cm⁻¹;

^b Only predicted bands with band strengths > 30 km mol⁻¹ are reported;

^c CO, CO₂ and H₂CO are from Schutte et al. (1993) and Hudgins et al. (1993);

^d Bands identified experimentally as 1,7-C₂₄H₁₀O₂ by (Guennoun et al. 2011a);

^e Bands identified experimentally as 1,6-C₂₄H₁₂O₂ by (Guennoun et al. 2011a).

Table 4

Rate Constants (k_p) and a constant a derived via experimental data fittings from Eq. (7).

Reactions	Cor:50	Cor:150	Cor:200	Cor:300	Cor:400
Rate Constants (k_p in 10^{-4} s^{-1})					
$C_{24}H_{12}^0$	0.07 ± 0.03	0.09 ± 0.01	0.10 ± 0.07	0.14 ± 0.08	0.23 ± 0.09
$C_{24}H_{12}^+$	6.2 ± 0.4	3.1 ± 0.3	3.5 ± 0.5	3.6 ± 0.6	3.8 ± 0.6
$C_{24}H_{13}^+$	4.7 ± 0.3	2.0 ± 0.2	2.1 ± 0.2	2.2 ± 0.2	2.5 ± 0.4
$1,6-C_{24}H_{12}O_2$	4.3 ± 0.3	1.7 ± 0.5	1.9 ± 0.4	2.3 ± 0.5	3.0 ± 0.5
$1,7-C_{24}H_{12}O_2$	6.1 ± 0.4	1.8 ± 0.1	2.3 ± 0.2	2.5 ± 0.1	2.8 ± 0.5
$1,6-C_{24}H_{10}O_2$	-	1.4 ± 0.8	2.1 ± 0.5	2.2 ± 0.4	2.5 ± 0.7
$1,7-C_{24}H_{10}O_2$	4.1 ± 0.5	2.3 ± 0.3	2.2 ± 0.3	2.1 ± 0.2	2.3 ± 0.4
Constant a (10^{-9} moles)					
$C_{24}H_{12}^+$	2.98 ± 0.67	3.55 ± 0.10	6.40 ± 0.17	10.1 ± 0.3	14.2 ± 0.32
$C_{24}H_{13}^+$	0.51 ± 0.09	0.67 ± 0.16	1.03 ± 0.06	2.19 ± 0.36	2.99 ± 0.29
$1,6-C_{24}H_{12}O_2$	1.77 ± 0.07	2.93 ± 0.19	3.77 ± 0.22	7.05 ± 0.40	7.77 ± 0.38
$1,7-C_{24}H_{12}O_2$	1.72 ± 0.14	2.99 ± 0.16	2.98 ± 0.15	6.34 ± 0.11	8.09 ± 0.41
$1,6-C_{24}H_{10}O_2$	-	0.08 ± 0.01	0.09 ± 0.02	0.13 ± 0.06	0.17 ± 0.05
$1,7-C_{24}H_{10}O_2$	0.15 ± 0.03	0.15 ± 0.05	0.16 ± 0.05	0.15 ± 0.05	0.26 ± 0.08