Photochemistry of Coronene in Cosmic Water Ice Analogs at Different Concentrations

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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_{2}O at concentrations of (1:50), (1:150), (1:200), (1:300), and (1:400). Previous UV irradiation studies of anthracene:H_{2}O, pyrene:H_{2}O, and benzo[ghi]perylene:H_{2}O ices at 15 K have shown that aromatic alcohols and ketones, as well as CO_{2} and H_{2}CO, are formed at very low temperatures. Likewise, 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 Polycyclic Aromatic Hydrocarbons (PAHs) and their UV induced PAH:H_{2}O 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. as C_{1}–C_{5}. Our results suggest that oxygenated and hydrogenated PAHs could be in UV-irradiated regions of the interstellar medium where water-rich ices are important.

Key words: astrochemistry – ISM: clouds – ISM: kinematics and dynamics – ISM: molecules – protoplanetary disks – techniques: spectroscopic

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., Verstraete et al. 2001; Geers et al. 2006; Draine & Li 2007). 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 μm have been detected, in IR absorption, for several lines of sight (Smith et al. 1989; Sellgren et al. 1995; Brooke et al. 1999). Furthermore, PAHs are thought to contribute to the blended absorption features in the 5–8 μm region in the spectra of young stellar objects (YSOs; Boogert et al. 1996; Keane et al. 2001; Cook et al. 2014; Hardegree-Ullman 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_{2}O 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_{2}O 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) photo-dissociation of H_{2}O into the radicals H and OH, and (iii) subsequent reactions between photoproducts (Gudipati & Allamandola 2003; Bouwman et al. 2011a).

Subsequent studies of pyrene:H_{2}O 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_{2}O, pyrene:H_{2}O, and benzo[ghi]perylene:H_{2}O ices at 14 K have shown that aromatic alcohols and ketones, as well as CO_{2} and H_{2}CO, form at 10–15 K for PAH:H_{2}O 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 cm^{-1}) study. They followed the photo-reactivity of coronene trapped with water in an argon matrix, Cor:H_{2}O: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, and, upon irradiation, produces 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 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 at 15 K and suspended in a high vacuum chamber (P ∼ 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 on 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 (10.6 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. The actinometry measurements method was used to calculate the UV photon flux for the lamp. A polyethylene film with a thickness of 15 μm 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 minutes with intervals of 20 minutes, taking an IR spectrum at the end of every irradiation period (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 ± 0.5) × 10¹⁴ photon/(cm² s) for our lamp. The 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 N₂-cooled MCT detector. A complete spectrum consists of a background spectrum (I₀), 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 a resolution of 0.5 cm⁻¹ and the coaddition of 225 scans. VUV photolyzed spectra were collected after 2, 4, 8, 16, 32, and 60 minutes of VUV. Mid-IR spectra were taken after each photolysis event and compared to the unphotolyzed spectra to 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 photoproduction bands, and the subtraction factor, Y (0 < Y < 1), directly reflects the amount of neutral coronene (N₀) converted to photoproducts during photolysis:

\[ N_0(1 − Y) = N_{\text{products}}. \] (1)

The factor Y is derived by determining the fraction of neutral to be subtracted so that all neutral species are completely removed from the irradiation spectrum. For the coronene, in an argon matrix after 16 minutes 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 photoproduction 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; 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 μm region, and 0.975 for the region greater than 9 μm. 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 A₁ and the two B₂g bands summarized by Behlen et al. (1981) and the one A_u and one B₁g bands summarized by Cané et al. (1997).

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
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⁻¹), Theoretical Band Positions (in cm⁻¹), and Intensities (in km mol⁻¹) of Bands

| Cor:Ar<sup>b</sup> Relative<sup>b,c</sup> Cor:H₂O<sup>d</sup> Relative<sup>b,c</sup> Cor:H₂O<sup>d</sup> Relative<sup>b</sup> Intensity Intensity Assignments | Intensity Brackets | Intensity | Intensity | Intensity | Intensity | Intensity | A-values | A-values | A-values | 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 | ... | ... | 1504.1 | 2.7 | 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 |

Notes. The data for coronene in argon are from Hudgins & Sandford (1998) and those for Cor:H₂O (1:160) are from Bernstein et al. (2005).

<sup>a</sup> Hudgins & Sandford (1998).

<sup>b</sup>This work. Only the Cor:H₂O (1:150) is reported; the band positions at different concentrations vary by ±3 cm⁻¹.

<sup>c</sup>Intensities relative to the strongest band at 857.0 cm⁻¹ for argon and 858.1 cm⁻¹ for water.

<sup>d</sup>Bernstein et al. (2005).

<sup>e</sup>Theoretical values were determined for the gas phase with errors of ±4.4 cm⁻¹ (average) and ±11.7 cm⁻¹ (maximum).
were normalized to the most intense band at 857.0 cm\(^{-1}\) for argon and 858.1 cm\(^{-1}\) for H\(_2\)O. A comparison of our results for Cor:H\(_2\)O (1:150) with those of Bernstein et al. (2005) for Cor:H\(_2\)O (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 overlapping H\(_2\)O vibration 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 H\(_2\)O vibrational band.

Comparison of coronene band positions in H\(_2\)O 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:H\(_2\)O (15 K) at a concentration of (1:50). It clearly shows that the H\(_2\)O 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 H\(_2\)O ice, reveals that their observed CH-stretching bands near 3030 cm\(^{-1}\) (3.3 \(\mu\)m) are imperceptible in our sample. The strong C–H out-of plane bending bands between 900 and 500 cm\(^{-1}\) (11–20 \(\mu\)m) suffer from severe blending with the H\(_2\)O ice libration mode. This makes the PAH IR bands between 1650 and 1000 cm\(^{-1}\) (~6.06–10 \(\mu\)m) the most promising for studying PAH:H\(_2\)O photochemistry, as well as for identifying astronomical PAHs and PAH-related photoproduct species in interstellar ices (e.g., Sandford et al. 2004).

Figure 1. Non-irradiated FTIR absorption spectra (4000–450 cm\(^{-1}\)) of Cor:H\(_2\)O (1:50) at 15 K. The inset shows the spectrum in the range 1650–1000 cm\(^{-1}\). The modes attributed to water are labeled in the spectrum as the H\(_2\)O stretch, libration, and bend.
strengths for the higher water concentration, Cor:H2O (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 H2O ices are slightly lower than those in argon, varying between 0.81 for the 1:50 ratio and 0.89 for the 1:400 ratio.

Bossa et al. (2015), used MIR 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 H2O:CH4 ices, whereas a water dilution can considerably alter them. They have shown that the A-values related to the C–H stretching and CH4 bending modes undergo considerable attenuations with water dilution. This effect was also observed by Hudgins et al. (1993). Our data show a slight decrease (∼15%, see Figure 2(c)) in the band strength of coronene in water ices compared to argon. However, Hardegree-Ullman 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-Ullman et al. (2014) utilize UV–Vis absorptions measurements in their determination of the A-values for the mid-IR (MIR). While H2O does not obscure the electronic transitions visible in the UV–Vis region, these transitions are highly influenced by their environments, much more so than the vibrational transitions measured in the MIR (see Mattioda et al. 2012).

3.2. Photochemistry of Coronene in Water Ices

3.2.1. Decay of Coronene

The Cor:H2O ratio photolysis experiments were performed for a Cor:H2O ratios of 1:50, 1:150, 1:200, 1:300, and 1:400. Integrated band areas for neutral coronene bands, namely the 858.1, 1137.3, 1317.3, and 1603.0 cm⁻¹ bands, 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 concentrations (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:

$$\Lambda(t) = \Lambda_0 \exp\left(-\frac{t}{\tau}\right)$$  \hspace{1cm} (4)

where $\Lambda_0$ is the initial value and $\tau$ is the time of decay, as revealed by the red fitting curves in Figure 3. Table 2 displays the fitting parameters for all the Cor:H2O concentrations. These parameters are used in the rate constant calculations in Section 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 H$_2$O 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 the spectra 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 1650–1000 cm$^{-1}$ spectral region, since this region does not suffer from overlap with the broad H$_2$O bands.

Figure 6 shows the spectra of Cor:H$_2$O (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 MIR absorption bands shown in Figure 6 (Cor:H$_2$O at 1:200), where the coronene cations (structure b from Figure 5) located 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 Figure 6). Three cation bands have been reported for coronene in an argon matrix (Hudgins & Allamandola 1995a, 1995b), namely the 876.6, 1387.9, and 1580.1 cm$^{-1}$ bands.

The identified bands are summarized in Table 3, with the structures of the photoproducts shown in Figure 6. Upon increasing photolysis time, the photoproduct 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 1650–1000 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 Equation (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 H$_2$O concentration increases, new bands, not seen in the lower concentration, become visible in the spectrum. The negative peaks are due to the subtraction of neutral coronene.

### 3.2.3. Cor:H$_2$O Concentration Effects

#### 3.2.3.1. Coronene Cations

The H and OH radicals, produced by the H$_2$O photodissociation, react with coronene to form the photoproducts shown in Figure 5. Table 3 contains the band positions, intensities, and assignments of the bands detected at lower and higher concentrations. Due to the overlap of the bands of the multiple photoproducts we only give the positions of the most predominate peaks in H$_2$O bands, the positions given in H$_2$O indicate the most predominant peaks.

The Cor:H$_2$O photoproduct absorption bands were decomposed by Gaussian fits and the peak positions of these bands were measured in water at different concentrations. The photoproduct 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:H$_2$O (1:50), (1:150), (1:200), (1:300), and (1:400) concentrations. 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 for 1:300 Cor:H$_2$O concentrations. 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:H$_2$O (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 to identify bands belonging to a single photoproduct, in that all the bands attributed to the coronene cations grew in at the same rate. Figures 8(c) and (d)) show the integrated band areas of 876.6 cm$^{-1}$ plotted versus the

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\Lambda_0$</th>
<th>$\tau$ (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cor:50</td>
<td>0.28</td>
<td>32.3</td>
</tr>
<tr>
<td>Cor:150</td>
<td>0.39</td>
<td>25.1</td>
</tr>
<tr>
<td>Cor:200</td>
<td>0.49</td>
<td>23.2</td>
</tr>
<tr>
<td>Cor:300</td>
<td>0.62</td>
<td>18.9</td>
</tr>
<tr>
<td>Cor:400</td>
<td>0.79</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Figure 7 shows the spectra of the photoproducts obtained using Equation (4) in the Cor:H$_2$O concentrations ranging from 1:50 to 1:400.
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 $R^2$ fitting parameters and Pearson’s $r$ values are given (see the inset in the figure). In both instances, the $R^2$ and Pearson’s $r$ values are almost 1, indicating a very strong correlation.
<table>
<thead>
<tr>
<th>Positions in H$_2$O$^a$</th>
<th>Relative Intensity in H$_2$O</th>
<th>Theoretical Band Positions$^b$</th>
<th>Theoretical Absolute Intensities (km mol$^{-1}$)</th>
<th>Assigned Photoproducts</th>
<th>Assignments/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>656.05</td>
<td>...</td>
<td>650$^c$</td>
<td>...</td>
<td>CO$_2$</td>
<td>$\nu_2$ bend (only seen for Cor:H$_2$O ratios of 1:50 and 1:150)</td>
</tr>
<tr>
<td>876.6</td>
<td>...</td>
<td>880.7</td>
<td>144.7</td>
<td>C$_3$H$_4$I$_2$</td>
<td>C-H out-of-plane bend (hard to see because of water band)</td>
</tr>
<tr>
<td>1006.8$^d$</td>
<td>0.22</td>
<td>1000.5</td>
<td>25.5</td>
<td>C$_4$I$_3$</td>
<td>CH$_2$ wag and C-H in plane bend (seen for the Cor:H$_2$O ratios 1:50 and 1:150)</td>
</tr>
<tr>
<td>1027.6$^{d,e}$</td>
<td>0.72</td>
<td>1032.5</td>
<td>208.4</td>
<td>1,7-C$<em>{24}$H$</em>{13}$O$_2$</td>
<td>C-O stretch (Peaks at 1032, 1028 (seen for the Cor:H$_2$O ratios 1:50 and 1:150)</td>
</tr>
<tr>
<td>1148.5$^e$</td>
<td>0.38</td>
<td>1148.1</td>
<td>90.6</td>
<td>1,6-C$<em>{24}$H$</em>{12}$O$_2$</td>
<td>C-H scissor and O-H in plane bend—Stronger/well-defined</td>
</tr>
<tr>
<td>1189.0</td>
<td>...</td>
<td>1162.3</td>
<td>66.6/46.1</td>
<td>1,6-C$<em>{24}$H$</em>{12}$O$_2$/1,7-</td>
<td>C-H scissor/C-H bend (Peaks at 1192, 1189, 1183, 1179, 1176)</td>
</tr>
<tr>
<td>1207.8$^{e,d}$</td>
<td>...</td>
<td>1206.0</td>
<td>209.2/113.0</td>
<td>1,7-C$<em>{24}$H$</em>{13}$O$_2$/1,6-</td>
<td>C-H rock and O-H in-plane bend (Broad peaks at 1208, 1219)</td>
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<tr>
<td>1217.9$^{e,d}$</td>
<td>0.28</td>
<td>1213.7</td>
<td>95.1</td>
<td>1,7-C$<em>{24}$H$</em>{12}$O$_2$</td>
<td>C-H rock and O-H in-plane bend (Broad peaks at 1208, 1219)</td>
</tr>
<tr>
<td>1234.1$^d$</td>
<td>0.34</td>
<td>1257.9</td>
<td>107.3</td>
<td>1,7-C$<em>{24}$H$</em>{12}$O$_2$</td>
<td>C-C stretch $\alpha$ to the carbonyl (Peaks at 1237, 1234, 1239)</td>
</tr>
<tr>
<td>1281.2</td>
<td>0.45</td>
<td>1272.6</td>
<td>136.9</td>
<td>1,6-C$<em>{24}$H$</em>{12}$O$_2$</td>
<td>C-C stretch $\alpha$ to the carbonyl (not seen for Cor:H$_2$O ratio of 1:50)</td>
</tr>
<tr>
<td>1345.3$^e$</td>
<td>0.55</td>
<td>1345.7</td>
<td>213.1</td>
<td>C$_2$I$_3$</td>
<td>CH$_2$ scissor (Peaks at 1339, 1342.5, 1345.7)</td>
</tr>
<tr>
<td>1357.8$^e$</td>
<td>...</td>
<td>1356.5</td>
<td>146.0/869.0</td>
<td>1,7-C$<em>{24}$H$</em>{13}$O$_2$/C$_3$I$_3$</td>
<td>CH$_2$ wag and C-H in-plane bend (Peaks at 1366, 1357)</td>
</tr>
<tr>
<td>1376.9</td>
<td>0.56</td>
<td>1369.9</td>
<td>253.4</td>
<td>C$_2$I$_3$</td>
<td>C-C stretch (Broad peaks at 1360, 1370, 1377)</td>
</tr>
<tr>
<td>1387.7$^e$</td>
<td>0.19</td>
<td>1399.1</td>
<td>32.0</td>
<td>1,7-C$<em>{24}$H$</em>{13}$O$_2$</td>
<td>C-C stretch (Peaks at 1406, 1388) (only seen for Cor:H$_2$O ratios of 1:300 and 1:400)</td>
</tr>
<tr>
<td>1436.7</td>
<td>0.12</td>
<td>1435.7</td>
<td>33.5</td>
<td>1,6-C$<em>{24}$H$</em>{12}$O$_2$</td>
<td>C-C Stretch (Broad peaks at 1436.8, 1442.0) (not seen for Cor:H$_2$O ratio of 1:50)</td>
</tr>
<tr>
<td>1515.1</td>
<td>0.80</td>
<td>1516.9</td>
<td>137.5</td>
<td>C$_3$I$_3$</td>
<td>CH$_2$ sym. stretch</td>
</tr>
<tr>
<td>1545.5</td>
<td>0.21</td>
<td>1553.1</td>
<td>60.7</td>
<td>C$_3$I$_3$</td>
<td>C-C stretch (Peaks at 1545 and 1539)</td>
</tr>
<tr>
<td>1572.7$^d$</td>
<td>0.55</td>
<td>1569.0</td>
<td>107.1</td>
<td>C$_3$I$_3$</td>
<td>C-C stretch (Broad peaks at 1576, 1573, 1570)</td>
</tr>
<tr>
<td>1580.1</td>
<td>0.74</td>
<td>1584.4</td>
<td>408.0</td>
<td>C$_3$I$_3$</td>
<td>C-C stretch</td>
</tr>
<tr>
<td>1590.4</td>
<td>0.24</td>
<td>1598.4</td>
<td>67.4</td>
<td>C$_3$I$_3$</td>
<td>C-C stretch (Peaks at 1590 and 1600)</td>
</tr>
<tr>
<td>1606.1$^d$</td>
<td>1</td>
<td>1607.3</td>
<td>106.4</td>
<td>C$_3$I$_3$</td>
<td>C-C stretch (a band at 1590, 1588 was also seen)</td>
</tr>
<tr>
<td>1718.5</td>
<td>...</td>
<td>1723$^c$</td>
<td>...</td>
<td>H$_2$CO</td>
<td>$\nu_2$, $\nu_3$, C=O stretch</td>
</tr>
<tr>
<td>2136.9</td>
<td>...</td>
<td>2139$^c$</td>
<td>...</td>
<td>CO</td>
<td>$\nu_1$ CO stretch (only seen for Cor:H$_2$O ratio of 1:50 and 1:150)</td>
</tr>
<tr>
<td>2341.5</td>
<td>...</td>
<td>2342$^c$</td>
<td>...</td>
<td>CO$_2$</td>
<td>$\nu_3$, asymmetric stretch</td>
</tr>
<tr>
<td>2856.8</td>
<td>...</td>
<td>2850$^c$</td>
<td>...</td>
<td>H$_2$CO</td>
<td>$\nu_1$ CH$_2$ sym. stretch (only seen for Cor:H$_2$O ratio of 1:150)</td>
</tr>
</tbody>
</table>

Notes.

$^a$ Only the photoproducts for the Cor:H$_2$O (1:400) concentration; the other band positions vary by $\pm 3.0$ cm$^{-1}$.

$^b$ Only predicted bands with band strengths $>30$ km mol$^{-1}$ are reported.

$^c$ CO, CO$_2$, and H$_2$CO are from Schutte et al. (1993) and Hudgins et al. (1993).

$^d$ Bands identified experimentally as 1,7-C$_{24}$H$_{12}$O$_2$ by Guennoun et al. (2011a).

$^e$ Bands identified experimentally as 1,6-C$_{24}$H$_{12}$O$_2$ by Guennoun et al. (2011a).

$^f$ Bands identified experimentally as 1,6-C$_{24}$H$_{12}$O$_2$ by Guennoun et al. (2011a).

### 3.2.3.2. Oxygenated and Protonated Photoproducts

Figures 9(a) and (b) compare 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 Figures 9(a) and (b) that the production of 1,6- and 1,7-dihydroxycoronene increases with decreasing coronene concentration. A marked increase with dihydroxycoronene production occurs at the Cor:H$_2$O concentration of 1:300. Previous work has shown that H$_2$O ice chemistry is dominated by reactions that primarily involve the water photodissociation into the radicals OH and H (Woon & Park 2004; Gudipati & Allamandola 2006; Cuylple et al. 2014 and references therein). This behavior was also observed by Cook et al. (2015) for the formation of CO$_2$ and H$_2$CO during the irradiation of PAH water ice mixtures. The cation band at 1580.1 cm$^{-1}$ (Figure 8(a)), and the 1,7-dihydroxycoronene band at 1218.0 cm$^{-1}$ (Figure 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-corocquinone, respectively, through comparison with theory. Figures 9(c) and (d) show 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-corocquinone was not observed for the Cor:50 concentration. As can be seen in Figure 9(c), the band areas for 1,6-corocquinone are 5 times smaller than those for 1,7-corocquinone (Figure 9(d)). Overall, these areas for the corocquinones are 30 times smaller than those for the dihydroxycoronenes. While these photoproduction bands have very small areas, they exhibit increases, with increasing water concentration, as would be expected for a photoproduct. However, the Cor:H$_2$O (1:300) inflection point is not clearly defined for these species, and 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 the bands at 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\(^{-1}\). Figure 7. Neutral-subtracted spectra for the region from 1625 to 1000 cm\(^{-1}\) showing only the photoproduct features appearing after 32 minutes of in situ VUV photolysis of Cor:H\(_2\)O at different concentrations. Data have been baseline-corrected for presentation proposes. The structures of the photoproducts shown in Figure 5.

Figure 11(a) shows the growth of the protonated coronene (C\(_{23}\)H\(_{13}\), structure c in Figure 5) with the photolysis time (VUV fluence) for Cor:H\(_2\)O concentrations of (1:50), (1:150), (1:200), (1:300), and (1:400). Figure 11(b) shows the UV correlation plots for the growth of the three bands attributed to protonated coronene, namely the bands 1606.1, 1342.4, and 1545.5 cm\(^{-1}\) for the Cor:H\(_2\)O (1:300) concentration. Multiplicative factors were used to show the similarities in growth patterns (e.g., 1342.4 and 1545.5 cm\(^{-1}\)). Figures 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 straight lines to obtain 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\(_{15}\)), all the positions for H atom additions are equivalent, yielding only one chemically unique protonated cation structure (C\(_{24}\)H\(_{15}\)), 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 a 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 cations already have 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 band positions of C\(_{23}\)H\(_{13}\), their assignments, and their intensities are given in Table 3. Of the eight bands that can only be attributed to C\(_{23}\)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\(_{23}\)H\(_{15}\) 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:H\(_2\)O 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 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) \(2 \times 10^{-16}\), \(1.2 \times 10^{-17}\), and \(3.1 \times 10^{-17}\) cm molecule\(^{-1}\) for the stretching, bending, and libration modes, respectively (Hudgins & Sandford 1998). The H\(_2\)O column density was determined by taking the average of at least two of the H\(_2\)O bands, \(\sim 3300\) and \(\sim 1660\) cm\(^{-1}\), the reason for this being that the H\(_2\)O libration modes (\(\sim 833\) 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 H\(_2\)O, we used the theoretical molar absorbances to calculate the column densities of the photoproducts, applying the same procedure used for neutral coronene (Equations (1)–(3)); details are 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 Equations (1) and (2) and the amount of consumed neutral is given by
Equation (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:H$_2$O 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 discussed earlier, there is an increase of $\sim$20% in the loss of coronene between Cor:200 and Cor:300. This corresponds to a 11% increase of cations, a 10% increase in 1,6-$C_{24}H_{12}O_2$, a 9% increase in 1,7-$C_{24}H_{12}O_2$, a 3% increase in $C_{24}H_{15}^+$, and an increase of $\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 that these products are not dependent on the initial Cor:H$_2$O concentrations. One possibility is that 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 of UV photolysis time, we estimate that ~86% of the neutral coronene is converted into photoproducts (see Figure 12). Of this 86%, roughly 38% is converted into cations, 7% is converted to protonated coronene, 16% converts to 1,7-dihydroxycoronene, 13% converts to 1,6-dihydroxycoronene, 12% converts to 1,7-coroquinone, around 1% converts to 1,6-coroquinone, and ~11% convert into other species like CO₂, CO, and H₂CO (not shown in Figure 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 medium produces smaller PAH-like molecules as well as CO₂. Mattioda et al. (2012) studied the PAH photochemistry of the PAH

**Figure 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).
isoviolanthrene (C_{32}H_{18}) in different environments and showed that the growth of CO$_2$ appears with the loss of the PAH isoviolanthrene, when water vapor is present. The O and OH formed from water dissociation erode the PAH, leading to the formation of CO, CO$_2$, and H$_2$CO within the ice (Cook et al. 2015). The CO$_2$ 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 H$_2$CO $\nu_3$ CH scissor mode at 1718.5 cm$^{-1}$ is clearly seen at all concentrations, although it is much smaller compared to the CO$_2$ band. The integrated band strengths for CO$_2$ ($A_{CO_2} = 2 \times 10^{-16}$ cm molecule$^{-1}$, e.g., Hudgins et al. 1993 and references therein) and H$_2$CO ($A_{H_2CO} = 9.6 \times 10^{-18}$ cm molecule$^{-1}$ (Schutte et al. 1993) were used to track the growth of CO$_2$ and H$_2$CO shown in Figure 13.

Figures 13(a) and (b) show the growth of the integrated band area for the 2341.5 cm$^{-1}$ band of CO$_2$ and the 1718.5 cm$^{-1}$ band of H$_2$CO, respectively, plotted versus photolysis time for the different Cor:H$_2$O concentrations studied. It is interesting to note that, although the concentrations of CO$_2$, and to a lesser extent H$_2$CO, increase with increasing UV photolysis time, these two molecules do not exhibit the same Cor:H$_2$O concentration dependence as the coronene photoproducts (e.g., no abrupt increase at Cor:H$_2$O (1:300)). The CO$_2$ data were corrected by removing the CO$_2$ 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, which corresponds to a first order reaction given in Equation (5), which is equivalent to Equation (4). This equation can be used to fit the column density of the coronene molecule during the irradiation phase via Equation (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 taken into account by averaging all the observed bands for each species at different concentrations using the theoretical A-values determined by averaging the number of molecules (N) obtained from all the observed bands for each species (Equation (3) at different concentrations. As previously mentioned, theoretical A-values were used for the determinations.

$$\frac{d[C_{24}H_{12}]}{dt} = k_t[C_{24}H_{12}],$$

(5)

$$C_{24}H_{12}(t) = C_{24}H_{12}(t = 0)e^{-kt}.$$  

(6)

For the photoproducts shown in Figure 12, the cation can be assumed to be produced via the reaction of a first-order growth using Equation (7), were $k_1$ is the rate constant:

$$C_{24}H_{12}^+(t) = a[1 - e^{-kt}];$$

(7)

Assuming that all the photoproducts are also formed via first-order reactions, we used Equation (7) to fit the experimental data through 30 minutes of irradiation for Cor:H$_2$O (1:50) and 60 minutes of 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 $\times$ 10$^{-6}$ and 2.3 $\times$ 10$^{-5}$ s$^{-1}$.

Bouwman et al. (2010) and Cook et al. (2015) found two distinct reaction pathways for the PAHs that 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:H$_2$O < 1:300, favor PAH ion-driven and ion-dominated reaction networks and processes, while PAH:H$_2$O > 1:300 favors 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 protonated coronene cations, oxygenated photoproducts, and CO, CO$_2$, and H$_2$CO. This work is the first detailed IR study of the effect of different concentrations of coronene on its ionization efficiency in H$_2$O ice, and all the photoproducts formed. There is a clear link between coronene concentration and photoproduct yield and thus, by implication, between the types of coronene photoproducts present in the ice that are available for subsequent reactions and processes.

The ionization behavior of coronene in H$_2$O ice falls into two distinct concentration regimes. At low coronene concentrations, ionization yield and stabilization are high, ranging from around 70% for Cor:H$_2$O (1:400), to about 40% for Cor:H$_2$O (1:200), and dropping to nearly 15% for Cor:H$_2$O (1:50) (Figure 3). The PAH concentrations with respect to H$_2$O in interstellar ices are estimated to be on the order of up to 2%–3%. In this regime, PAH ionization occurs, with conversion efficiencies on the order of 10%–20% (e.g., Bouwman et al. 2011a and references within).

Rapacioli et al. (2006) suggested 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) and Madden (2000) 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 photo-driven 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 in planet-forming disks. A few observational studies have provided evidence for the absorption features of PAHs in molecular clouds (e.g., Chiar et al. 2000; Keane et al. 2001), while Hardegree-Ullman 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 μm range can be attributed to neutral PAHs frozen out in dust grain mantles (Boogert et al. 1996).

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 Section 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 $1.24 \times 10^{15}$ CO2 cm$^{-2}$ to $3.22 \times 10^{15}$ CO2 cm$^{-2}$ for this concentration regime. While this represents a threefold increase (5% error bar) in the number of CO2 molecules produced, as well as a threefold 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 that 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., Boogert et al. 1996, 2015; Keane et al. 2001; Gibb & Whittet 2002; Schutte & Khanna 2003; van Diedenhoven 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 5.3–7.7 μm interstellar ice spectra associated with 41 low-luminosity YSOs carried out by Boogert et al. (1996). After correcting for the broad 6 μm H2O-ice feature, Boogert et al. (1996) showed that the residual
absorption consists of at least five 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 five spectroscopic components identified by Boogert et al. (1996), labeled 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 μm reported here, as well as the photoproduct bands reported by Cook et al. (2015) for anthracene, pyrene, and benzo(ghi)perylen. Likewise, since the interstellar residual spectra do not extend beyond 7.8 μm due to the overlap with the interstellar silicate feature (Boogert et al. 1996), we do not show the computed features in this region.

Comparing the PAH photoproduction bands with the interstellar residual components shown in Figure 15 supports the suggestion that PAHs and their photoproduction trapped in interstellar ices should be considered as possible contributors to the components described by Boogert et al. (1996). 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 photoproduction trapped in water-rich ices, would produce very broad, slightly structured features.

The 5.5–6.5 μm 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 μm fall in the region characteristic of the very strong carbonyl (>C=O) stretch, with C1 reasonably well-accounted for by overlapping >C=O stretching bands of ice-bound HCOOH and H₂CO (see Boogert et al. 1996, 2015). The >C=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 >C=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...
Oxidation products of coronene and CO$_2$ growth as a function of VUV irradiation time for the C$_{24}$H$_{12}$:H$_2$O ices.

**Figure 14.** Neutral coronene loss (red close circles) and CO$_2$ growth (black open squares) as a function of VUV irradiation time for the C$_{24}$H$_{12}$:H$_2$O ices.

Quinones contribute to the dominant 5.5–6.5 $\mu$m portion of the C5 component seems reasonable.

It can be observed from Figure 15 that the ketones (RC(=O)R') dominate the region between 5.8 and 6.2 $\mu$m corresponding to C1 and C2 components. The cations (R$^+$ and R-H$^+$) are more abundant in the parts of C2, C3, and C4 (6.2–7 $\mu$m) and the alcohols (R-OH) dominate the C2 (6–6.2 $\mu$m) component. Further perusal of Figure 15 shows that the C2 component, which extends from about 5.8 to 6.5 $\mu$m, 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 $\mu$m (now known to be the C2 component from Boogert et al. 1996) 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 $\mu$m
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, and the other for PAH cations. Adopting the intrinsic strength for PAH cations, they calculated 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 that 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 6.5–7.8 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 ketone bands. Keane et al. (2001) and Schutte & Khanna (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. (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, 6.5–7.8 μm section of C5. Discussions of the weak substructure evident on C5, and possible assignments, have been published (e.g., Lacy et al. 1991; Schutte et al. 1996, 1999; Keane et al. 2001; Boogert et al. 2008, 1997). 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 >C=O stretching bands that we suggest contribute to the 5.8–6.5 μm portion of C5.

6. Discussion

The manuscript describes mid-IR absorption spectroscopy of C2H12:H2O UV photoproducts. Band positions and relative intensities of neutral coronene in H2O 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 the argon matrix. Additionally, band strengths are derived for neutral coronene isolated in an astrophysically relevant H2O ice at 15 K. The main conclusions of this manuscript are summarized below.
1. VUV photolysis of coronene-containing H2O ice causes the embedded coronene to ionize and react with H2O photoproducts. The band positions of coronene cations trapped in H2O ice are measured. Additionally, peak positions of C24H12:H2O photoproducts, other than the cation, are determined and tentatively assigned to C24H12:Xn species, with X being O, H, or OH.

2. The photochemistry is tracked as a function of C24H12:H2O ice concentration for Cor:H2O 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. In the same way, the fraction of neutral coronene converted into photoproduct species other than the C24H12 is larger in ices of higher water concentration.

3. The C24H12:H2O 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 10–16 minutes before slowing and growing steadily until an hour of irradiation.

4. It was found that the corresponding increases, over the different water concentrations, of the 1,6- and 1,7-C24H10O2 photoproducts, do not depend on the initial Cor:H2O concentrations.

5. Another interesting result is that the photoproducts 1,6- and 1,7-C24H10O2 do not depend on the initial Cor:H2O concentrations, strongly suggesting that they can be formed from the 1,6- and 1,7-dihydroxycoronene.

6. A comparison of the growth pattern of CO2 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:H2O (1:50) to ~60% for Cor:H2O (1:400). Therefore, the production of CO2 from coronene is only 2.5 × 10^{-15} CO2 cm^{-2} for this concentration regime, 0.01% of the carbon inventory.

In summary, in this study we have shown that neutral coronene is highly reactive with water ice, under UV irradiation, 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 concentrations, strongly suggesting that they can be formed from the 1,6- and 1,7-dihydroxycoronene.

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