

DEUTERIUM ENRICHMENT OF POLYCYCLIC AROMATIC HYDROCARBONS BY PHOTOCHEMICALLY INDUCED EXCHANGE WITH DEUTERIUM-RICH COSMIC ICES

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ABSTRACT

The polycyclic aromatic hydrocarbon (PAH) coronene ($C_{24}H_{12}$) frozen in D_2O ice in a ratio of less than 1 part in 500 rapidly exchanges its hydrogen atoms with the deuterium in the ice at interstellar temperatures and pressures when exposed to ultraviolet radiation. Exchange occurs via three different chemical processes: D atom addition, D atom exchange at oxidized edge sites, and D atom exchange at aromatic edge sites. Observed exchange rates for coronene ($C_{24}H_{12}$)- D_2O and $d_{1,2}$ -coronene ($C_{24}D_{12}$)- H_2O isotopic substitution experiments show that PAHs in interstellar ices could easily attain the D/H levels observed in meteorites. These results may have important consequences for the abundance of deuterium observed in aromatic materials in the interstellar medium and in meteorites. These exchange mechanisms produce deuteration in characteristic molecular locations on the PAHs that may distinguish them from previously postulated processes for D enrichment of PAHs.

Subject headings: ISM: abundances — ISM: molecules — meteors: meteorites — methods: laboratory — molecular processes — ultraviolet: ISM

1. INTRODUCTION

Isotopic anomalies represent the only unequivocal signatures of the survival of circumstellar and interstellar (IS) materials within the solar system. For example, significant deuterium enrichments have been found in the organic components of both meteorites (see Yang & Epstein 1983; Zinner 1988; Halbout, Robert, & Javoy 1990) and interplanetary dust particles (IDPs; Zinner, McKeegan, & Walker 1983; McKeegan, Walker, & Zinner 1985; Messenger et al. 1995, 1996), and these are understood to be remnants of presolar processes. Deuterium enrichments of several classes of extraterrestrial organic compounds have been measured, including aromatics in meteorites and IDPs (Kerridge, Chang, & Shipp 1987; Clemett et al. 1993) and meteoritic amino, hydroxy, dicarboxylic, and hydroxy-dicarboxylic acids (Pizzarello et al. 1991; Cronin et al. 1993).

Unlike isotopic signatures in circumstellar materials, D anomalies do not have a nucleosynthetic origin. Instead, they have been proposed to result from interstellar processes such as gas-phase ion-molecule reactions at low temperatures (Geiss & Reeves 1981; Dalgarno & Lepp 1984), gas-grain chemistry at low temperatures (Tielens 1983, 1992), and repeated unimolecular photodissociation of gas-phase interstellar PAHs (Allamandola, Sandford, & Wopenka 1987; Allamandola, Tielens, & Barker 1989).

PAHs are known to be ubiquitous in the ISM (Dwek et al. 1997; Allamandola, Hudgins, & Sandford 1999) because spectral features of the PAHs are observed in emission from planetary nebulae, reflection nebulae, H II regions, and the diffuse interstellar medium (ISM) (Allamandola et al. 1989; Schutte et al. 1998). They have also been observed in absorption toward protostellar objects embedded in dense

interstellar molecular clouds (Smith, Sellgren, & Tokunaga 1989; Sellgren et al. 1995). The PAHs seen in absorption in dense clouds are presumably frozen into icy mantles on grains because at the temperatures characteristic of these clouds (10–50 K) most molecules, including PAHs, would be expected to be efficiently condensed from the gas phase (Sandford & Allamandola 1993). Ices in these clouds are photochemically processed by ambient UV photons (Prasad & Tarafdar 1983). Laboratory studies have shown that the photolysis of interstellar ice analogs containing simple molecules like H_2O , CH_3OH , NH_3 , etc., lead to a surprisingly rich system of photochemistry that produces considerably more complex molecular species (cf. Bernstein et al. 1995). However, the photochemistry of PAHs in these ices is only poorly understood.

In a recent paper we reported our initial results from an experimental program designed to elucidate the photochemistry of the PAH coronene in H_2O ices under interstellar conditions (Bernstein, Sandford, & Allamandola 1999). Although gas phase PAHs are very stable, even when photoionized (Allamandola et al. 1999), Bernstein et al. (1999) reported that the UV photolysis of PAHs in low-temperature H_2O ices produces both partially oxidized and partially reduced aromatic photoproducts (see Fig. 1). This work also showed early results indicating that the peripheral H atoms on the PAHs can be replaced by D atoms as a result of irradiation in D_2O -rich ices. This result is very interesting because (1) the H atoms on PAHs are normally considered to be very nonlabile, and (2) PAHs represent a major carrier of D excesses in primitive meteorites (Kerridge et al. 1987).

In this paper we use standard isotopic substitution experimental techniques to expand on our earlier work and show that photo-oxidation of PAHs can occur on a much shorter timescale than was previously thought. We also demonstrate that PAHs can easily become D-enriched by photochemistry in D-rich interstellar ices to the levels

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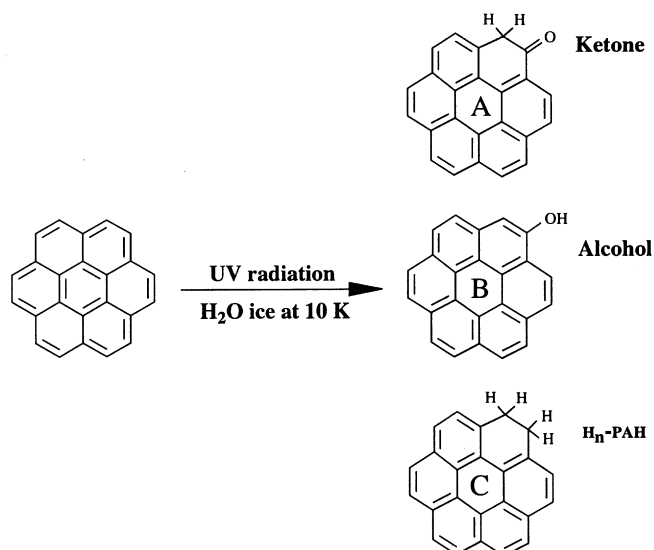


FIG. 1.—New molecular structures produced by the UV irradiation of coronene-H₂O ice samples. Oxygen atoms add to edge carbons to form ketone and alcohol side groups and the addition of H atoms yield aliphatic edge structures (H_n-PAHs). When bay regions are present, bridging ethers may also form (not shown; see Bernstein et al. 1999). The locations of the functional groups have been selected arbitrarily.

observed in meteorites. Thus, the photolysis of PAHs in D-rich interstellar ices may provide an explanation for the deuterium enrichment of aromatic molecules observed in meteorites and IDPs.

2. EXPERIMENTAL METHODS

Since the purpose of these experiments is to identify and understand the deuterium photoexchange processes that can occur to PAHs in low-temperature ices, we have used standard isotopic substitution techniques. In such experiments, one replaces *all* of the atoms of a specific element in one of the starting materials with an isotopic variant. That way, when that isotopic variant is seen in subsequent products, it is clear where it came from, and the mediating chemical processes can be studied. Once these processes are understood, it will be possible to better understand more complex astrophysical simulations (see § 5, especially § 5.1).

The sample preparation and irradiation apparatus at NASA-Ames and the microprobe laser-desorption, laser-ionization mass-spectrometer ($\mu\text{L}^2\text{MS}$) at Stanford University that were used in this study are described in detail elsewhere (Clemett & Zare 1997 for $\mu\text{L}^2\text{MS}$; Bernstein et al. 1999 for sample preparation).

Samples were prepared at the Astrochemistry Laboratory at NASA-Ames as follows: Coronene (C₂₄H₁₂; Aldrich 97%) or perdeuterated coronene (*d*₁₂-coronene; C₂₄D₁₂; Cambridge 98%) was vapor deposited under dynamic vacuum (10⁻⁸ mbar) onto a ~15 K metal or ~10 K CsI substrate simultaneously with H₂O or D₂O vapor. The temperatures given are accurate to ± 1 K. Water vapor was deposited from a glass sample bulb through a room-temperature copper inlet pipe while coronene was deposited from a separate Pyrex sample tube heated to ~150 °C. Deposition times were typically 30 minutes. Previous infrared spectral studies indicate that sample layers deposited in this manner have typical thickness of ~1 μm and H₂O/PAH ratios in excess of 500/1 (Bernstein et al. 1999). Experiments involving D₂O were preceded by a pass-

ivation step where a 2 liter bulb containing 20 mbar of D₂O was slowly pumped through the vacuum system to exchange any surface H for D.

Each PAH-H₂O layer was then UV-irradiated for a predetermined time using a pure hydrogen discharge lamp. This lamp emits $\sim 2 \times 10^{15}$ photons cm⁻² s⁻¹ nearly evenly divided between the Ly α line and a 20 nm wide molecular transition centered near 160 nm (Warneck 1962). The sequential deposition and irradiation of coronene-water layers was repeated multiple times, with 10 or 200 minutes of irradiation per layer, depending on the experiment, after which the sample was slowly warmed to room temperature to gently sublime away the H₂O/D₂O.

After warmup, the remaining nonvolatile material was removed and transported to the Stanford Chemistry Department where its mass spectrum was measured using the $\mu\text{L}^2\text{MS}$ technique (Clemett & Zare 1997). Note that the mass spectra of our photolysis residues are typically compared to unphotolyzed standards. These standards were prepared in the same manner as the samples except that no irradiation was made, i.e., the coronene was deposited in H₂O or D₂O and later warmed to room temperature without irradiation.

3. RESULTS

3.1. Atom Addition: O, H, and D

Figure 2 presents the $\mu\text{L}^2\text{MS}$ spectra of coronene (C₂₄H₁₂), and that of the nonvolatile residues resulting from the 10 minute UV irradiation per layer of coronene in H₂O and D₂O ices at ~15 K. The large peak that appears in all three spectra near 300 amu arises from unreacted coronene. The small peaks near 301 and 302 amu in the spectrum of the coronene standard (Fig. 2c), are caused by the natural abundance of the ¹³C isotopes in coronene, which also contribute to these peaks in the other two spectra. The peaks at 316, 332, and 348 amu in the spectra of the UV irradiated coronene-H₂O and coronene-D₂O

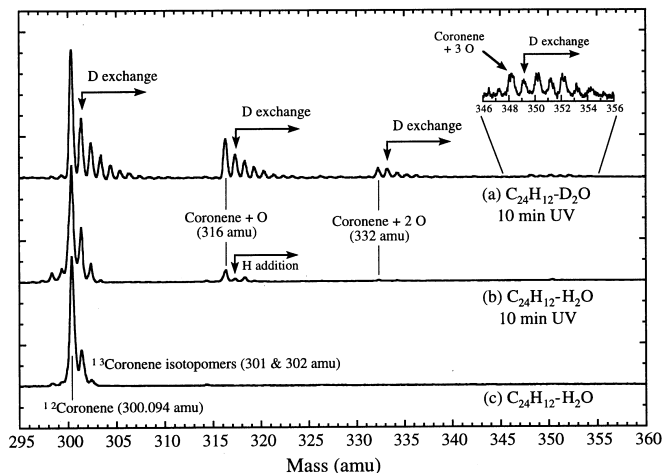


FIG. 2.—The $\mu\text{L}^2\text{MS}$ spectra of (a) a room temperature residue from 10 minute per layer UV irradiations of five layers of coronene (C₂₄H₁₂; 300 amu) in D₂O at ~15 K, compared with (b) a room-temperature residue made using 10 minute per layer UV irradiations of five layers of coronene in H₂O at ~15 K, and (c) a coronene standard deposited into H₂O at ~15 K, and warmed to room temperature but not photolyzed. Each layer was deposited for ~30 minutes. The radiation causes oxidation of the coronene as well as some H-atom addition. The top spectrum also shows that UV photolysis also drives rapid H/D exchange between the water matrix and both coronene and its photoproducts.

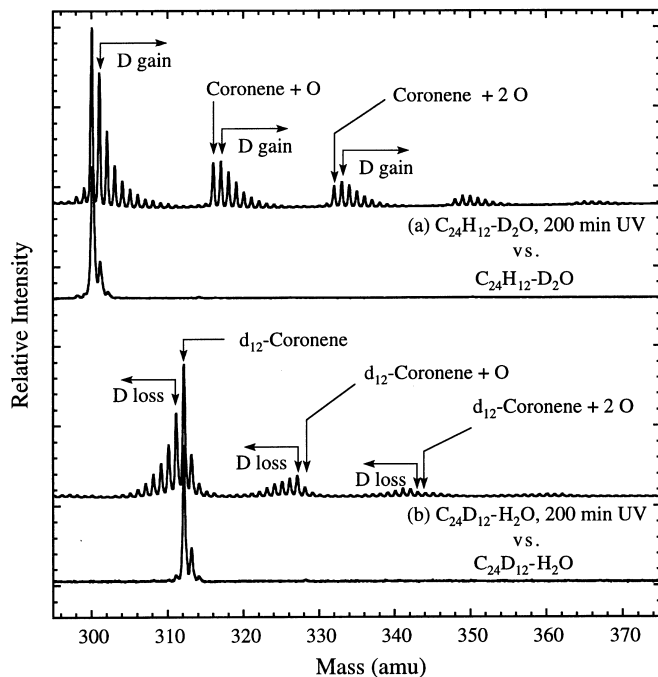


FIG. 3.—The $\mu\text{L}^2\text{MS}$ mass spectra of coronene ($\text{C}_{24}\text{H}_{12}$) and d_{12} -coronene ($\text{C}_{24}\text{D}_{12}$) standards compared with room-temperature residues made by (a) 200 minute per layer UV irradiations of five layers of coronene ($\text{C}_{24}\text{H}_{12}$) in D_2O at ~ 15 K and (b) 200 minute per layer UV irradiations of five layers of perdeuterated coronene ($\text{C}_{24}\text{D}_{12}$) in H_2O at ~ 15 K. Both unreacted coronenes (300 and 312 amu) and oxidized coronenes (300 or 312 plus increments of 16 amu), are subject to both H/D atom exchange and addition reactions.

ices correspond to the addition of one, two, and three oxygen atoms, respectively, to the coronene starting material (Bernstein et al. 1999). In Figure 2b the smaller peaks at 318 and 334 amu correspond to the addition of two H atoms to the mono- and dioxidized coronenes at 316 and 332 amu, respectively. Similarly, when coronene is photolyzed in D_2O ice (Fig. 2a) D-atom addition reactions must also be occurring, although we show in § 3.2 that exchange reactions appear to dominate in these samples. The implications of these atom addition reactions for the photo-deuteration of PAHs are discussed in §§ 4.2 and 4.3.

3.2. Deuterium Exchange

In the mass spectrum of the UV-irradiated coronene- D_2O mixture in Figure 2a, the peaks at 300, 316, 332, and 348 amu (coronene and coronene plus 1, 2, and 3 oxygens, respectively) are followed by a series of peaks decreasing in intensity with increasing mass over the 301–312, 317–328, 333–344, and 349–354 amu mass ranges. These series provide clear evidence for the UV-mediated exchange of D atoms from the D_2O ice matrix for H atoms on the coronene. After only 10 minutes of photolysis a majority of the oxidized coronenes have exchanged at least one H atom for a D atom from the D_2O ice. During this exposure period even the unoxidized coronene starting material has become appreciably deuterated.

While the relative heights of the peaks from 301 to 312 amu diminish rapidly with increasing mass, consistent with a purely statistical process, those following the oxygen addition peaks at 316, 332, and 348 amu do not. Compare, for example, the relative heights of the peaks from 348–354 amu (Fig. 2a, inset) with those from 301–312. While the peak at

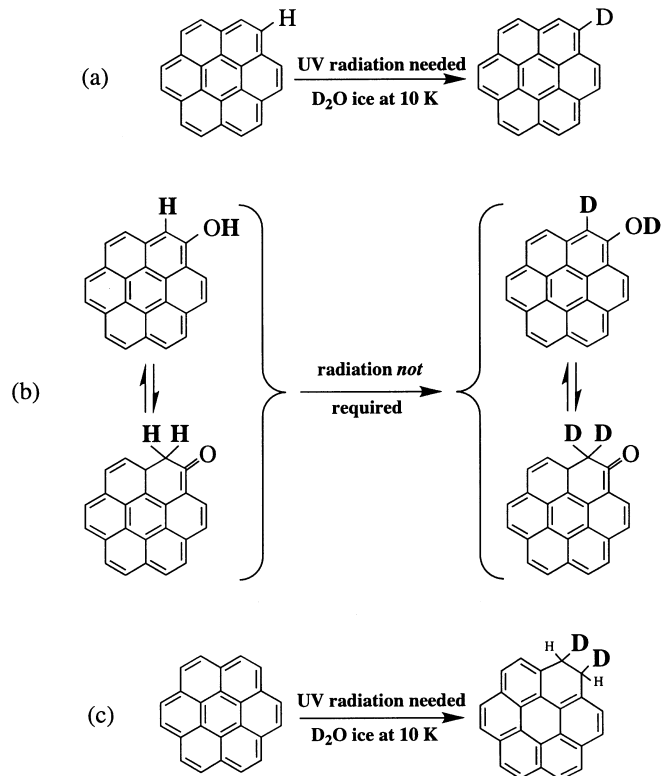


FIG. 4.—Several coronene photoreactions that lead to deuterium exchange. (a) Exchange of fully aromatic C–H bonds requires UV radiation and do not occur in its absence. (b) Hydrogen exchange via keto-enol tautomerism. Only the H atoms on carbon atoms next to a C=O and next to or on a C–OH group are subject to this exchange mechanism. This exchange mechanism can occur even in the absence of UV radiation (such as during aqueous alteration). (c) UV-stimulated addition of D atoms across a double bond to yield an aliphatic ring. This deuterium, once added, is not labile under aqueous alteration.

300 is clearly much larger than those that follow it, the peak at 348 is comparable to those at 350 and 352. To quantify this observation, the ratio of the sum of the areas of the first two deuterated peaks (corrected for ^{13}C contributions) to their associated undeuterated parent peak are 0.42, 0.72, 1.05, and 1.38, respectively, for the original coronene and the 1-, 2-, and 3-added oxygen variants. Clearly, coronene molecules that have acquired oxygen atoms are more likely to acquire D atoms than the unoxidized coronene starting material and the more oxygen present, the greater the exchange. Note that the variant with three added oxygen atoms (Fig. 2a, inset) shows a pronounced preference for even masses (i.e., 350 and 352 amu peaks are larger than 349 and 351 amu) although this pattern is not obvious for the peaks following the 316 and 332 amu, 1 and 2 oxygen variants, in Figure 2c.

The preference of oxidized coronenes for deuteration is even more pronounced in the mass spectra of the ices exposed to higher doses of UV radiation. Figure 3 shows a comparison of the mass spectra of the residues resulting from 200 minute per layer UV-photolysis (20 times that of the samples in Fig. 2) of $\text{C}_{24}\text{H}_{12}\text{-D}_2\text{O}$ and $\text{C}_{24}\text{D}_{12}\text{-H}_2\text{O}$ ices at ~ 15 K, and unphotolyzed coronene standards.

The top two traces (Fig. 3a) are from the photolysis residue of a $\text{C}_{24}\text{H}_{12}\text{-D}_2\text{O}$ sample and a $\text{C}_{24}\text{H}_{12}$ standard (300 amu), respectively. As in Figure 2, the peaks at 316, 332, and 348 amu correspond to the singly, doubly, and triply oxidized coronenes and those to higher masses indi-

cate the extent to which the coronene and its oxidized photoproducts have undergone D for H exchange from the D₂O ice matrix. The longer photolysis time in this case has resulted in more extensive D atom-exchange than was observed in Figure 2a, where the exposure was only 10 minutes. For example, the oxidized coronenes that have exchanged an H atom for a D atom are all visibly more abundant than those that retained all their H atoms (for example, the peak at 317 amu is greater than that at 316 amu). Furthermore, as with the shorter photolysis time, the more oxygen added to the coronene, the greater the effect. For example, not only is the triply oxidized coronene (348 amu) less abundant than that which has a D atom (349 amu), it is actually less abundant than that which has acquired *three* (351 amu).

The two spectra at the bottom of Figure 3b are the mass spectra of the residue of a C₂₄D₁₂-H₂O mixture UV-photolyzed for 200 minutes per layer at ~15 K and a C₂₄D₁₂ standard (312 amu). A careful examination of the mass spectra of the C₂₄D₁₂-H₂O photolysis residue in Figure 3b shows that D atoms from C₂₄D₁₂ are replaced by H atoms from the H₂O ice matrix in a manner that is similar to the reverse of the case described above. Again, the extent of the exchange is clearly enhanced in the oxidized species relative to the unoxidized coronene. The possible causes and implications of the role of oxygen in the exchange of H and D are discussed in §§ 4.2 and 5.2. It is interesting to note that in addition to the cascade of peaks to lower masses, i.e., to the left of the 312, 328, and 344 amu peaks in Figure 3b, peaks also appear at *higher* masses (i.e., to the right of these peaks). Because these species are already fully deuterated and cannot increase their mass by exchange, this observation is a clear demonstration that H- and D-*atom addition* reactions (Fig. 4c) take place. This behavior is discussed further in § 4.3.

4. MOLECULAR INTERPRETATIONS

We have presented evidence (§ 3) that the photolysis of coronene in D₂O results in H/D exchange reactions and O, H, and D addition reactions. The following sections focus on these reactions and the resulting molecular structures observed under our experimental conditions. The implications of these reactions for extraterrestrial materials are considered in § 5.

Throughout the discussion, keep in mind that the deuterium levels measured from our samples by mass spectroscopy should strictly be regarded as lower limits. It is possible that some of the more labile D atoms (i.e., those on alcohols and adjacent to ketones) may have been exchanged with H atoms, caused by exposure of the samples to atmospheric moisture during transport.

4.1. H/D Exchange on Coronene

The exchange of H atoms on the otherwise unreacted coronene starting material with D atoms from the D₂O ice is demonstrated by the series of peaks decreasing in intensity with increasing mass over the 301–312 amu range in Figure 2a. This exchange of H for D, represented schematically in Fig 4a, was somewhat unexpected. Aromatic C–H bonds are normally not labile, even at much higher temperatures than those employed in our experiments (Hart 1979). This H/D exchange is not seen in control experiments when we freeze and thaw C₂₄H₁₂ in D₂O without photolysis. Clearly the exchange is facilitated by exposure to UV

radiation and occurs very rapidly with at least one third of the unoxidized coronene acquiring one or more D atoms after only 10 minutes of UV photolysis (Fig. 2a).

We would note that all the H atoms on an unoxidized coronene are equivalent, i.e., there is no molecular edge site that has special structural significance. The relatively smooth decline in intensity with increasing D-atom exchange seen in the 301–312 amu range in Figures 2a and 3a is consistent with simple statistical exchange being the main process occurring under our experimental conditions.

4.2. Coronene Oxidation Enhances H/D Exchange

As described in § 3, the different mass patterns produced by the deuterated species with and without added oxygen (Figs. 2 and 3) indicate that the extent of exchange of H and D between the coronene and the ice matrix is greater for oxidized coronene than it is for unoxidized coronene. This enhanced exchange is not necessarily surprising for several reasons. Oxidized PAHs have an additional means of deuterium exchange not available to unoxidized PAHs. Both unoxidized and oxidized PAHs can directly exchange their peripheral aromatic hydrogen/deuterium atoms with the surrounding matrix (§ 4.1 and Fig. 4a). As mentioned above, this process is expected to produce a statistical fall off in the degree of exchange.

Aromatic molecules bearing oxygen atoms also have an additional way to exchange those H atoms that reside on the same aromatic rings as the oxygen. It is well known that oxidized PAHs in solution can exchange certain H atoms with surrounding water molecules by keto-enol tautomerism, the process that inter-converts the alcohol and ketone forms (Hart 1979; Fig. 4b). Because the two H atoms associated with the oxidized ring *are* labile, this second mechanism should cause H atoms on oxidized coronenes to exchange with D atoms from the ice far more rapidly than unoxidized coronene, just as is observed and discussed in § 3.2. Note that while the exchange of aromatic H for D (Fig. 4a) requires UV radiation, this keto-enol exchange, at least in liquid water, does not. We have not yet determined if these oxidized PAHs, once generated *in situ*, require UV to undergo D/H exchange under our experimental conditions.

Note that two labile H atoms result from the addition of each oxygen atom to coronene (Fig. 4b). If this mechanism is operative in general, then oxidized coronenes would be expected to show a tendency to exchange deuterium in pairs. This pattern of mass peaks is clearly seen in the 349–354 amu range for the coronene variant with three added oxygen atoms (Fig. 2a), but is less apparent in the variants with fewer O atoms, presumably because a greater fraction of the exchange is associated with the more abundant normal aromatic rings. The even-odd pattern is also not obvious in the spectra shown in Figure 3, but the longer photolysis time of these samples generates increased atom addition (§ 3.1, § 4.3) that complicates interpretation of the mass spectra.

The increasing extent of deuterium exchange with oxidation and the even-odd pattern of deuterium exchange in pairs both strongly suggest that the oxidized coronene molecules are acquiring some deuterium from the D₂O when they undergo keto-enol tautomerism of their oxidized rings.

4.3. Atom Addition Reactions

The addition of H atoms to PAHs results in H_n-PAHs, aromatic systems where one or more of the aromatic rings

have been converted to aliphatic rings (Bernstein et al. 1996). We have noted previously (Bernstein et al. 1999) that one of the reactions that occurs when coronene is photolyzed in H_2O is the addition of H atoms to partially reduce the coronene. As an example, the structure shown in Figure 1c is that of dihydro-coronene ($\text{C}_{24}\text{H}_{14}$), a coronene that has gained two H atoms, thereby converting one of its outer aromatic rings into an aliphatic ring. For closed-shell, stable PAHs, these atom additions to PAHs must always occur in pairs, yielding an H_n -PAH where n is a multiple of two, but less than or equal to the number of carbon atoms in the parent PAH. As can be seen from the mass spectrum of coronene exposed to UV radiation in H_2O (Fig. 2b), H-atom addition to the unoxidized coronene is measurable but not appreciable after only 10 minutes of UV radiation (see 302 amu in Fig. 2b). However, H-atom addition to the oxidized coronenes is clearly indicated by the heights of the peaks at 318 and 334 seen in Figure 2b and noted in § 3.1. By analogy one might expect that the coronene oxidized in D_2O would be subject to the addition of pairs of D atoms, which would add 4 amu per pair.

These observations highlight an ambiguity in the assignment of particular peaks in these mass spectra because either deuterium exchange or addition reactions (or both) could account for the presence of certain peaks. This problem exists for all peaks with an added mass of multiples of 4 because they could be produced by either multiples of four $\text{H} \rightarrow \text{D}$ exchanges or the addition of multiples of two D atoms. For example, the peak at 350 amu in the inset of Figure 2a can only be produced by molecules that have exchanged two H atoms for D atoms (onto the triply oxidized coronene at 348 amu), whereas the peak at 352 could contain contributions from molecules that have added two D atoms and molecules that have exchanged four H atoms for D atoms. The absence of a clear pattern of peaks spaced by 4 amu in Figure 2a suggests that neither coronene nor its oxidized variants are experiencing significant D-atom addition after being exposed to only 10 minutes of UV irradiation.

The results of the 200 minute coronene- D_2O photolysis experiment shown in Figure 3b confirm however that atom addition reactions must be taking place at longer exposure times. Because hydrogen is lighter than deuterium, the d_{12} -coronene- H_2O photolysis experiments shown in Figure 3b could not be producing the mass peaks on the high side of d_{12} -coronene (314–316 amu) and its photoproducts (329–331, 345–348 amu, etc.) if only exchange were taking place. These peaks make sense only if H atoms are being added to some of the d_{12} -coronene (and their photoproducts) under these experimental conditions. Thus, the mass peaks in Figure 3 provide unequivocal evidence of H-atom addition to d_{12} -coronene. The fact that atom addition becomes obvious only at higher UV doses suggests that the atom addition reactions are slower than the oxidation and exchange reactions.

4.4. No Isotopic Exchange Asymmetry?

The comparable extent of $\text{H} \rightarrow \text{D}$ and $\text{D} \rightarrow \text{H}$ exchange seen in the mass spectra present in Figure 3 indicates that the two rates of exchange are the same under these conditions (15 K, 200 minutes of UV per ice layer), within our experimental uncertainties. This balance indicates that the exchange is largely a statistical process, not one that preferentially places deuterium onto the PAH. This behavior is

very different from the other processes that could lead to the D enrichment of PAHs, namely gas-phase ion-molecule reactions at low temperatures (Geiss & Reeves 1981; Dalgarno & Lepp 1984), gas-grain chemistry at low temperatures (Tielens 1983, 1992), and repeated unimolecular photodissociation of gas-phase interstellar PAHs (Allamandola et al. 1987, 1989). These other mechanisms enrich PAHs in deuterium through isotope effects resulting from the differences in the zero-point energies (ZPEs) of aromatic C–H and C–D bonds.

Perhaps we have not observed the expected isotope effect because our experiments have not achieved equilibrium after 200 minutes per layer of UV radiation. Unfortunately, much longer UV doses would be neither practical nor, in some cases, of much astrophysical relevance (see below).

4.5. Reaction Mechanisms

The exact reaction mechanisms by which PAHs add oxygen and add and exchange H atoms during photolysis in low temperature ices are not currently understood. Several possibilities exist. These include reaction schemes controlled by photoproducted PAH cation intermediates and the attack of the PAHs (neutral or ionized) by “hot” O, H, and OH photofragments produced from the photolysis of H_2O . The results presented here are consistent with all these possibilities. Preliminary results of PAH- H_2O irradiation experiments involving PAHs other than coronene suggest that the rate of PAH alteration can vary widely from one PAH to another, even for PAHs having similar edge structures (unpublished results). This observation may favor the possibility of a PAH cation intermediate because PAHs with similar edge structures might be expected to react with hot O and H atoms in a similar manner. If photoionization of the PAH is, indeed, a rate determining step in the addition and exchange reactions discussed in this work, we would expect the degree of deuterium exchange of different PAHs might correlate with a parameter relating to photo-reactivity, such as ionization potential or UV cross section at wavelengths capable of ionizing the PAH. Additional experiments are currently underway to better understand this issue.

5. ASTROPHYSICAL IMPLICATIONS

5.1. Interstellar Deuterium Levels and UV Fluxes

The extent to which interstellar PAHs will be photo-deuterated in interstellar ices is affected by the concentration of deuterium in the ices and the UV fluences to which they are exposed. Interstellar *gas-phase* molecules have been measured to have D/H ratios as high as $\text{D}/\text{H} = 10^{-1}$ in certain cases (see Gerin et al. 1987). Certainly a degree of deuteration of interstellar gas-phase molecules is expected from low-temperature gas-phase ion-molecule reactions (Geiss & Reeves 1981; Dalgarno & Lepp 1984). At the low temperatures characteristic of dense interstellar molecular clouds, most of these molecules should be efficiently frozen onto grains (Sandford & Allamandola 1993). Thus, on the basis of gas-phase ion-molecule reactions alone, interstellar ices would be expected to be enriched in deuterium over cosmic abundances. Perhaps more importantly, the ices would be expected to be further enriched by fractionation during gas-grain reactions occurring on the surfaces of the ices (Tielens 1983, 1992), potentially up to values as high as $\text{D}/\text{H} = 10^{-3}$ – 10^{-2} . Infrared observations of dense clouds show that such enrichments do exist in interstellar ice

mantles. Recent measurements of the ratio of HDO to H₂O in interstellar ice grain mantles in three dense molecular clouds yielded D/H ratios ranging from 8×10^{-4} to 1×10^{-2} (Teixeira et al. 1999). Since H₂O is one of the most abundant molecular species in interstellar ices (cf. Sandford 1996), these values are likely to be representative of the ice mantles as a whole. Thus, both observation and theory suggest that D/H ratios of 10^{-3} to 10^{-2} are likely to be common in interstellar ice mantles.

Our results indicate that photolysis of PAHs in deuterium-enriched interstellar ices should lead to the PAHs becoming themselves deuterium-enriched. In § 3 we demonstrated that H → D and D → H exchange is quite rapid under experimental conditions analogous to those in the interstellar medium. Even brief exposures to UV radiation causes PAHs in ices to exchange measurable amounts of hydrogen. Thus, these processes could easily account for aromatics being deuterium-enriched to the level seen in the Murchison meteorite (D/H $\sim 10^{-4}$; Kerridge et al. 1987).

The amount of time in astrophysical environments to which our experimental exposures correspond depends on the ambient radiation field. The 10- and 200-minute irradiations in our experiments are roughly comparable to exposures of about 5×10^3 and 1×10^5 years, respectively, at the edge of molecular clouds where H₂O ice bands are observed ($A_v \approx 5$; Whittet et al. 1988). Even in the densest regions, where external radiation is attenuated and most UV is induced by cosmic rays (Prasad & Tarafdar 1983), our 200 minute-per-layer exposures correspond approximately to what an interstellar ice might experience over the lifetime of a cloud ($\sim 10^7$ yr). Thus, the UV irradiations shown in Figures 2 and 3 roughly bracket the exposures expected for PAHs in the denser parts of typical interstellar dense clouds, but may lie at the lower end of the exposures expected at cloud edges or in the radiation-rich environs of star formation regions.

The mass spectra shown in Figures 2a and 3a clearly indicate that the coronene has not reached equilibrium with its matrix D₂O in either case. This behavior is not surprising, however. Although these experiments realistically simulate reasonable interstellar temperature, pressure, and UV radiation dosage conditions, interstellar ices are obviously *not* expected to be as highly deuterated as they are in our isotopic substitution experiments. Our irradiations in pure H₂O or D₂O matrices were carried out to assist with interpretation of the mass spectral measurements and to allow us to more clearly discern the deuteration exchange mechanisms for aromatics in ices. Obtaining a better quantitative understanding of the rate and extent to which interstellar PAHs are deuterium-enriched in dense clouds via exchange in interstellar ices will clearly require additional experiments using more complex molecular ice mixtures and lower, more astrophysical, D/H ratios. Such experiments require much more sensitive D detection techniques, for example the use of an ion probe, and are currently underway. We should stress, however, that although the levels of D-enhancement in the experiments reported here are higher than those expected in true interstellar ices, the chemical reaction mechanisms are unaffected by the actual amount of deuterium in the ices.

5.2. Relevance to Meteoritic Materials

If the photolysis of PAHs in ices is responsible for a significant fraction of the deuterium enrichments seen in the

aromatics in meteorites, this work predicts that meteoritic aromatics will show characteristic patterns of deuteration that are consistent with our observations and differ from those predicted by other D-enrichment processes for PAHs. Specifically, whereas unimolecular photo-dissociation provides largest enrichments for PAHs in the 10–40 C size range and diminish with increasing carbon number (Allamandola et al. 1987, 1989), photolysis of PAHs in ices probably would not. Instead, the degree of deuterium enrichment via exchange should correlate with reactivity and hence molecular structure. If a size effect exists, it will probably favor larger PAHs, but only if an ion intermediate is the rate determining step of the alteration process and then only inasmuch as larger PAHs tend to ionize more easily or better stabilize ion intermediates. If hot-atom attack is involved in the rate determining step, deuterium excesses would probably correlate more with PAH edge structure.

As a result, D enrichment of PAHs by photolysis-driven exchange in ice is expected to produce a D content that correlates with the photoreactions that have occurred to the PAHs in the ice. For example, replacement of the H atom on an aromatic C–H with a D atom from the ice (§ 4.1 and Fig. 4a) results in a partially deuterated PAH, but the structure remains unchanged. Such plain aromatic C–H or C–D bonds are not labile, that is, they will retain their deuterium through subsequent non-radiative processes such as dissolution in liquid water. In addition, our experiments indicate that D atoms that are on an alcohol or are adjacent to either an aromatic alcohol or a ketone (§ 4.2 and Fig. 4b) should be acquired more rapidly through low-temperature ice photolysis than those on plain aromatic carbons. In contrast to the aromatic C–H or C–D bonds, however, these D atoms are labile so the level of deuteration in such bonds could be reset during subsequent aqueous alteration, such as is believed to have occurred on the parent bodies of many meteorites, including the CM carbonaceous chondrite Murchison (cf. Zolensky & McSween 1988 for a review). Finally, the rate of D-atom addition to coronene (§ 4.3 and Fig. 4c) is slower than the exchange processes but results in deuterated (cyclic) aliphatic domains, groups (-CH₂-, -CD₂-) with concomitant loss of aromaticity in that ring. These C–H and C–D bonds are not labile and are chemically distinct from the others.

The fact that deuteration goes hand in hand with the formation of an ensemble of chemical groups complicates matters in two ways. First, a meteoriticist trying to understand the interstellar deuteration of a certain PAH should attempt to measure not only its D/H ratio but also should distinguish between the different amounts and locations of deuterium in structurally-related compounds, such as the corresponding alcohols, ketones, and H_n-PAHs. Second, the fact that some of the D atoms that the PAH has acquired from photolysis are labile (such as on an alcohol or adjacent to an alcohol or a ketone, see above) means that these D atoms can be lost to moisture in the air or solution. Consequently, measured values in both our experiments and in meteoritic materials would represent lower limits.

The presence of the chemical classes of PAHs, oxidized PAHs, and H_n-PAHs in carbonaceous chondrites (cf. Cronin & Chang 1993) is qualitatively consistent with photo-processing of aromatics in ice grains. The further observation that the aromatic materials in these meteorites are enriched in deuterium (Kerridge et al. 1987) is compat-

ible with deuteration driven by PAH photolysis in D-enriched ices. We predict that, if this process is really responsible for the deuterium enrichments of a significant portion of the aromatic compounds in meteorites, then the abundance of aromatic deuterium should show some dependence on the structure of aromatics and their chemical sidegroups.

As with the level of deuterium in the ice, the PAH for this study was chosen to be practical as well as germane to astrochemistry. All the C–H bonds of coronene are equivalent, so a reaction occurring on one is equivalent to any other, removing confusion arising from structural isomers for the product molecules (seen in Fig. 4) and thereby making analysis more straightforward. Understanding how deuteration depends on PAH structure will require similar experiments on additional PAHs that sample a range of molecular sizes and structures. Studies using other PAHs are currently underway.

6. CONCLUSIONS

The PAH coronene (and its photoproducts) rapidly become deuterium-enriched via exchange when UV irradiated in D₂O ices under conditions mimicking those in dense interstellar clouds. This suggests that PAHs can attain elevated D/H ratios in the ISM as a result of ice photochemistry.

Both the kinds of molecules and the extent of deuteration measured in meteoritic aromatics are compatible with that

expected to result from the photolysis of PAHs in D-enriched interstellar ices over the lifetime of a single dense cloud. If this process were responsible for a significant portion of the deuterium enrichment measured in meteoritic aromatics, then we would predict that the distribution of deuterium in these molecules in meteorites should correlate with molecular structures formed during the photolysis of PAHs in low temperature ices. For example, simple aromatic exchange, keto-enol tautomeric exchange, and D-atom addition should all have occurred, each producing different compounds with characteristic deuteration patterns and labilities.

The relationship between deuteration and molecular size and structure resulting from this process is expected to be different from other processes, such as unimolecular photodissociation, that may also deuterium-enrich interstellar PAHs.

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