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Planetary and Space Science 50 (2002) 1145–1154

Planetary and Space Science

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Interstellar processes leading to molecular deuterium enrichment and their detection

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Received 12 November 2001; received in revised form 4 March 2002; accepted 11 March 2002

Abstract

Large deuterium (D) enrichments in meteoritic materials indicate that interstellar organic materials survived incorporation into parent bodies within the forming Solar System. These enrichments are likely due to one or more of four distinct astrochemical processes. These are (i) low-temperature gas phase ion–molecule reactions, (ii) low-temperature gas–grain reactions, (iii) gas phase photodissociation, and (iv) ultraviolet photolysis in D-enriched ice mantles. Each of these processes should be associated with molecular carriers having distinct structural signatures (D placement on the product molecules, correlation with specific chemical functionalities, etc.). These processes are reviewed and specific spectroscopic signatures for the detection of these processes in space are identified and described.
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Keywords: Deuterium enrichment; Interstellar medium; Interstellar chemistry; Polycyclic aromatic hydrocarbons; Isotopic anomalies; Ultraviolet photolysis; Organics

1. Introduction

Isotopic measurements, primarily in the form of deuterium (D) enrichments, provide definitive evidence for presolar interstellar materials within meteoritic samples (Robert and Epstein, 1982; Yang and Epstein, 1983; Kerridge and Chang, 1985; Kerridge et al., 1987). These enrichments are seen both in bulk meteoritic materials (Zinner, 1988), in meteoritic subfractions, and in specific classes of molecular species, such as amino and carboxylic acids (Epstein et al., 1987; Pizzarello et al., 1991; Krishnamurthy et al., 1992; Zinner, 1997).

The traditional explanation of these meteoritic D excesses has been to invoke the presence of materials made in the ISM by low-temperature gas phase ion–molecule reactions (Geiss and Reeves, 1981; Dalgarno and Lepp, 1984). The D/H ratios of simple interstellar molecules amenable to measurement using radio spectral techniques are generally higher than those of Solar System materials (Robert et al., 2000). However, comparisons of meteoritic and interstellar D/H ratios are obscured by several effects. First, D enrichments in interstellar molecules have been detected in only a few simple species, molecules that are not the principle carriers of D in Solar System materials. Second, some of the observed interstellar D enrichments reside on labile molecular sites that would be expected to exchange to some degree with more isotopically normal material during incorporation into a warm protosolar nebula, parent body processing, delivery, recovery, and analysis. Finally, ion–molecule reactions represent only one of four different processes that can produce strong D–H fractionation in the ISM (Sandford et al., 2001).

The four chemical processes that can lead to D enrichment are briefly reviewed in Section 2. These processes are expected to manifest in ways that are amenable to telescopic observation. Section 3 provides a discussion of the infrared spectral signatures that should be associated with D enrichment in the ISM and that may serve to delineate the contributions of the different chemical processes to D enrichment. Finally, Section 4 provides a very brief discussion of how isotopic investigations of meteoritic organics may help establish the relative contributions of these interstellar processes to the D enrichments found in solar system materials.

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0032-0633/02/$ - see front matter Published by Elsevier Science Ltd.
PII: S0032-0633(02)00075-2

2. Interstellar chemical processes for deuterium enrichment

Interstellar molecules, including PAHs, can become D-enriched through the processes of gas phase ion–molecule reactions at low-temperatures (Dalgarno and Lepp, 1984; Tielens, 1997), gas–grain reactions (Tielens, 1983, 1992, 1997), unimolecular photodissociation (Allamandola et al., 1987, 1989), and radiation processing of D-enriched ice grains (Sandford et al., 2000). Each of these processes manifests itself in the production of D-enriched molecules with distinctive structural signatures (Sandford et al., 2001). These differences are summarized in Table 1.

For the purpose of inter-process comparisons, the chemistry of polycyclic aromatic hydrocarbons (PAHs) will be highlighted since PAHs are abundant and widespread in the universe (Puget and Leger, 1989; Roelfsema et al., 1996; Allamandola et al., 1989, 1999), and PAHs are extremely stable molecules that represent one of the few classes of materials that can survive in all the interstellar environments associated with the four chemical processes listed above. In addition, PAHs and related aromatic materials are common in primitive meteorites (Cronin and Chang, 1993; Gardinier et al., 2000; Cody et al., 2001; and references therein) and interplanetary dust particles (IDPs) (Allamandola et al., 1987; Clemett et al., 1993), both of which contain significant carriers of D (Kerridge and Chang, 1985; McKeegan et al., 1985; Keller et al., 2000; Messenger, 2000).

For a more detailed description of these processes, as well as a discussion about how these processes are expected to effect C, N, and O isotopic ratios, see Sandford et al. (2001) and references therein.

2.1. *Low-temperature gas phase ion–molecule reactions*

Deuterium fractionation by ion–molecule reactions occurs only at the very low temperatures characteristic of dense interstellar clouds ($T < 50$ K). At such temperatures, chemical reactions between most neutral gas phase species will not proceed at any appreciable rate, but exothermic ion–molecule reactions can occur even at very low temperatures (cf. Geiss and Reeves, 1981; Herbst, 1987; Tielens, 1997). Thus, most of the gas phase chemistry occurring in dense clouds is the result of ion–molecule reactions and exoergic reactions involving radicals.

Such reactions are expected to produce mass fractionation at low temperatures due to the different zero-point energies of H and D, D having a lower energy and the potential to form slightly stronger chemical bonds (Dalgarno and Lepp, 1984; Tielens, 1997; Millar et al., 2000). At high temperatures fractionation is a minor effect, but as the gas drops below about 70 K, fractionation becomes increasingly significant (e.g. Millar et al., 1989). This process can proceed with most H-bearing gas phase molecules. This includes gas phase PAHs (Tielens, 1997, Fig. 1 shows the case for the PAH pyrene). This process is expected to initially preferentially deuterate PAHs that are larger or less condensed since they have relatively more H atoms, but all PAHs in the gas phase should show increasing D/H ratios as they approach steady-state equilibrium with H in the gas phase. Since PAHs are considerably more stable and more abundant in the ISM than many of the smaller species that show D enrichments ($PAH/H_2 \sim 10^{-7}$ compared to $HCN/H_2 \sim 10^{-8}$; cf. Allamandola et al., 1989; Hirota et al., 1998), and PAHs carry more H atoms per molecule than simpler

Table 1
PAH interstellar D-enrichment processes and their signatures

Process	Low temperatures required?	UV photons directly involved?	Deuterium labile?	Fractionation in other elements?	Signature
Gas phase ion–molecule reactions	Yes	No	No	Yes	Favors PAHs with larger numbers of peripheral H atoms (larger PAHs). Probably independent of regiochemistry
Unimolecular photodissociation reactions	No	Yes	No	Probably no	Favors smaller PAHs (Number of C atoms $\leqslant 50$). Probably independent of regiochemistry
Gas–grain reactions	Yes	No	No	Yes?	May not occur. If it does, the enrichment will reside on the reduced rings of H_n-PAHs
Ice-PAH photolysis reactions	Yes	Yes	Variable[a]	Possibly	Size independent. Enrichment will correlate with oxidation, reduction, and regiochemistry

[a] The deuterium associated with oxidized rings on aromatic alcohols and ketones will be labile. Deuterium residing on the reduced rings of H_n-PAHs and on the fully aromatic rings of PAHs will be non-labile.

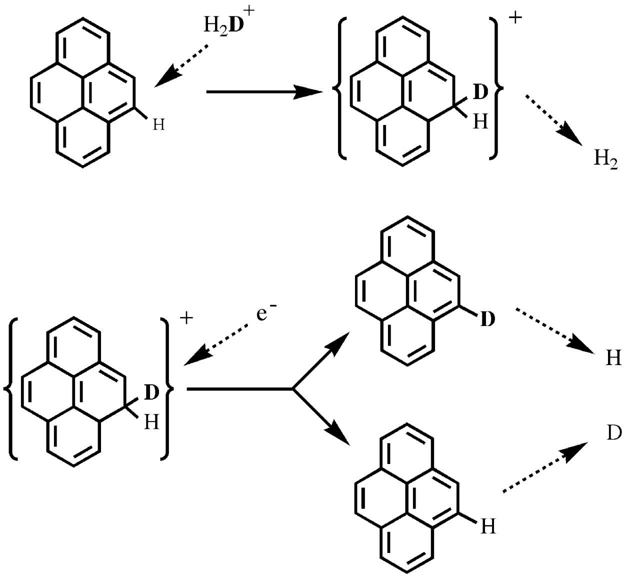

Fig. 1. PAHs become enriched in D via gas phase ion–molecule reactions in a two step process (shown here for the PAH pyrene). First, a PAH reacts with H_2D^+ to pick up an excess D atom and charge. Subsequent reaction with an e^- neutralizes the charge and the PAH eliminates an excess H or D atom. This process should initially preferentially deuterate *larger* PAHs in dense clouds, but all gas phase PAHs would ultimately become D enriched as they approach steady-state equilibrium with the gas phase.

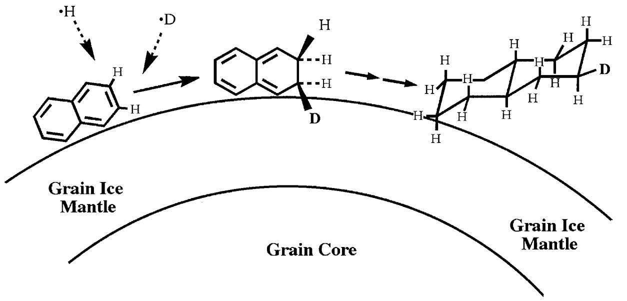

Fig. 2. In dense clouds where H/H_2 is large, gas–grain reactions primarily serve to hydrogenate, and D-enrich, species in the ice. It is not clear if PAHs can be hydrogenated in this manner, but to the extent that this process occurs, any D enrichments generated would be expected to correlate with the presence of H_n-PAHs and cyclic aliphatics.

molecules, PAHs are likely to represent the largest reservoir of materials D-enriched by ion–molecule reactions.

Observational evidence that D fractionation occurs in the ISM via gas phase ion–molecule reactions comes from radio telescopic studies that have demonstrated that several *simple* molecules are often highly D-enriched in dense interstellar clouds (Mauersberger et al., 1988; Jacq et al., 1990; Roueff et al., 2000; Turner, 2001). Deuterium enrichments in interstellar PAHs have not yet been detected (or carefully searched for).

2.2. Low-temperature gas–grain reactions

Ion–molecule reactions can only occur in the gas phase. However, at the temperatures typical of dense clouds ($T < 50$ K) most volatile species are condensed out of the gas phase into icy grain mantles (Sandford and Allamandola, 1993), as evidenced by the large quantities of mixed-molecular ices (Sandford, 1996; van Dishoeck and Blake, 1998; Gibb et al., 2000) and gas phase depletions (Mauersberger et al., 1992; Goldsmith, 2001) seen in dense clouds. The composition of these ices does not simply reflect gas phase abundances, however, since additional species are formed when condensing species participate in gas–grain reactions on the grain surfaces (Tielens and Hagen, 1982; d'Hendecourt et al., 1985; Brown and Charnley, 1990; Hasegawa et al., 1992). The compositions of these new species are strongly dependent on the local H/H_2 ratio. In environments where H/H_2 is large, surface reactions with H atoms dominate and species like CH_4, NH_3, and H_2O are produced. If H/H_2 is small, reactive species such as O and N can react with one another to form O_2 and N_2.

Gas–grain chemistry should produce large D enrichments in grain mantles where reduction is occurring (Tielens, 1992, 1997). In this case, the role of the zero-point energy difference between H and D counterparts is limited (Tielens, 1983). Instead, D enrichment results primarily from the atomic D fractionation of the accreting gas. Both the atomic H and D accreted onto grain surfaces can tunnel through activation barriers and hydrogenate species that are not fully reduced. Models indicate that such a process could yield mantle D/H ratios as high as 0.1 for simple molecules like H_2O and CH_3OH (Tielens, 1983, 1992, 1997; Charnley et al., 1997). Values in this range have been reported for HDO/H_2O in interstellar ices (Teixeira et al., 1999), although this detection remains controversial. Since the grain mantles in dense clouds represent a much larger fraction of the total reservoir of material than does material in the gas phase (H_2 excepted), grain surface processes are probably responsible for a larger portion of the total inventory of D fractionated species in dense clouds than ion–molecule reactions.

Naturally, D fractionation during gas–grain reactions should only proceed efficiently for molecules that can be hydrogenated. Fully reduced species will not accept additional D in this fashion and simple exchange is unlikely under these low-temperature conditions. In the case of PAHs, such reduction would result in the production of H_n-PAHs, aromatic species in which excess H atoms convert some of the aromatic rings to aliphatic rings (Bernstein et al., 1996, Fig. 2). There is currently no laboratory evidence suggesting that PAHs can become further reduced in this manner through simple H-atom exposure on grain surfaces. Thus, while gas–grain reactions may dominate the mass distribution of D in dense clouds, it may leave PAHs largely unaffected. However, to the extent that this process does occur

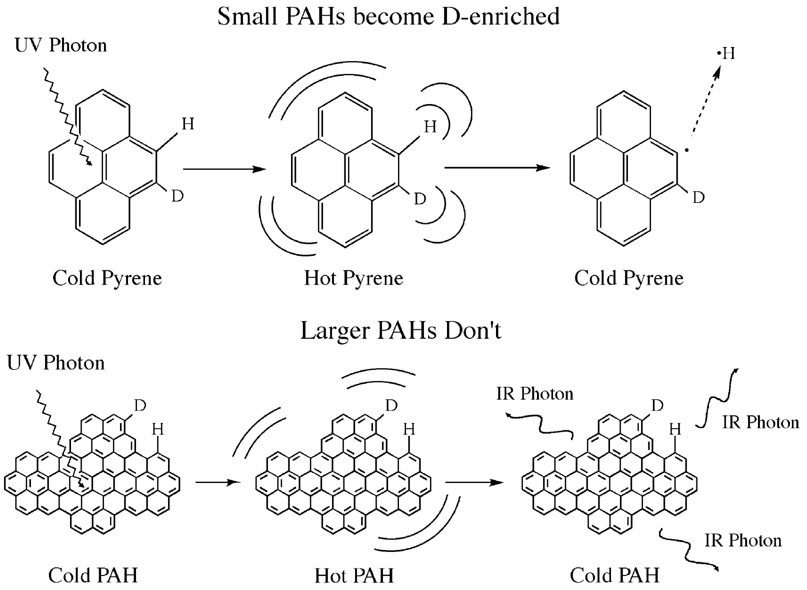

Fig. 3. Gas phase PAHs can become D-enriched by repeated gas phase photodissociation events that favor retention of D over H. The extent of the enrichment depends on the size of the PAH, with the most significant fractionations occurring for PAHs in the range of sizes spanned by naphthalene ($C_{10}H_8$) and hexabenzocoronene ($C_{42}H_{18}$). Enrichment in larger PAHs is not expected because they have large numbers of vibrational modes and are stable against photolytic bond rupture. D enrichment by unimolecular photodissociation does not require low ambient temperatures.

to PAHs, any D enrichments generated would be expected to correlate with the presence of H_n-PAHs, increasing H/C ratios, and the presence of aliphatic structures (Table 1).

2.3. *Gas phase photodissociation reactions*

In contrast to ion–molecule and gas–grain reaction processes, D-enrichment by gas phase photodissociation does not require low temperatures and is expected to be restricted *solely* to PAHs (Allamandola et al., 1987, 1989; Tielens, 1997). Because of their multiple C bonding and π electrons, PAHs are fairly resistant to photolytic destruction and can survive in environments where other species would be quickly fragmented. While relatively immune to *complete* photodestruction by interstellar UV photons, individual PAHs may still absorb UV photons that contain more energy than they can vibrationally accommodate. In such cases, a bond or bonds will break, the most likely being a peripheral C–H bond followed by loss of the H atom. Because of the zero-point energy difference of the C–D and C–H bonds, the rate of D loss from interstellar PAHs should be lower than that of H (Fig. 3). The resulting PAH radical will subsequently react with ambient H/D atoms, and repeated processing should gradually enrich interstellar PAHs in D relative to the ambient gas. Steady-state equilibrium is expected to be reached in most PAHs in photodissociation regions. In dense clouds, where the UV radiation field is weaker and the exchange rate slower, equilibrium may only be attained for the smallest PAHs. At equilibrium, the fraction of peripheral D relative to H will be 3 times the local gas phase ratio of D to H (10^{-5}–10^{-3}) (Tielens, 1997). Thus, in these interstellar environments, many PAHs having less than $\sim$ 25 C atoms should have peripheral D atoms (Allamandola et al., 1989).

This process is unique in two ways. First, low ambient temperatures are *not* required to produce fractionations by this process. Second, the extent of the D-enrichment depends on the size of the PAH. D enrichment is expected to be most significant for PAHs in the size range from $C_{10}H_8$ (naphthalene) to $C_{42}H_{18}$ (hexabenzocoronene). Enrichment in PAHs having more than $\sim$ 40 C atoms is not expected because these larger PAHs have larger numbers of vibrational modes, and can therefore accommodate the maximum energy of typical UV photons without photodissociation occurring (Fig. 3).

2.4. *Ultraviolet photolysis reactions in deuterium-enriched ice mantles*

Most of the volatile species in dense clouds reside in icy grain mantles. The dominant species in these ices is usually H_2O, but they also contain CO, CO_2, CH_3OH, NH_3, H_2CO, CH_4, and a number of other simple species in abundances greater than 1% of H_2O (see Sandford, 1996; Whittet et al., 1996; Gibb et al., 2000). Many of these species should be significantly enriched in D, either by enrichment in the gas phase by ion–molecule reactions followed by condensation onto the grain mantle, or via gas–grain reactions occurring on the mantle surface, as explained above. Once in the ice, these molecules can serve as a D-enriched reservoir for the synthesis of other enriched species.

One would normally expect few chemical reactions to occur within these ice mantles because of their low temperatures. However, interstellar ices in dense clouds can be further modified by energetic processing by cosmic rays (and secondary radiation generated by their interaction with matter), the attenuated diffuse ISM UV field, and UV photons from stars forming within the cloud (cf. Norman and Silk, 1980; Prasad and Tarafdar, 1983). When these ices are irradiated and warmed, bonds are broken, molecules are destroyed, and new molecules, radicals, and ions are formed. Thus, irradiation and thermal processing of ices made of simpler (D-enriched) molecules are expected to form a host of more complex species in dense interstellar clouds (Moore et al., 1983; Agarwal et al., 1985; Allamandola et al., 1988; Bernstein et al., 1995; Palumbo et al., 2000; Dworkin et al., 2001). Infrared spectra of the ices in dense clouds provide evidence for this process (Tegler et al., 1993; Pendleton et al., 1999; Bernstein et al., 2000). Furthermore, laboratory studies of mixed-molecular ices in which some of the original species are D-enriched have shown D incorporation into many of the reaction products (Bernstein et al., 1994, 1995, 2000; Sandford et al., 2000). Unlike the previously described processes, the effect is not to *produce* a fractionation of H from D, but instead to *propagate* previous fractionations into new molecular species, i.e., the "global" D/H ratio of the ice mantle remains fixed, but the D/H ratios in individual molecular families may be redistributed into other species.

The presence of PAHs in these environments has been demonstrated by detection of their infrared vibrational bands in absorption in the spectra of stars embedded within dense clouds (Sellgren et al., 1995; Brooke et al., 1996, 1999; Chiar et al., 2000; Bregman et al., 2000). Once condensed into interstellar ice mantles, PAHs will be subjected to the same radiation processing as the other ice components. Laboratory irradiation simulations have shown that under interstellar conditions PAHs undergo both oxidation and reduction reactions that affect their edge structures (Bernstein et al., 1999, 2001). Oxidation results in the production of aromatic alcohols, ketones, and ethers, while reduction leads to the formation of H_n-PAHs. Laboratory studies of PAHs in D-enriched H_2O ices have shown that UV photolysis results in rapid D enrichment of the PAHs through aromatic D → H exchange, D-atom addition, and exchange through keto–enol tautomerism. Each of these processes produce different compounds with characteristic deuteration patterns and D labilities (Sandford et al., 2000): D → H exchange reactions result in enriched PAHs in which the D resides in relatively non-labile locations (Fig. 4a), D-atom addition reactions result in enriched H_n-PAHs in which the D resides in relatively non-labile aliphatic rings attached to aromatic rings (Fig. 4b), and enrichment via keto–enol tautomeric exchange results in the D being located exclusively on rings that contain oxygen atoms in sites that are relatively labile (Fig. 4c).

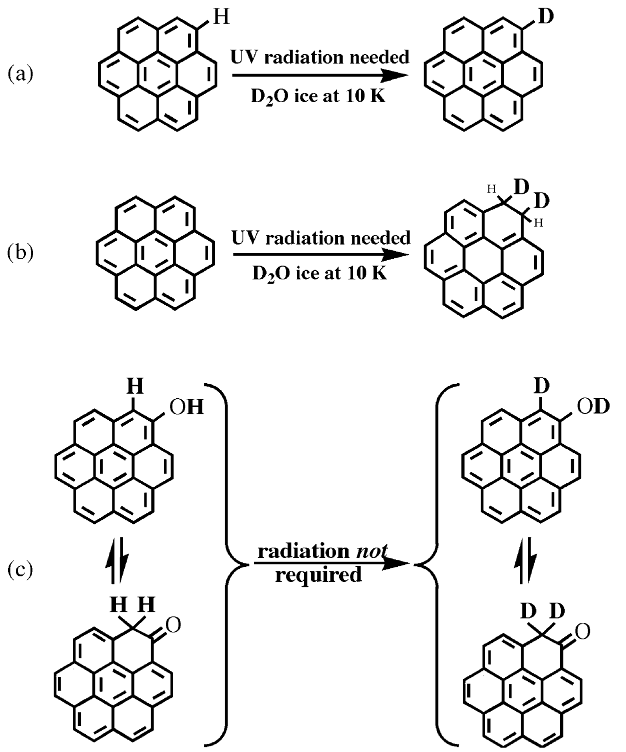

Fig. 4. The UV photolysis of PAHs in D-enriched ices results in rapid D enrichment of the PAHs through (a) aromatic D → H exchange, (b) D-atom addition, and (c) exchange through keto–enol tautomerism. Deuterium enrichments produced in this manner are largely independent of PAH molecular size, but should show specific regiochemical patterns and would be expected to correlate with the presence of both reduced PAHs (H_n-PAHs) and oxidized PAHs (aromatic alcohols, ketones, and ethers).

These deuterium enrichments are expected to occur largely independent of PAH molecular size, but should show specific behaviors with respect to their structures and the placement of the deuterium. In addition, since this same irradiation process produces both reduced PAHs (H_n-PAHs) and oxidized PAHs (aromatic alcohols, ketones, and ethers) (Bernstein et al., 1999), D enrichments produced by this process would be expected to correlate with the presence of these other species (Table 1).

3. Searching for D enrichments in interstellar molecules

3.1. The difficulties associated with detecting deuterated molecules in space

The chief difficulty of studying deuterated molecules in space is the low intrinsic abundance of D. The current cosmic D/H ratio is on the order of 1×10^{-5} (cf. Vidal-Madjar et al., 1998). In environments where D fractionation is occurring this ratio will be larger in select molecules, but even under the most efficient fractionation this ratio is generally not expected to exceed a value of 0.01, or perhaps 0.1. Thus, studies of the fractionation of D within specific molecular species require the measurement of both the protonated molecule and its deuterated variant, which will be *at least* an order of magnitude less abundant, but more likely less abundant by factors of 10^2–10^4. This places stringent requirements on the required sensitivities and signal-to-noise ratios of such studies.

The best technique for the detection of D-enriched molecules in space is the spectroscopic measurement of bands whose positions are shifted by the presence of D, i.e., molecular rotational and vibrational transitions. Past studies have concentrated almost exclusively on the use of spectroscopy at the radio frequencies where many of the rotational lines of molecules with significant dipole moments are found. The greater relative mass of the D atom in deuterated molecules can cause significant displacement in the rotational band positions and allows for the quantitative determination of D/H ratios through the comparison of the line strengths of gas phase molecules and their deuterated counterparts. For example, radio observations have lead to the detection of large D enrichments in simple molecular systems like HDO/H_2O, DCN/HCN, $ND_2H/NH_2D/NH_3$, and CH_3OD/CH_3OH (Mauersberger et al., 1988; Jacq et al., 1990; Roueff et al., 2000; Turner, 2001). Such observations are well suited to the study of D enrichments in small gas phase molecules, particularly as they serve as probes to the fractionation processes associated with ion–molecule reactions.

Enrichment studies at radio wavelengths have some limitations, the most significant being that the technique is restricted to molecules in the gas phase. Three of the four fractionation processes operate only at very low temperatures, where most molecular species will be condensed *out* of the gas phase and into icy grain mantles. In addition, even in the gas phase, molecules will be undetectable if they have very small dipole moments or are very large. This precludes the use of these techniques for the study of D enrichment in gas phase PAHs and the photodissociation enrichment process. Thus, while radio observations provide an excellent means of probing the D/H ratios of certain specific molecular systems, they cannot be used to study most of the material that is likely to be carrying excess deuterium. Thus, radio observations alone cannot provide an understanding of the relative importance of the four different fractionation processes.

If the bulk of the carriers of D in space are to be identified and understood, it will be necessary to probe the solid components of the interstellar medium. The chief means of doing this is also spectroscopic, although at infrared (IR) wavelengths where the principal *vibrational* transitions of molecules lie. IR spectroscopy has the advantage of not being restricted solely to gas phase species. Unfortunately, relatively little work has been done on the measurement of D enrichments at these wavelengths. The Earth's atmosphere is a significant obstacle to the infrared measurement of D-enriched molecules. The principle means of measuring D in molecules in the infrared is through the detection of vibrational stretching or bending modes involving C–D, O–D, and N–D bonds. Unfortunately, these are obscured by the asymmetric stretching and bending modes of telluric CO_2 (Figs. 5 and 6). Thus, spaceborne platforms are required for such studies (the work by Teixeira et al., 1999 was done using the ISO space telescope).

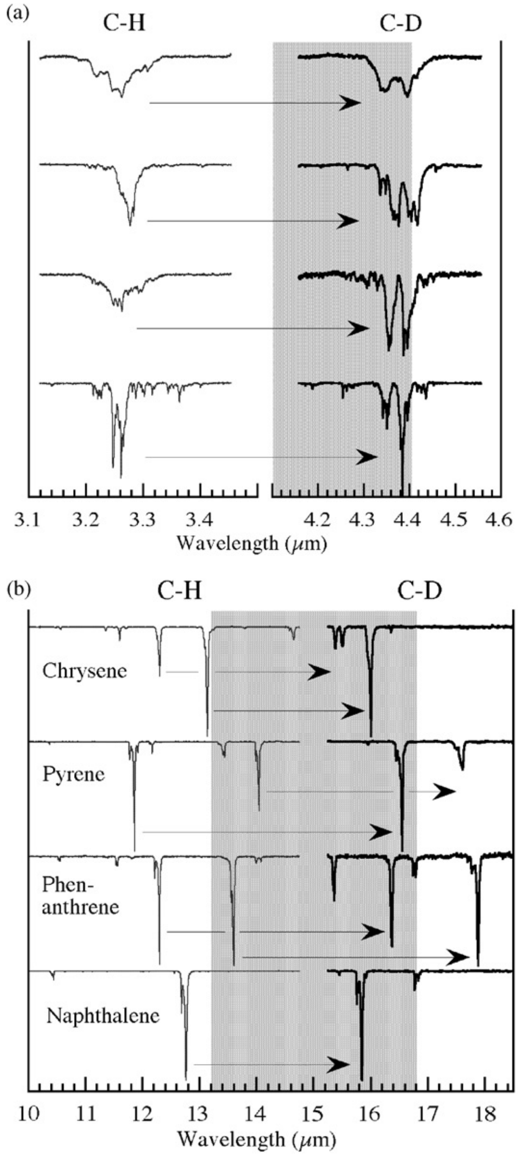

Fig. 5. Substitution of D for H moves the (a) C–H stretching and (b) C–H bending mode vibrations of organics (represented here by several different PAH species) to longer wavelengths. The C–D stretching and bending mode vibrations fall in wavelength regions (shaded gray) that are blocked from ground-based and airborne observation by telluric CO_2.

3.2. *Using infrared spectra to study interstellar deuterium fractionation processes*

Key to the IR spectral study of interstellar D fractionation is the ability to measure very high signal-to-noise spectra of appropriate interstellar environments at the wavelengths

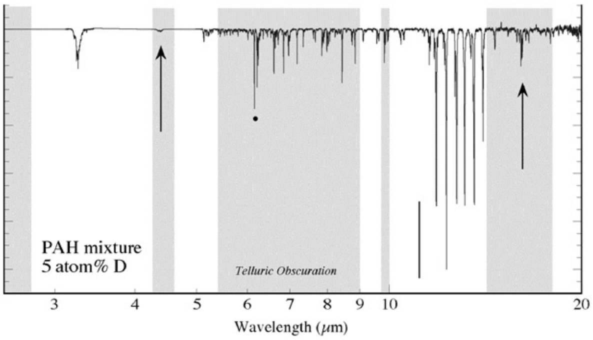

Fig. 6. The infrared spectrum of a mixture of PAHs that contain D-enriched members. The D/H ratio of the total mixture is 0.05. The gray bands represent spectral regions that are blocked from ground-based observation by telluric H_2O and CO_2. The arrows point to the bands produced by C–D stretching modes (left) and C–D bending modes (right).

characteristic of C–H, O–H, and N–H, and their corresponding C–D, O–D, and N–D, stretching and bending mode vibrations. As an example, Figs. 5a and b show the infrared C–H stretching and bending mode bands, respectively, of four different PAHs and their perdeuterated counterparts. Both the C–H stretching and bending modes are significantly shifted to longer wavelengths in the deuterated variants; the aromatic C–H stretch shifts from near 3.3 μm to around 4.4 μm and the various C–H bending modes shift from the 11–15 μm region to the 15–18 μm region.

Thus, in principle, the D/H ratios in PAHs (as one example) in different astrophysical environments could be measured by comparing the relative strengths and types (aromatic vs. aliphatic, see Table 1) of the corresponding C–H and C–D modes. As noted earlier, this will require a space-borne telescope and very high quality spectra. Fig. 6 shows the spectrum of a mixture of PAHs having an overall D/H ratio of 0.05, i.e., an enrichment comparable to the *biggest* that might be expected in favorable environments space. It is immediately apparent that the C–D modes of D-enriched molecules will only be detectable in spectra with high signal to noise.

With sufficient sensitivity, spectral coverage, and spectral resolution, there are several tests that could help constrain the relative importance of the various interstellar D fractionation mechanisms. In the case of D enrichment via ion–molecule reactions, it would be useful if the presence of D-containing PAH^+ ions could be verified in the gas phase in dense interstellar clouds. In principle, it may be possible to determine PAD/PAH ratios at infrared frequencies using the relative strengths of the aromatic C–H and C–D stretching emission bands near 3050 and 2270 cm^{-1}, respectively (Hudgins et al., 1994). However, the low expected gas phase abundances of PAHs in such cold environments will make this very difficult. In addition, PAHs are most easily observed in the gas phase when they are excited by UV photons and then radiatively cooled by emitting a cascade of infrared photons. At the relatively low UV fluxes present in typical dense cloud environments, this excitation mechanism is strongly curtailed. There may be more hope of measuring the relative strengths of the C–H and C–D aromatic stretching bands in absorption, but in this case the bands would presumably be dominated by PAHs frozen onto grains and it would be difficult to assign any observed fractionation specifically to ion–molecule reactions, as opposed to other processes.

The same UV excitation that makes gas phase PAHs observable via infrared emission should also produce D enrichment by gas phase photodissociation reactions, with the largest enrichments occurring in PAHs smaller than $\sim C_{50}$. This is in contrast to ion–molecule reactions, which should tend to preferentially enrich larger PAHs. The challenge will be to use the infrared C–D and C–H stretching emission bands near 4.40 and 3.28 μm, respectively, to measure the PAD/PAH ratio in a variety of interstellar environments that sample different UV radiation fields and astrochemical evolutionary histories. If D-enrichment by unimolecular photodissociation is occurring, PAD/PAH ratios should be very low in the outflows from carbon stars, where D is largely absent, having been consumed in the star. PAD/PAH ratios should be much larger in diffuse interstellar “cirrus” clouds, H II regions, and reflection nebulae, environments where PAHs have longer UV exposures in environments with higher gas phase D/H ratios.

3.3. *The dependence of deuterium enrichment on environment*

Previous sections have described how different chemical processes are expected to produce different D/H ratios among co-spatially located molecular species. However, these multiple chemical routes to D fractionation have different dependencies on various environmental parameters (temperature, H/H_2 ratio, UV and cosmic ray flux, etc.), and it is expected that the D/H ratios of a given molecular species should vary between environments. Since many environments, dense molecular clouds for example, can support more that one D fractionation process, the dependence of fractionation on environmental conditions could be difficult to determine.

In general, significant D fractionations are not expected in molecular species found in the outflows of aging stars (AGB stars, novae, etc.). This is largely because most of the D original to the star would have been destroyed and little D would be expected in their outflows. In addition, the materials in outflows are quite young and therefore will have had time to participate in relatively little chemical and isotopic exchange. For this reason, it is not anticipated that molecular species in C-rich planetary nebulae, where PAHs are very abundant, will show any appreciable level of D.

It should be easier to detect deuterated species, including PAHs, in dense clouds. This is both because all four of the possible D enrichment mechanisms can operate in these environments and because the contents of these clouds represent materials that have been exposed to much longer periods of chemical evolution during which D excesses could have accumulated. However, the possible simultaneous action of all four processes will also make it more difficult to delineate which processes are responsible for any detected enrichments. A clear understanding will require the correlation of D enrichments with environmental conditions spanning a wide range of temperatures, densities, dynamics, radiation fluxes, etc.

4. Some implications for meteoritic organics

The relative importance of these various astrochemical processes can, in principle, be garnered from the identities, abundances, and chemical structures of the carriers of excess D in meteorites and IDPs (Sandford et al., 2001). Unfortunately, there is currently little information about the nature of the D carriers within the organic fraction of meteorites, either in terms of their distribution among the various molecular species present or the siting of the D within these species.

Deuterium enrichments have been identified in a number of specific classes of molecules in meteorites, including amino and carboxylic acids (Epstein et al., 1987; Pizzarello et al., 1991; Krishnamurthy et al., 1992) and aromatic hydrocarbons (cf. Robert and Epstein, 1982; Kerridge et al., 1987; Krishnamurthy et al., 1992). Aromatic hydrocarbons and related materials are the main carriers of carbon in primitive meteorites (cf. Cronin et al., 1987; De Vries et al., 1993; Gardinier et al., 2000; Cody et al., 2001) and IDPs (Allamandola et al., 1987; Clemett et al., 1993) and are therefore likely to be the main carriers of the D excesses as well (Kerridge et al., 1987).

On the basis of current knowledge, it is not possible to exclude potential contributions to the inventory of excess meteoritic D from any of the four processes outlined above. For example, the report by Aléon et al. (2000) that the value of D/H increases with increased C/H in IDPs, with most enrichments occurring when $C/H > 1$ is qualitatively consistent with a fractionation of the D enrichment occurring in PAHs via ion–molecule reactions. However, the observation that the D/H ratio in the main carrier of carbon in primitive meteorites, an acid insoluble, highly aromatic kerogen, drops slightly as the C/H ratio increases from 2.3 to 3.0 (Robert and Epstein, 1982) is also qualitatively consistent with enrichment by gas phase photodissociation (Allamandola et al., 1987). The suggestion that the D in IDPs may be carried in C-rich materials that contain aldehydes (Keller et al., 2000) is consistent with the photoenrichment of PAHs frozen in D-rich ices since the very same photolysis that drives the enrichment is expected to convert some of the PAHs into aromatic aldehydes/ketones (Bernstein et al., 1999). The lack of correlation of D enrichment with C and O isotopic ratios and the poorly defined relationship between D enrichments and ^{15}N enrichments are also compatible with these processes. The same processes that produce the D fractionations are not expected to produce significant systematic C and O isotope effects and should yield only modest N isotopic effects whose degree should depend differently on environmental conditions (cf. Sandford et al., 2001).

Specific tests designed to address these meteoritic issues have been suggested (Sandford et al., 2001), and the capabilities needed to make these tests are fast becoming available. It can be anticipated that a great deal will be learned about the carriers of D in meteorites, and the chemical processes whereby they formed, in the next few years.

5. Conclusions

There are at least four interstellar astrochemical processes that can produce significant D fractionation in their products: gas phase ion–molecule reactions, low-temperature gas–grain reactions, gas phase photodissociation, and ultraviolet photolysis in D-enriched ice mantles. In the case of PAHs, these processes are associated with distinct structural signatures. Gas phase ion–molecule reactions initially preferentially deuterate the *larger* PAHs in dense clouds, but if sufficient time is available, all PAHs in the gas phase should reach equilibrium with the gas phase. Thus, the signature of this process would be fully aromatic PAHs whose D/H ratios are uniform across the PAH population or that increase with increasing PAH size. Gas–grain reactions produce D fractionations in dense clouds manifested primarily in simple hydrogenated molecules. PAHs probably cannot be enriched in D in this manner, but if they are, D enrichments would be found in H_n-PAHs, i.e., hydrogenated PAHs that contain cyclic aromatic and aliphatic rings. Enrichment via gas phase photodissociation reactions should produce a fractionation pattern in which PAHs below the C_{50} size range show the largest enrichments. Finally, photochemistry of ices containing pre-existing enrichments may preserve the fractionations generated by other mechanisms in new forms that can survive incorporation into forming stellar systems. Deuterium enrichments produced in aromatic species by this process will be largely independent of PAH size and should show specific structural behaviors, such as correlations between D/H and the presence of both reduced PAHs (H_n-PAHs) and oxidized PAHs (aromatic alcohols, ketones, and ethers).

These are signatures that can be searched for spectroscopically in the interstellar environments where these processes are operant, as well as in the molecular carriers of the excess D found in the organic fractions of primitive meteorites. Deuterium-enriched molecules in space can be detected through their spectral signatures, both through rotational transitions (at radio wavelengths) and through vibrational transitions (at infrared wavelengths). Since they are not restricted to gas phase species, infrared measurements are more likely to provide information about the distribution of the bulk of D-enriched species. Deuterated species are most easily identified in the infrared through their characteristic X–D stretching and bending mode vibrations, which fall in the spectral regions around 4.4 and 16.5 μm, respectively. Because of interferences from atmospheric CO_2, such measurements require the use of a spaceborne telescope.

Acknowledgements

This work was supported by NASA grants 344-37-44-01 (Origins of Solar Systems), 344-38-12-04 (Exobiology), and 344-50-92-02 (Astrobiology). The author gratefully acknowledges useful discussions with M.P. Bernstein and J.P. Dworkin and insightful reviews by T. Teixeira and an anonymous referee.

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