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Final Report: Chemical and isotopic analysis of trace organic matter on meteorites and interstellar dust using a laser microprobe instrument

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Polycyclic Aromatic Hydrocarbons (PAHs) are of considerable interest today because they are ubiquitous on Earth and in the interstellar medium (ISM). In fact, about 20% of cosmic carbon in the galaxy is estimated to be in the form of PAHs (Allamandola, 1995; Dwek 1997; Li 1997). Investigation of these species has obvious uses for determining the cosmochemistry of the solar system. Work in this laboratory has focused on four main areas:

1) Mapping the spatial distribution of PAHs in a variety of meteoritic samples and comparing this distribution with mineralogical features of the meteorite to determine whether a correlation exists between the two.

2) Developing a method for detection of fullerenes in extraterrestrial samples using $\mu L^2 MS$ and utilizing this technique to investigate fullerene presence, while exploring the possibility of spatially mapping the fullerene distribution in these samples through *in situ* detection.

3) Investigating a possible formation pathway for meteoritic and ancient terrestrial kerogen involving the photochemical reactions of PAHs with alkanes under prebiotic and astrophysically relevant conditions.

4) Studying reaction pathways and identifing the photoproducts generated during the photochemical evolution of PAH-containing interstellar ice analogs as part of an ongoing collaboration with researchers at the Astrochemistry Lab at NASA Ames.

All areas involve elucidation of the solar system formation and chemistry using microprobe Laser Desorption Laser Ionization Mass Spectrometry ($\mu L^2 MS$). A brief description of $\mu L^2 MS$, which allows selective investigation of subattomole levels of organic species on the surface of a sample at 10-40 μm spatial resolution, is given in Appendix A. Sections on the progress of all four areas are given in order below:

1) Spatial resolution of organic content with mineralogical features

Meteorites have long been of interest as possible probes into the history of the solar system. The history of meteorites has been dealt with in detail elsewhere. However, meteorites are aggregates of particles of distinctly different histories. Once accreted, they are then subject to further processing, the results of which will vary depending upon the suite of chemical components which have been left in place. There have been bulk analyses of carbon-rich meteorites revealing many organic compounds such as amino acids, alkanes, aromatic compounds, and macromolecular organic material (e.g. for Murchison: Gilmour, 1994; Levy, 1973; Oro, 1971; Sephton, 1998; Shock, 1990, for Allende: Hahn, 1969; Hahn, 1988; Zenobi, 1989). This includes $\mu L^2 MS$ analysis of both crushed and uncrushed material (Hahn,

1988; Zenobi 1989). While the uncrushed material did offer some information on compositions in different areas, the spectra shown were 50-shot averages of the regions. There has been a need expressed in the literature as far back as 1993 for spatially resolved analyses of the lighter elements and organic content of meteorites (Buseck, 1993) in order to fully investigate the association of the different organic species with the different features in the meteorite. $\mu L^2 MS$ is ideally suited to give these analyses for aromatic species, in particular the PAHs.

For the carbonaceous chondrites, there are three main components: matrix, chondrules, and calcium-aluminum inclusions. Chondrules are spherical objects that show evidence of solidification from a melt and are thermally processed to the extent that they should contain no organic species. Controversy exists as to the nature of the formation mechanism for chondrules, via shock waves, meteor ablation, bipolar outflows, etc. (e.g. Connolly Jr., 1998; Galy, 2000; Hewins, 1997; Rubin, 1998; Sears, 1998; Wood, 1996 and references therein). However, it is known that the material has been heated to at least several hundred degrees Kelvin. The chondrules generally possess a dark rim which is high in carbon content (Alexander, 2001). It is unresolved as to whether this material is accreted before inclusion into the meteorite or acquired during post-processing in the parent body. Two carbonaceous chondrite meteorites are reported on here; Allende and Murchison. Allende is a class $CV3_{OxA}$: oxidized, moderate amount of thermal/shock alteration, whereas Murchison is a class CM2: moderate amounts of aqueous alteration.

In our work, meteorites were sectioned to give a profile of material that is flat, such that adjacent $\mu L^2 MS$ shots should give results whose intensities are comparable. Each shot gives a complete mass spectrum and hence, in this manner, the spatial profile of multiple PAHs is acquired across the sample. The intensity of an individual PAH depends on its concentration in the sample, its desorption characteristics (including desorption cross-section and plume expansion), and its photoionization cross-section. Hence, the intensity of a given PAH is not directly comparable to the intensity of any other PAH[i]. However, the change in intensity from shot to shot for one PAH and the relative change in intensity for two PAHs do have significance. It was hoped that this work would give a PAH signal that would be significantly different in different regions and would reproducibly tie to different types of features within the meteorite. This hope has been realized, as will be discussed in detail later.

Figure 1 shows a composite (120x magnification) picture of a 5 mm long section of the Allende meteorite. The single-shot mass spectrum was recorded for a series of points of 40 μm diameter along this line. Overlaid on the photo is a graph showing the integrated intensity of mass 128 Da (naphthalene) for each shot. Features visible in the matrix (such as chondrule inclusions) show a low intensity of PAHs. We see that rims around features that are likely to be chondrules have high PAH content and the dark matrix surrounding these features has an intermediate PAH content. These observations have been repeated several times for two different Allende sections, and for a freshly exposed, curated sample of Murchison. In the interest of brevity, not all the data are presented here. A clear correlation is apparent which holds true for all PAHs found so far and also for investigation at different ionization wavelengths. Extensive tests were performed on both doped and undoped controls to ensure that the sectioning and sample introduction process, as well as residence in the vacuum chamber of the mass spectrometer, do not introduce contamination. (See Appendix B.)

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[i] However, this laboratory has done some work on characterizing the relative peak intensities of the different PAHs. The relative intensities of a parent PAH and its alkylated homologs are comparable to a first approximation. Manuscript under preparation.
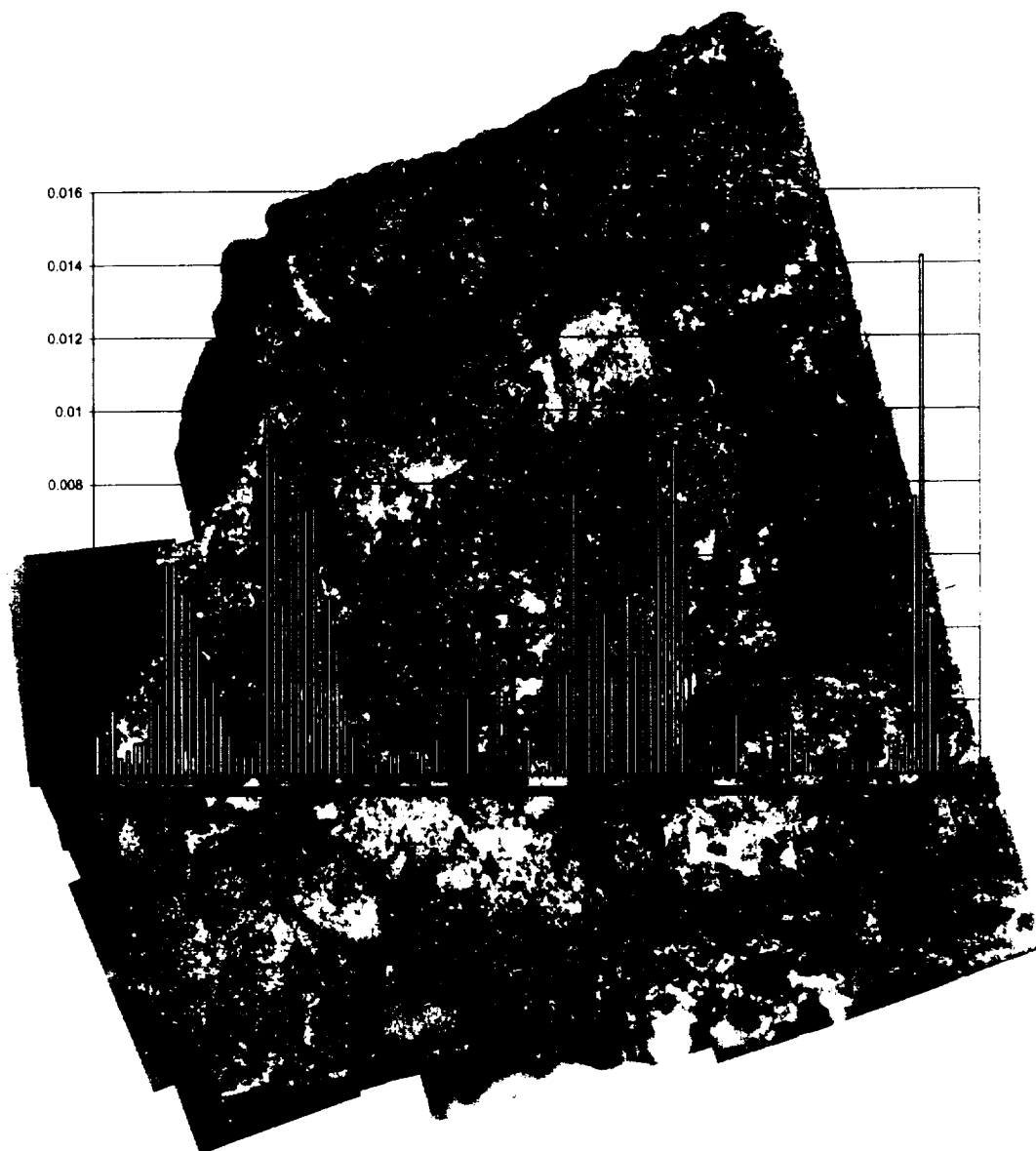
Figure 1: Overlay showing correlation of intensity of mass 128 with mineralogical features. The thick line denotes the desorption path. Arrows indicate features visible along this line and the corresponding drop in peak intensity. This correlation holds for all PAHs.

Figure 2 shows the intensity of several masses across a line of a chondrule evident on a freshly exposed Murchison surface. Masses 128 Da (naphthalene), 178 Da (anthracene/phenanthrene) and 202 Da (fluoranthene/pyrene) are shown. In addition, the intensities for peak mass 142 Da and 156 Da

3

(alkylation series of naphthalene) are also present. Although the absolute intensities vary, the same trend is apparent in each case. Very few, if any, PAHs are present in the chondrules themselves. The PAH signal intensity is much higher in the rim around the chondrule and drops off to an average value for the matrix. However, the distribution of PAHs does not change. The alkylated peaks investigated show a simple thermal-equilibrium distribution. This finding implies that the PAHs present in the meteorite are the result of one formation event that was prior to incorporation into the meteorite as no evidence exists for localized reactions and processing post incorporation.

PAHs across chondrule
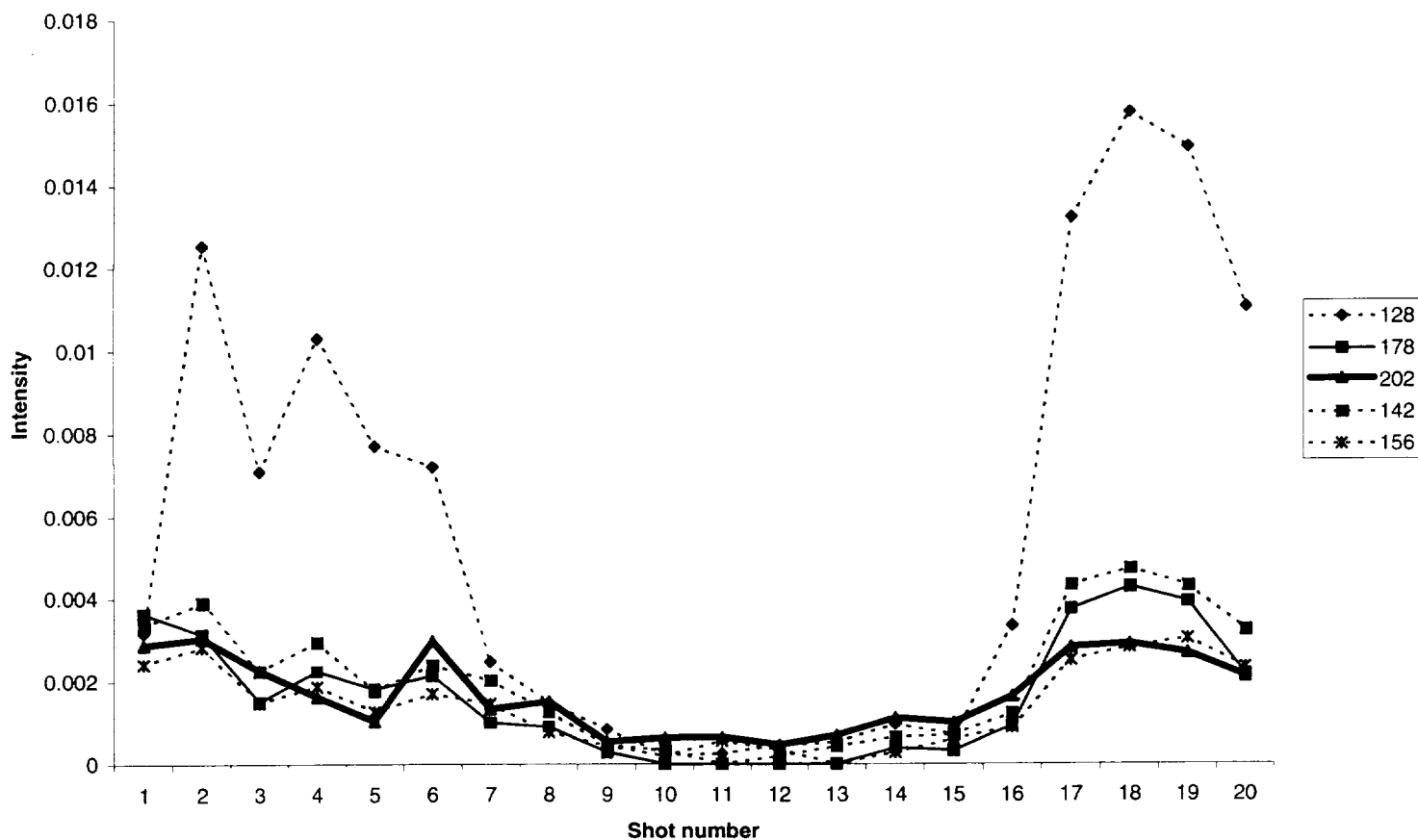
Figure 2: Intensities of three different PAHs across a portion of a freshly exposed chondrule in the Murchison meteorite. Shot numbers 7 and 15 are the chondrule limits.

The dark rims around the chondrules are carbon-rich whereas the chondrules themselves are carbon-depleted. Three main origins for the rims are proposed (Sears, 1993). 1) accretionary origin; 2) secondary product formed by alteration of the host chondrule; and 3) the rims reflect different degrees of zoning in the precursor chondrules.

4

There are two main theories as to the formation of matrix material for the chondritic meteorites (McSween, 1979; Sears, 1993 and references therein). One states that the material is accreted during the formation process and hence is primitive material. The other view is that the matrix material itself is derived primarily from chondrules that are incorporated into the aggregate and then altered. Assuming that all chondrules start out with PAH-rich rims and -depleted interiors, it is unlikely that PAHs would be so clearly absent from chondrules yet have managed to mix essentially uniformly with processed chondrules to form the matrix. Our results are more consistent with PAHs already present in the matrix material from the point of meteorite formation. Because chondrule formation involves heating events that remove PAHs from at least the interior of the chondrule, this suggests that matrix material was formed in an accretionary process and not from the post-incorporation alteration of chondrules.

Presuming that the material that formed the chondrules had cosmic abundances, the characteristic carbon-denuded chondrule with a carbon-rich 'dark rim' may result from a fractionation of the silicon and carbon during the heating event that formed the chondrule. Extremely high heating would result in partial or complete breakdown of any organic species, probably followed by recondensation into a soot or kerogen-type matrix on the outside of the chondrule. Lower formation temperatures would result in simple fractionation, possibly with breakdown of more complex species. The high PAH yields that are seen from these regions might result from a simple concentration effect or from trapping of mobile PAH species after rim formation. PAHs sorb easily to complex carbon systems and hence, if mobile in a meteorite, could well preferentially build up in these regions. Our desorption process would probably liberate such species (Mahajan, 2001). However, for the resultant steep concentration gradient observed between the rim and the chondrule to be preserved a big difference in the permeability of the chondrule as compared to the matrix material would be required.

Although the permeabilities of the chondrules themselves have not been measured directly, measurements have been performed for both the bulk and the matrix material (Corrigan, 1997). These give very similar results, and the authors' conclusion is that the chondrules on average have similar permeabilities to the bulk material. This again indicates that PAH distribution is fairly primitive; if the matrix formed from processed chondrules concurrent with PAH redistribution though the pores, then PAHs should also have permeated the unprocessed chondrules. It is interesting to note that the same type of correlation is seen both for the slightly aqueously altered Allende and the extensively altered Murchison. This fact again argues for a pre-accretionary origin for the PAHs present in these meteorites and a fairly primitive distribution. PAHs are extremely insoluble in water (Clemett, 1998) and so this is chemically consistent with a model for pre-accretionary origin.

Although this work does not distinguish between I) alteration and mixing of chondrules prior to incorporation in meteorites to form matrix, and II) simple accretion of matrix around meteorite constituents, it is consistent with the theory that the PAHs were mainly formed prior to incorporation in the meteorite. Nevertheless, further work is required in order to confirm this hypothesis. It seems unlikely that such extensive alteration and mixing of material to form matrix could take place while leaving material of similar porosity in pristine condition. Future work will include investigation of other pristine meteorite samples, along with a more complete characterization of those features apparent on the sample. This work will include utilization of cutting techniques that allow as flat a surface as possible in order to obtain maximum mineralogical information. This will allow a greater understanding of the PAH formation and distribution mechanisms.

Regardless of the history of the PAHs present in the rims and their matrix, the complete absence of these molecules within the chondrules requires either fractionation or complete loss during the chondrule formation process. This gives a lower bound to the formation temperature, of a few hundred

degrees Kelvin. An upper bound is given by the presence of the semi-volatile elements Na and K which evaporate at temperatures above ca. 970K (Connolly Jr., 1998). Conversely, the presence of PAHs throughout these meteorites implies that the meteorite as a whole has not experienced heating above the PAH destruction temperatures for any significant length of time and therefore gives upper bounds to the post-accretional temperature processing. Finally, the presence of a higher concentration of carbon in the chondrule rims argues for fractionation of the carbon in the chondrules during formation followed by a fast cooling which does not allow rediffusion back into the interior, and hence supports mechanism 3) for rim formation, involving zoning of the host chondrule.

## 2) Detection of fullerenes within extraterrestrial samples

Since the discovery of fullerenes in 1985 (Kroto et al., 1985) and their subsequent detection in natural samples (Buseck et al., 1992), there has been great interest in searching for extraterrestrial fullerenes. The proposal that fullerenes may exist in interstellar space was made almost immediately (Kroto, 1988; Kroto, 1992; Kroto et al., 1985). This was soon followed by the recognition that the ability of fullerenes to trap gases within their cages may help explain the anomalous isotopic compositions of noble gases within meteorites. Numerous investigations have been performed to detect fullerenes in interstellar space with minimal success (Bohme, 1992; Herbig, 2000; Leger et al., 1988; Petrie et al., 1993; Pillinger, 1993; Somerville and Belis, 1989). Fullerenes were observed, however, in an impact crater on the Long Duration Exposure Facility (LDEF), a spacecraft that was flown to collect interplanetary and interstellar particles prior to their likely destruction when entering Earth's atmosphere (di Brozolo et al., 1994).

The search for fullerenes in meteorites by standard extraction and analytical methods has yielded more mixed results. Numerous unsuccessful attempts to locate fullerenes in meteorites have been reported (Ash et al., 1991; de Vries et al., 1993; de Vries et al., 1991; Gilmour et al., 1991; Heymann, 1995). Becker and co-workers have, in contrast to other groups, successfully located fullerenes in meteorites (Becker et al., 1994; Becker and Bunch, 1997; Becker et al., 1999; Becker et al., 2000). They also reported both terrestrial and meteoritic fullerene molecules that contain trapped He (Becker et al., 1996; Becker et al., 2000; Becker et al., 2001). The successful detection of fullerenes in these samples was made using laser desorption mass spectrometry (LDMS), a technique that is similar to $\mu L^2 MS$. LDMS uses one UV laser to both desorb and ionize particles from a sample's surface, whereas $\mu L^2 MS$ is a two-step process involving spatial and temporal separation of desorption and ionization, performed with IR and UV wavelengths respectively.

We have investigated the limits and capabilities of $\mu L^2 MS$ for fullerene detection. Experiments will be conducted to investigate the abundance of fullerenes in terrestrial and meteoritic samples, with the possibility of developing a method for *in situ* detection of fullerenes. This work will help us to understand better both meteoritic chemistry and the limits of reliability we can place on laser desorption techniques as a means for fullerene detection. In the past few months, we have modified the $\mu L^2 MS$ instrument to optimize fullerene detection.

The typical setup for $\mu L^2 MS$ involves use of the fourth harmonic of a Nd:YAG laser (266 nm) for ionization of desorbed aromatic species. The efficiency of the ionization depends on the strength of the 266 nm absorption band for a specific species, as well as the internal processes involved in the two-photon excitation scheme. Fullerenes, owing to their extended aromatic system, do have a strong

6

absorbance that peaks at 258 nm (Berkowitz, 1999). Direct two-photon ionization at this wavelength, however, is complicated by the existence of a pathway for delayed ionization (Wurz and Lykke, 1991). This pathway leads to a broadened molecular ion peak in the resulting mass spectrum (see Figure 3a). Fragmentation of the C_{60} molecule is also observed. By modifying the $\mu L^2 MS$ system to use the fifth harmonic of the Nd:YAG (212 nm) for ionization, we are able to utilize the fullerene molecule's strong absorption band at 206 nm and avoid the delayed ionization pathway. The resulting mass spectrum is cleaner, with a C_{60} peak that is stronger and more defined (see Figure 3b). The direct ionization pathway combined with high-mass optimal settings for the time-of-flight extraction field also allow for better mass resolution of these species and the detection of ^{13}C isotopes.
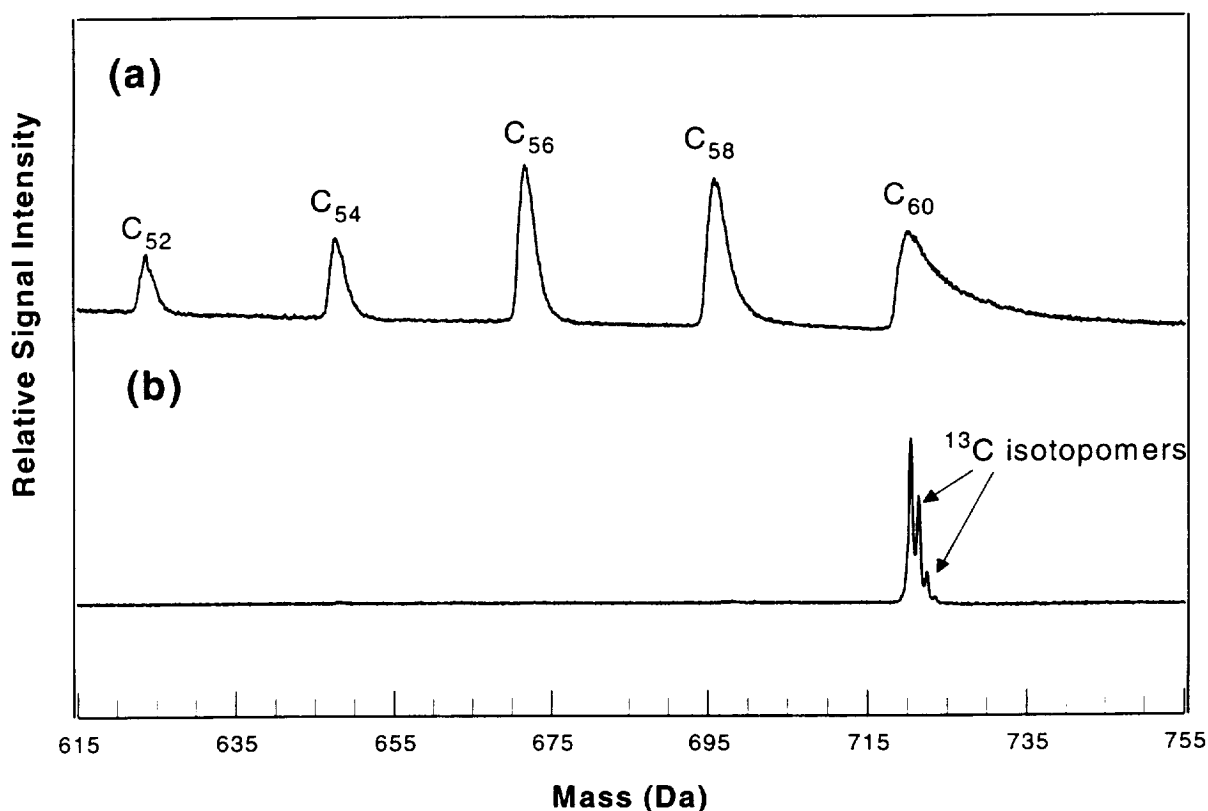
Figure 3: The $\mu L^2 MS$ spectrum of C_{60} using (a) 266 nm and (b) 212 nm for ionization.

Fragmentation of C_{60} can occur even with the 212 nm ionization light if the laser power is sufficiently high. While a lower laser fluence limits C_{60} fragmentation, it also reduces the sensitivity and, hence, the detection limits of the $\mu L^2 MS$ technique. We have examined the C_{60} spectrum obtained with a range of laser powers and have determined the optimal conditions for both C_{60} detection sensitivity and for decreased fragmentation. This work was primarily interested in confirming the presence or absence

of C_{60} in a sample; thus, we usually use a laser power consistent with high sensitivity, even at the cost of increased fragmentation.

Further work involved using our optimized system to examine the C_{60} content of terrestrial samples. The published studies that have successfully identified C_{60} have been carried out on extracted samples. Test samples that have been doped with known amounts of C_{60} have been investigated. We have optimized our extraction conditions, as well as analyzing the extracts to characterize the response of the $\mu L^2 MS$ instrument to varying concentrations of C_{60}. This allows us to determine the limits of sensitivity of $\mu L^2 MS$ to extractable fullerenes. Should our detection limits be sufficiently low, this work will be extended to *in situ* spatially resolved detection of fullerenes.

3) Photochemical alkylation of PAHs: plausible mechanism for the formation of C-C bonds on the early Earth and the interstellar medium

In general, PAHs are unusually stable compounds because the π electrons in PAHs are delocalized over the aromatic rings and these molecules have large resonance energies. In spite of the intrinsically low chemical reactivities of PAHs, they absorb light in the near UV and undergo numerous photochemical reactions. Although Allamandola and co-workers have reported the formation of a variety of compounds such as hydrogenated-PAHs, quinones, alcohols, and ethers from the photoreaction of PAHs in ices under simulated interstellar conditions (Bernstein, 1999), little information exists about possible photochemistry of PAHs with alkanes in the ISM.

The reaction of PAHs and alkanes is interesting because these compounds are abundant in certain environments, and it is likely that photoreactions between these molecules may provide a facile mechanism for linking them to each other through the formation of new carbon-carbon (C-C) bonds. C-C bonds are extremely strong, with average bond energies of 348 kJ/mol. Elaborate conditions are used to produce them chemically in the laboratory today. These bonds connect PAHs to other molecules, and therefore this step is integral in the synthesis of large and complex aromatic compounds.

We are exploring the photochemistry of PAHs with alkanes under conditions relevant to the prebiotic Earth and the ISM. Alkanes are abundant in the ISM, (Lacy, 1991) interplanetary dust particles, comets, and meteorites (Cronin, 1988; Cronin, 1990). Moreover, there is little doubt that they were plentiful components of the organic inventory deposited on Earth during the heavy bombardment period (Chyba, 1990; Chyba, 1992). UV light was the primary source of energy in the early solar system (Deamer, 1997), and would have impinged on surfaces of planets and on dust particles of the molecular cloud. In the absence of the ozone layer 4 billion years ago, the shorter and more energetic wavelengths of UV light should have reached the Earth's surface, making photochemical reactions possible. The photochemical linking of PAHs and alkanes in the ISM may prove relevant in the formation of meteoritic kerogen, which is a highly complex, cross-linked, three-dimensional network of aliphatic and aromatic hydrocarbons.

In our work thus far, we have examined the reaction of PAHs and alkanes in the presence of UV light. The photoreactions of PAH:alkane solutions were carried out in a commercial microscale immersion well reactor purchased from Ace Glass Inc, KY (Penn, 1989). The source of UV energy was a mercury lamp (UVP Model-11-SC-1) that primarily emits 254 nm light. Standard solutions were prepared by

dissolving 0.001 moles of a particular PAH in 0.1 moles of alkane. For each reaction, 2 mL aliquots of the PAH:alkane solution were placed in the outer jacket of the reactor and argon was passed through for an hour to remove any O_2 that may have been present. The UV lamp was then turned on, and CO_2 was bubbled through the solution for a period of five hours to ensure that the solution was uniformly mixed during irradiation and that O_2 was excluded.

The first experiments were performed using phenanthrene ($C_{14}H_{10}$) and hexadecane [$CH_3(CH_2)_{14}CH_3$] as the model test compounds for PAH and alkane respectively. Figure 4 shows the mass spectra resulting from a phenanthrene:hexadecane sample exposed to UV light (Figure 4a) and from a similar sample that was not exposed to UV radiation (Figure 4b). In both cases CO_2 gas was bubbled to ensure that the PAH and alkane were constantly in contact with each other and to exclude O_2 from the reaction mixture.
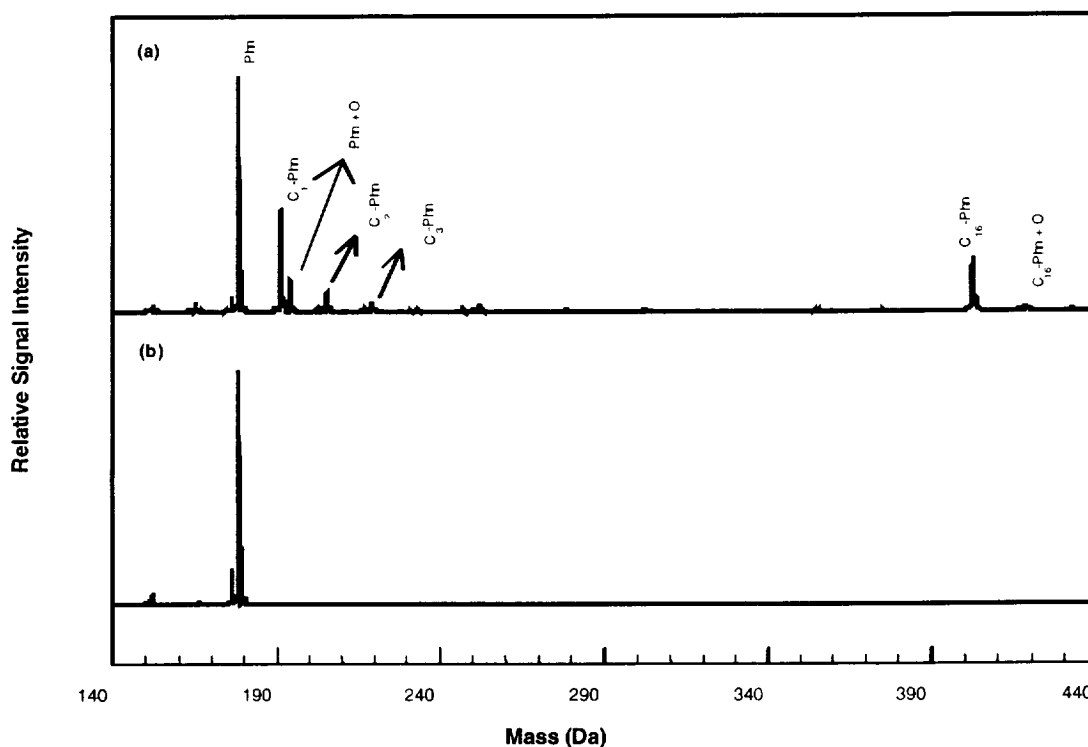
Figure 4: $\mu L^2 MS$ spectra of products formed during the reaction of solutions of phenanthrene and hexadecane (1:100) (a) in the presence of UV light, and (b) in the absence of UV light.

In the presence of UV light (see Figure 4a), the solution forms a prominent peak at 402 Da that corresponds to the substitution of the hexadecane chain (226 Da) onto the phenanthrene ring (178 Da). Alkylated products resulting from the addition of methyl, ethyl, or propyl groups to the phenanthrene rings were also observed. In Figure 4 and Table 1 alkylated products have been labeled as C_n-PAH, with n indicating the number of carbon atoms that have added to the PAH. In addition, products resulting from the addition of an oxygen atom (O) or a hydroxyl group to the phenanthrene ring were detected at 194 Da (Phn + O) and at 418 Da (C_{16}-Phn + O). These oxidation products probably result from the O_2 gas dissolved in the alkanes.

No products were formed in the dark control (Figure 4b), indicating that UV radiation is driving the alkylation reaction. A control sample of UV-irradiated hexadecane without phenanthrene present also

9

yielded no products (spectrum not shown). The UV absorption of hexadecane is negligible, so absorption of light by phenanthrene is the key factor. The excited phenanthrene then transfers energy to the hexadecane, driving the substitution reaction. The presence of methyl, ethyl, and propyl product species suggests that the excited state PAH has sufficient energy to activate fragmentation of the hexadecane chain, and the alkyl fragments also undergo substitution reactions where they replace hydrogen atoms on the PAH rings.

After completing the phenanthrene-hexadecane studies, a number of different PAHs and alkanes were examined to test the robustness of the photoalkylation process. Anthracene, 9-methyl anthracene, pyrene, and fluoranthene were dissolved in hexadecane and irradiated with UV light under the same conditions as the phenanthrene experiments reported in the previous section. The products formed in each case and approximate yields of the reactions are given in Table 1.

Table 1: Products and percent yields for photoreactions of different PAHs in Hexadecane (1:100)

PAH	ALKYLATED PRODUCTS	YIELDS AT THE END OF THE REACTION		
		% Alkylated	% Oxidized	% Unreacted
Phenanthrene	C_1-phenanthrene, 192 Da C_2-phenanthrene, 206 Da C_3-phenanthrene, 220 Da C_{16}-phenanthrene, 402 Da	47	7	46
Anthracene	C_1-anthracene, 192 Da C_2-anthracene, 206 Da C_{16}-anthracene, 402 Da	19	4	77
9-methyl anthracene	C_2-anthracene, 206 Da C_{17}-anthracene, 416 Da	18	3	79
Pyrene	C_1-pyrene, 216 Da C_2-pyrene, 230 Da C_{16}-pyrene, 426 Da	23	6	71
Fluoranthene	C_1-fluoranthene, 216 Da C_2-fluoranthene, 230 Da C_{16}-fluoranthene, 426 Da	22	5	73

All the PAHs underwent alkylation and yields ranged from 18% for 9-methyl anthracene to 47% for phenanthrene. The most prominent alkylated products are the methylated or the hexadecylated species of the particular PAH. In all cases there were also peaks for dimethylated/ethylated products, but the yields were considerably lower. In addition to the alkylated products, small amounts of oxidation products (approximately 5%) appear from the addition of one or two oxygen atoms or hydroxyl groups to the starting PAH. It is clear that some source of oxygen is present in the reaction mixture, despite careful efforts to exclude O_2 gas. Phenanthrene is the most efficient PAH for undergoing alkylation reactions, with a yield of 47%. The other PAHs tested all produce yields of approximately 20%. The reason for the higher reactivity of phenanthrene is unclear.

Photoreactions of phenanthrene were also carried out with five other alkanes. In all cases alkylated and oxidized products were formed. The yield for the photoreaction of phenanthrene in nonane (23%) is

lower than that for the corresponding reaction in hexadecane (47%). The result implies that as the carbon chain of the alkane becomes longer, the yield of alkylated products increases. Cyclodecane gives much lower amounts of product than decane, which suggests that normal chain alkanes are more reactive than their cyclic counterparts. Nonane is more reactive than 4-methyl nonane, indicating that the presence of side groups on an alkane chain reduces the yield of alkylated PAHs. 1,1'-(1,1,3-trimethyl-1,3-propanediyl)biscyclohexane was found to be the most reactive of all the alkanes investigated in the study, based on the low percentage of PAH remaining after the photoreaction.

A wide variety of PAHs and alkanes examined react to give alkylated PAHs and hence the photoalkylation reaction is very robust. Irrespective of the structure of the PAH, length of the alkane chain, and cyclic structure of two of the alkanes investigated, new carbon-carbon bonds were produced. It should be noted that controls were performed for all the PAH-alkane mixtures investigated. In the absence of light no products were observed.

This study indicates that alkylated PAHs are readily produced when a mixture of PAH and alkane is exposed to UV irradiation. The detailed investigation of pure PAH-alkane solutions has indicated that PAHs and alkanes photoreact easily and robustly to form a variety of alkylated PAHs. Although PAHs and alkanes are fairly unreactive compounds, the alkylation reaction occurs for a number of PAHs and a wide range of starting materials including cyclic, normal, long-chain, short-chain, substituted, and unsubstituted alkanes. Different experimental conditions such as the physical state of the sample irradiated, the presence or absence of gas, the identity of the gas bubbled, and the ratio of PAH:alkane do not affect photoalkylation. Moreover, although the lamp used as a source of UV photons was relatively weak, fairly significant product yields ranging from 18% to 47% were obtained when solutions were irradiated for a period of five hours.

To the best of our knowledge, this work is the first investigation of photochemical formation of alkylated PAHs. The photoreaction of PAHs is proven to be a feasible, robust, and facile way to produce C-C bonds in reasonably high yields, one of the key requirements in the synthesis of complex compounds. It also shows the probability that this type of reaction is feasible under prebiotic and interstellar conditions.

4) Photochemistry in interstellar ice analogs

We are engaged in an ongoing collaboration with researchers[ii] in the Astrochemistry Laboratory at NASA Ames Research Center to study the photochemical reactions of PAH-containing interstellar ice analogs. PAHs are known to be widespread components of the ISM and their characteristic infrared emission bands have been detected in a variety of diffuse interstellar environments (Allamandola et al., 1999; Allamandola et al., 1989; Boulanger et al., 1998; Puget and Leger, 1989). They are also expected to be abundant components of the icy grain mantles that form around silicate cores inside dense molecular clouds (Chiar et al., 2000; Sandford, 1996; Sellgren et al., 1995). Energetic processing by UV photons and cosmic rays drives photochemical reactions within these ice grains, creating new and more complex compounds (Allamandola et al., 1988; Bernstein et al., 1995; Dworkin et al., 2001; Greenberg, 1982; Schutte, 1988; Strazzulla, 1997). The identification of these reactions and their products will enhance our understanding of the chemical evolution of organic compounds in the universe.


[ii] Louis Allamandola, Scott Sandford, Max Bernstein and Jason Dworkin

The interstellar ice analogs examined in our work are prepared and irradiated at NASA Ames. The ices are created by deposition of the constituent gases onto a 10 K substrate in a high-vacuum chamber ($\sim10^{-8}$ torr), and are subsequently irradiated by a flowing-hydrogen discharge lamp, the output of which simulates interstellar ultraviolet radiation. After irradiation, the ices are warmed to room temperature, causing loss of the more volatile components. The residue remaining on the substrate contains the more complex, less volatile photoproducts of the reactions. This residue is then analyzed in our laboratory by μL^2MS, which reveals the presence of PAH derivatives that have formed during irradiation. Additional analyses on the residue using HPLC, IR spectroscopy, and UV-Vis absorption-luminescence spectroscopy are performed at NASA Ames.

Our previous work examined the photochemistry of PAHs in water-rich ices and showed the formation of partially oxidized PAH products including quinones and aromatic alcohols (Bernstein et al., 1995). In our current work, we have analyzed ices composed of binary mixtures of PAHs and other interstellar ice components such as methanol, ammonia, and carbon dioxide.

During the past year, we have studied a series of ices consisting of coronene in binary mixtures with ammonia, methanol, carbon monoxide, carbon dioxide, formaldehyde, and acetaldehyde. Some trinary mixtures (coronene/argon/methane, coronene/water/ammonia, and coronene/argon/HCN) have also been irradiated and analyzed. The residues remaining after irradiation of these ices have shown the presence of PAH derivatives formed from oxidation, reduction, alkylation, and nitrogen addition reactions. Figure 5 presents the spectra of the residues remaining after irradiation of coronene:methanol and coronene:ammonia ices, while Table 2 summarizes the products observed in the ices studied.
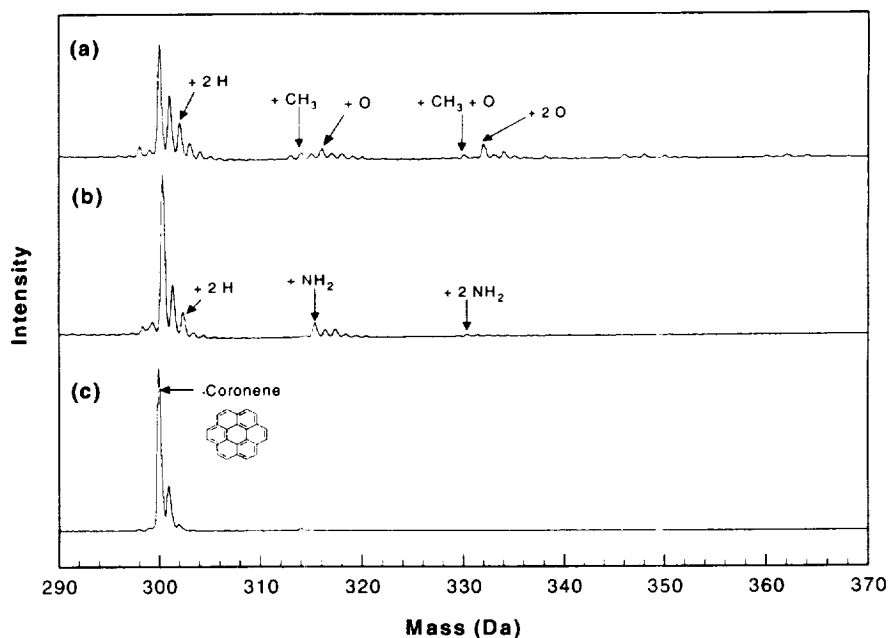
Figure 5: μL^2MS spectra of coronene ($C_{24}H_{12}$) after freezing at 10 K into (a) CH_3OH ice followed by UV irradiation, (b) NH_3 ice followed by UV irradiation, and (c) NH_3 ice with no UV irradiation (unpublished collaboration with The Astrochemistry Laboratory, NASA Ames).

Coronene is the simplest PAH to investigate in $\mu L^2 MS$ experiments because of its low volatility and high symmetry. Although most of the ices studied have been coronene-containing, we have also recently examined irradiated ices containing phenanthrene, anthracene, and pyrene. The PAH derivatives observed in these ices are analogous to those seen in the coronene-containing ices.

Work has been completed on the binary PAH-containing ice analogs. We are continuing studies of more complex ice mixtures which may more closely mimic the composition of true interstellar ices.

Table 2: Products and reactions observed from irradiated interstellar ice analogs.

| Ice Composition	Hydrogen Addition	Oxygen Addition	Alkyl Addition	Nitrogen Addition	
	+ 2H	+ O	+ CH_3	+ NH_2	+ CN
coronene + H_2O	x	x			
coronene + CH_3OH	x	x	x		
coronene + CO_2		x			
coronene + CO		x			
coronene + Ar/CH_4	x		x		
coronene + H_2CO	x	x			
coronene + CH_3CHO			x (very small)		
coronene + NH_3	x			x	
coronene + H_2O/NH_3	x	x		x	
coronene + Ar/HCN	x	x			x

5) Summary

Significant progress has been made in various areas relating to PAHs and fullerenes. The formation, cosmochemistry, processing and early-Earth chemistry are all under investigation in ongoing projects with this laboratory. Laboratory model chemistry of photochemical reactions has given insight into the formation mechanisms and subsequent possible reactions of the PAHs, while work on the detection and spatial resolution of these species allows their use as indicators of meteoritic chemistry and processing. This may help to resolve some of the issues bound up with chondritic meteorite formation and processing and hence shed light on solar system formation mechanisms.

Appendix A: Mechanism of the $\mu L^2 MS$ technique

Microprobe laser-desorption laser-ionization mass spectrometry is a highly sensitive technique capable of spatially resolving the distribution of organic molecules on complex surfaces and particulates. The technique combines focused laser-assisted thermal desorption with ultrasensitive laser ionization methods to produce a combination of sensitivity, selectivity, and spatial resolution unmatched by traditional methods of analysis. We have already applied our $\mu L^2 MS$ instrument to problems of cosmochemical interest and have been able to show the presence of organic species in a wide range of extraterrestrial materials, in some cases where previously none had been detected owing to limitations in detection sensitivity (Clemett et al., 1994; Clemett et al., 1993; McKay et al., 1996; Thomas et al., 1995).

A detailed description of our technique has been presented elsewhere (Clemett and Zare, 1997; Kovalenko et al., 1992), and is summarized here for convenience. The principle of $\mu L^2 MS$ is illustrated in Figure 6. Constituent neutral molecules of the sample are first desorbed with a pulsed infrared laser beam focused down to a spot, presently adjustable between 10 and 40 μm. The laser power density is kept well below the plasma threshold to ensure desorption of neutral organic species with little or no fragmentation. In the second step, a selected class of molecules in the desorbed plume is preferentially ionized by a single-frequency pulsed ultraviolet (UV) laser beam that passes through the plume. The resultant ions are then extracted and injected into a reflectron time-of-flight mass spectrometer and analyzed according to mass. A complete mass spectrum is obtained for each shot.
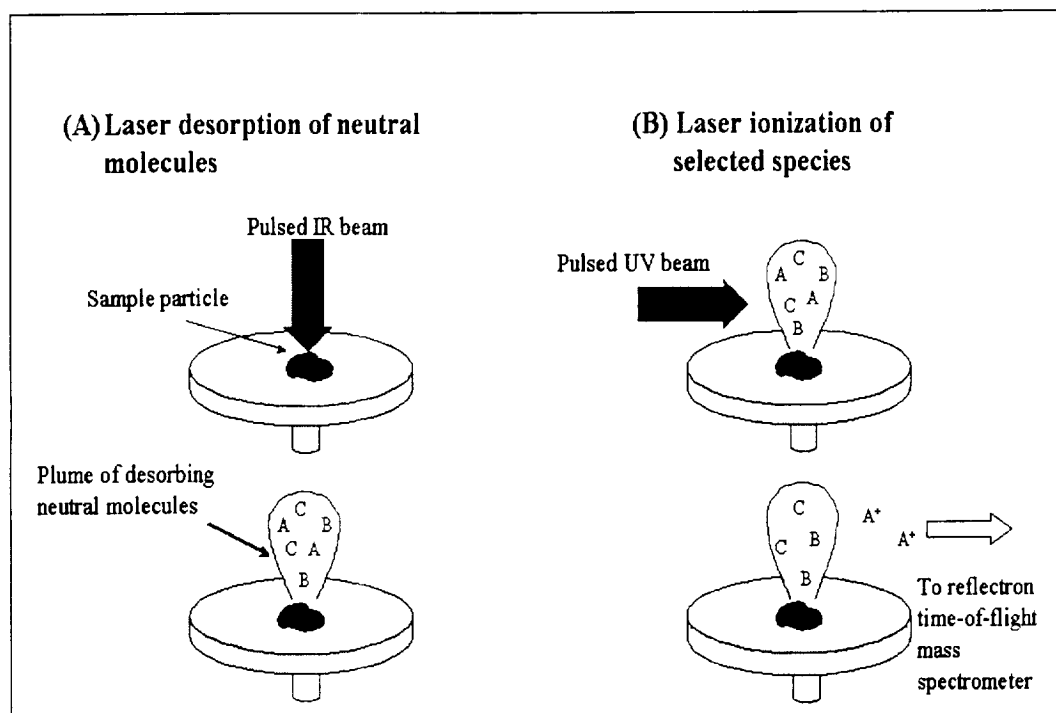
Figure 6: The $\mu L^2 MS$ technique consists of (a) laser desorption followed by (b) laser ionization to selectively produce ions, which are then extracted into a time-of-flight mass spectrometer for mass analysis.

Species-selective ionization, that is, ionization of molecules containing a characteristic functional group, is achieved through (1+1) resonance enhanced multiphoton ionization (REMPI). In this process, absorption of a single photon causes a molecule to make a transition to an electronically excited state; absorption of a second photon promotes the excited molecule to the ionization continuum. Molecular selectivity is achieved by virtue of the fact that only species having an electronic transition in resonance with the wavelength of the incident laser radiation will be appreciably ionized. Our system typically uses an ionization wavelength of 266 nm, which is strongly absorbed by the phenyl moiety and provides a selective ionization window for PAHs. We are also able to produce an ionization wavelength of 212 nm, which is more effective for the ionization of derivatized aromatics such as polychlorinated biphenyls (PCBs) (Mahajan et al., in press). In addition to being highly species-selective, REMPI has the advantage of providing a "soft" ionization route in which ion formation is accompanied by minimal fragmentation (Shibanov, 1985; Winograd et al., 1982). μL^2MS requires minimal sample processing and handling, and therefore allows analysis of samples with little possibility of contamination. It also utilizes extremely small amounts of sample, desorbing only from the surface layers of any given sample, which leaves the bulk of the sample intact and available for further investigation.

The key attributes of our instrument are summarized as follows:

- High spatial resolution and mapping capabilities, providing complete mass spectral analysis of a region as small as 10 μm in diameter
- Desorption with minimal decomposition and ionization with minimal fragmentation, resulting in spectra consisting of primarily parent ions.
- Selective ionization of only those molecules which have a transition in resonance with the UV laser photon energy, simplifying the spectra of complex mixtures
- High sensitivity, capable of detecting PAHs at the subattomole ($<10^{-18}$ M) level
- *In situ* analysis, requiring little sample handling and minimizing the possibility of contamination and chemical alteration

Appendix B: Control experiments on meteorite sectioning process

A series of control experiments were performed in order to investigate possible contamination associated with sectioning.

1) Clean glass pieces were sectioned and investigated. No PAHs were observed on the surface within detection limits. For at least one of the pieces marks from the diamond blade used for the cut were clearly observed on the surface. Hence if any contamination were to be introduced by the blade it should also be clearly observed on the surface. Investigation was also made of small fragments/powder produced during the cut. Such fragments were picked up with adhesive from a fresh foil surface placed in front of the blade before starting the cut. Any extraneous small particulate material which was introduced onto this surface should be incorporated into the mix of small fragments. However, no PAHs were observed. Hence, cutting introduces either no contamination or contamination below the limits of detection of the apparatus.

2) The control experiment was duplicated with a piece of common terrestrial rock. This relatively flat piece was halved. One piece was left blank while the other was doped with a solution of (ca. 10-4M, ca. 1ml) coronene. The control piece was sectioned and analyzed. Few PAHs were observed either on the sectioned surface or around the edge. Analysis of a small fragment of the doped piece revealed no background signal from vaporizing dopant, whereas signal was clearly observable upon laser desorption from the outside of the sample. The rest of the doped piece was sectioned and analyzed. Signal from the dopant is clearly seen at the edge of the sample, dropping away to nothing within a small number of shots. Consequently, material contaminating the outside is not introduced onto the freshly exposed inner surface used for analysis.

3) A clean glass plate was placed in the vacuum chamber. No PAHs were present initially, and none were observed after the sample was left in the system for several days.

4) The blank piece from 2) was placed in the vacuum chamber and left for several days in order to investigate the cleanliness of the system itself in case any material present sorbed preferentially to rocky material. There are a few very small PAH peaks intrinsically present in the rock sample chosen, most notably at 178 Da (phenanthene/anthracene) and 202 (fluoranthene/pyrene), although it has some 128 (naphthalene) present. 50-shot averages over the sample show most peaks decreasing slightly over a time period of several days, although peaks at 118 (unknown, possibly inorganic) and 128 increase slightly. All changes are within the level of change expected for heterogenous natural samples and so may be due either to this or to some effect in the chamber. It is unlikely that a contamination source such as pump oil would match the naturally-occurring peaks within the sample and hence any changes over time are more likely due to vacuum effects, e.g., degradation of the matrix allowing for easier release of the more volatile species.

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