SUMMARY OF RESEARCH REPORT

<u>Final Report: Understanding Organics in Meteorites and the Pre-Biotic Environment</u>
<u>Period: 08/01/01 – 07/31/02</u>

<u>Specific Aims and Objectives</u>

The work funded by this research grant included four specific purposes:

(1) Refinement of the analytic capabilities of our experiment via characterization of molecule-specific response and the effects upon analysis of the type of sample under investigation;

(2) Measurement of polycyclic aromatic hydrocarbons (PAHs) with high sensitivity and spatial resolution within extraterrestrial samples;

(3) Investigation of the interstellar reactions of PAHs via the analysis of species formed in systems modeling dust grains and ices;

(4) Investigations into the potential role of PAHs in prebiotic and early biotic chemistry via photoreactions of PAHs under simulated prebiotic Earth conditions.

To meet these objectives, we use microprobe laser-desorption, laser-ionization mass spectrometry ($\mu L^2 MS$), which is a sensitive, selective, and spatially resolved technique for detection of aromatic compounds. Appendix A presents a description of the $\mu L^2 MS$ technique.

The initial grant proposal was for a three-year funding period, while the award was given for a one-year interim period. Because of this change in time period, emphasis was shifted from the first research goal, which was more development-oriented, in order to focus more on the other analysis-oriented goals. The progress made on each of the four research areas is given below. Four publications based on the work funded by this grant have been produced:

F. L. Plows, J. E. Elsila, R. N. Zare, and P. R. Buseck, "**Evidence that Polycyclic Aromatic Hydrocarbons in Two Carbonaceous Chondrites Predate Parent-Body Formation**," *Geochim. Cosmochim. Acta*, in press.

M. P. Bernstein, J. E. Elsila, J. P. Dworkin, S. A. Sandford, L. J. Allamandola, and R. N. Zare, "**Side Group Addition to the PAH Coronene by UV Photolysis in Cosmic Ice Analogs**," *Astrophys. J.* (2002), 576 (2, Pt. 1) 1115–1120.

M. P. Bernstein, M. H. Moore, J. E. Elsila, S. A. Sandford, L. J. Allamandola, and R. N. Zare, "**Side Group Addition to the Polycyclic Aromatic Hydrocarbon Coronene by Proton Irradiation in Cosmic Ice Analogs**," *Astrophys. J.* (2003), 582, L25-L29.

T. B. Mahajan, J. E. Elsila, D. W. Deamer, and R. N. Zare, "**Formation of Carbon-Carbon Bonds in the Photochemical Alkylation of Polycyclic Aromatic Hydrocarbons,**" *Orig. Life Evol. Biosphere*, in press.

Objective 1: Refinement and Characterization of the $\mu L^2 MS$ Instrument Response

$\mu L^2 MS$ provides an extremely sensitive and selective technique for the spatially resolved detection and identification of molecular species. This technique, however, is not quantitative because the instrument response depends on a variety of factors. These include photoionization cross-section and sample desorption characteristics. The goal of this work was to investigate and characterize these factors and to use this information to make the $\mu L^2 MS$ technique more quantitative.

In order to investigate both desorption and photoionization effects, we developed a technique in which known concentrations of different PAHs were incorporated into three nonvolatile plastic matrices [poly(acrylic acid), poly(styrene-*co*-maleic acid), and poly(methyl vinyl ether-*alt*-maleic acid)]. These plastics were chosen because they have significant absorptions at both the 10.6 and 2.94 μm desorption lines, allowing soft desorption from the same sample with both of our desorption laser systems. Several 50-shot averages were taken from each sample with both desorption lasers. We then integrated the areas of the PAH peaks in the resulting mass spectra and used this quantitative information to calculate relative instrument response factors for each PAH in the matrix.

Table 1 shows the resulting response factors for plastic samples containing the PAHs naphthalene, acenaphthene, and phenanthrene. The response factors for the PAHs have been normalized to naphthalene. It is easy to see that the PAHs have different responses, as expected owing to different photoionization cross-sections. The effect of desorption conditions does not seem as strong, however, as indicated by the matching of response factors for the two desorption lasers and the three plastic matrices. Although the response factors do match within experimental errors for the different desorption conditions, the errors themselves are higher than would be needed for precise quantitative results of PAH concentrations in unknown samples. These errors probably result from differences in desorption energies or in the shape of the desorbed plume.

TABLE 1. Instrument response factors normalized to naphthalene for the two desorption lasers and three plastic matrices. Errors represent one standard deviation.

	Er:YAG acrylic	Er:YAG styrene	Er:YAG ether	CO_2 acrylic	CO_2 styrene	CO_2 ether
naphthalene	1	1	1	1	1	1
acenaphthene	1.32±0.44	0.92±0.11	1.04±0.18	1.90±1.15	1.08±0.25	0.88±0.26
phenanthrene	3.39±1.82	2.98±0.60	2.31±0.52	11.37±8.34	6.34±2.67	3.79±2.77

The results of the work carried out over the period covered by this grant award have provided a method with which to measure instrument factors as well as information

on the relative responses of several PAHs. More work will need to be done in order to apply this information to the quantitation of PAH concentrations in samples.

Objective 2: Spatial distribution of PAHs and mineralogical features in meteorites

The goal of this work was to investigate the presence and distribution of PAHs in meteorites and to correlate the spatial distribution of PAHs with meteoritic features. The chemical and mineralogical characteristics of a meteorite provide a wealth of information about the meteorite's formation and development. Although numerous studies have investigated the mineralogy and organic content of meteorites (1, 2, 3), little work has been done on correlating the distribution of meteoritic organics with mineralogical features. We have chosen to investigate PAHs because they are among the most abundant compounds in the universe, comprising ca. 10-20% of all carbon (4, 5). PAHs have been previously identified in meteorites, but their spatial distribution has not been extensively mapped.

During the period funded by this grant, we began work on this project by examining samples of the Allende and Murchison carbonaceous chondrite meteorites. The carbonaceous chondrites are of particular interest because they are among the most primitive solid samples in the solar system and may reflect the conditions present in the early solar system. Carbonaceous chondrites originated from planetesimals or asteroids that accreted during the formation of the solar system. They are aggregates of many components including chondrules, calcium-aluminum inclusions (CAIs), dark inclusions, and individual mineral grains, all of which can be surrounded by fine-grained rims and occur within a fine-grained matrix. Some of these components experienced temperatures sufficient to cause them to melt, while the minerals contained in other components have low decomposition temperatures that show that they never reached high temperatures. CAIs and chondrules were formed from materials heated to ca. 1400 – 2400 K (6, 7), whereas the matrix material accreted at lower temperatures (8). Allende and Murchison are important examples of carbonaceous chondrites, and their mineralogy and bulk organic composition have been extensively investigated (9, 10, 11, 12).

Samples of Allende and Murchison were dry-cut in our laboratory to produce thick sections. These sections were then photographed under a stereomicroscope and introduced into the $\mu L^2 MS$ instrument quickly to avoid possible contamination from exposure to laboratory air. Single-shot $\mu L^2 MS$ spectra were taken to determine PAH intensities in a series of 40-μm spots tracking across the sample surface. The PAH intensities were then compared to the stereomicroscope photographs to determine correlations between the PAH distribution and the visible features.

Figure 1 shows a chondrule on the surface of the Murchison sample and a map of the naphthalene intensity across this region. Maps made for other PAHs have similar appearances. The chondrule shows very low levels of PAH intensity compared with the surrounding matrix. This low PAH intensity for visible non-matrix features was observed for a series of desorption lines across both the Allende and Murchison samples studied.
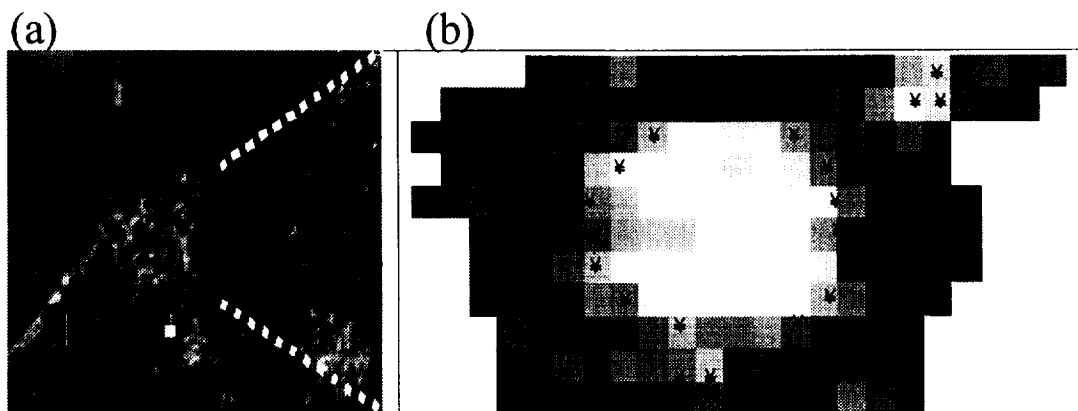
FIGURE 1. (a) Photo of Murchison sample surface showing a chondrule (scale bar = 400 μm). (b) Intensity map of the PAH naphthalene for the boxed area in (a). Scale goes from white (low intensity) to black (high intensity). The dots mark the feature limits observed during the experiment.

Figure 2 shows the normalized integrated intensities for several PAHs along a desorption line across the Allende sample. All PAH intensities follow the same distribution. Similar results were observed along several desorption lines for both the relatively unaltered Allende and the moderately aqueously altered Murchison.
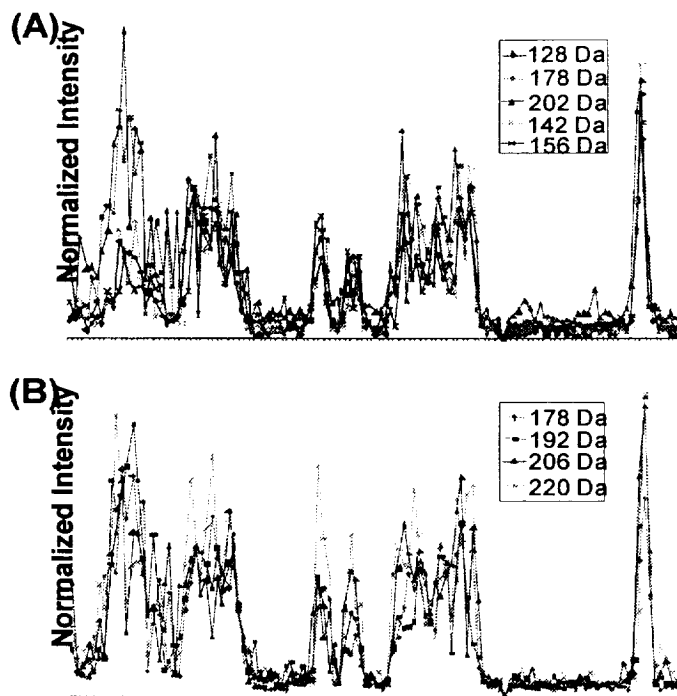

FIGURE 2: Normalized integrated intensities along a desorption line across the Allende sample for (A) mass 128 Da (naphthalene), mass 178 Da (phenanthrene), mass 202 Da (fluoranthene/pyrene), mass 142 Da (methylnaphthalene), mass 156 Da (dimethylnaphthalene/ethylnaphthalene) and (B) the alkylation series for phenanthrene. Trends are the same for all PAHs.

The sharp PAH gradients observed between the high-temperature components such as chondrules and CAIs and the low-temperature matrix suggest that the PAHs were in their host materials from the time of meteorite formation. It is unlikely that *in-situ* migration or alteration of the PAHs would allow the meteorites to retain such sharp chemical gradients and leave some PAH-free areas while mixing PAHs essentially uniformly with the matrix. These observations are consistent with a distribution for the PAHs that has not been significantly altered since the meteorite formed. Hence, our findings suggest an origin for the meteorite PAHs that is contemporary with or prior to parent-body formation.

Figure 3 presents the ratios of the main molecular PAHs and their alkylation series relative to naphthalene for the desorption shots taken across Murchison. Although the data are for single laser shots, the uncertainties shown by the error bars are consistent and modest. The ratios are constant within a factor of two for all spots. We have excluded data corresponding to areas with a signal-to-noise ratio of less than three. Similar data exist for Allende; the data for both meteorites is summarized in Table 2.
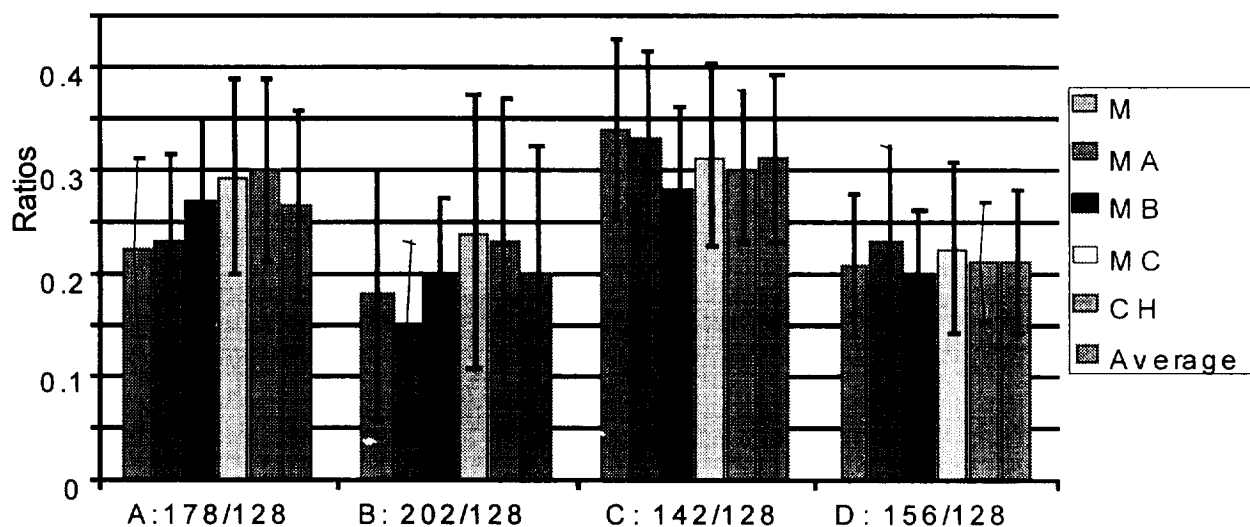

FIGURE 3: Intensity ratios of PAHs in Murchison normalized to naphthalene. Error bars represent one standard deviation. Regions with a signal-to-noise ration greater than three are excluded. M, MA, MB, and MC are desorption lines across the sample surface consisting of 114, 63, 110, and 65 included shots respectively, while CH is the area over the chondrule in Figure 1, consisting of 160 included shots.

Considering that the meteorites are agglomerations of many components, different origins for the PAHs contained within each component is a plausible assumption. It is unlikely, however, that material from unrelated samples would give PAH distributions that correlate so closely with one another. The similarity of the ratios for all points across a sample argue that the PAHs within a meteorite result from a common formation event that occurred prior to incorporation into the meteorite; no evidence exists for localized reactions and/or post-incorporation redistribution. The fact that the ratios between the two unrelated meteorites also match within experimental error suggests the possibility

that all of the meteoritic PAHs in Allende and Murchison come from a common origin, perhaps predating the formation of the solar system.

TABLE 2: Comparison of PAH ratios of Murchison and Allende. Ratios compare PAHs of mass 178 Da (phenanthrene, $C_{14}H_{10}$), 202 Da (pyrene or fluoranthene, $C_{16}H_{10}$), 142 Da (methylnaphthalene, $C_{11}H_{10}$), and 156 Da (dimethylnaphthalene or ethylnaphthalene, $C_{12}H_{12}$) to mass 128 Da (naphthalene, $C_{10}H_8$). Uncertainties represent one standard deviation.

Ratio	Murchison	Allende
178:128	0.27 ± 0.09	0.27 ± 0.21
202:128	0.20 ± 0.12	0.12 ± 0.09
142:128	0.31 ± 0.08	0.29 ± 0.10
156:128	0.21 ± 0.07	0.14 ± 0.07

The results of this work are being published in *Geochimica et Cosmochimica Acta* (13) and were also presented at the 65th Annual Meeting of the Meteoritical Society in 2002. **We consider this study to be the most important result obtained during this grant period.**

Objective 3: Determination of reaction pathways and photoproducts of PAH-containing interstellar ice analogs

The aim of this project is to investigate the processing of PAHs in interstellar ice analogs. PAHs are known to be widespread components of the interstellar medium, having been detected in a variety of diffuse interstellar environments through infrared astronomy (4, 5, 14, 15). They are also expected to be abundant components of the icy grain mantles that form around silicate cores inside dense molecular clouds (16, 17, 18). Energetic processing by UV photons and cosmic rays drives photochemical reactions within these ice grains, creating new and more complex compounds (19, 20, 21, 22). The identification of these reactions and their products adds to our understanding of the chemical evolution of organic compounds in the universe.

We have investigated the UV-driven photoreactions of PAH-containing interstellar ice analogs. The ices were prepared and irradiated at the NASA Ames Astrochemistry Lab (23). After warming to room temperature, the remaining residue, which contains the more complex, less volatile photoproducts of the reactions, was analyzed by $\mu L^2 MS$. Previous work examined PAH-containing water-dominated ices and revealed the formation of oxidized PAHs, including aromatic alcohols and quinones.

During the year covered by this grant award, we investigated interstellar ice analogs consisting of binary mixtures of coronene and other interstellar ice components, including ammonia, methanol, carbon monoxide, hydrogen cyanide, methane, and carbon dioxide. We observed products resulting from various addition reactions, including addition of amine, methyl, methoxy, nitrile/isonitrile, acid, ketone, and alcohol groups. The oxidized

coronenes were the most abundant products in all our photolysis experiments containing H_2O, and in most ices where oxygen was present in any form, suggesting that aromatic alcohols and ketones will be the dominant products of PAH-ice photolysis in the solar system and in the ISM, where many ices are H_2O-rich. Even in the presence of H_2O, however, UV-induced reactions between PAHs and other species do occur, forming new carbon-hydrogen, carbon-carbon, carbon-oxygen and carbon-nitrogen bonds. These results suggest the possible existence of a rich suite of organic compounds not only in the ISM but also on the surface of icy solar system bodies and planetary polar caps where aromatics in ices are exposed to radiation. A paper based on these findings has been published in *The Astrophysical Journal* (24).

In addition to examining UV-driven photoreactions of these ices, we exposed some coronene-containing ices to high-energy protons to determine the effect of cosmic rays on interstellar ices. The reactions observed were similar to those seen from the UV-driven reactions. A paper presenting these results has appeared in *The Astrophysical Journal*(25).

Objective 4: Investigation of prebiotic and meteoritic PAH reactions

Much of the bulk of carbonaceous chondrites and other meteorites is in the form of an insoluble polymeric kerogen-like material. This meteoritic kerogen is a highly complex, cross-linked three-dimensional network of aromatic and aliphatic hydrocarbons (26, 27). Not much is known about the reaction pathways leading to kerogen formation. We investigated the photoreactions of PAHs and alkanes under various conditions to determine if these reactions could play a role in the synthesis of larger, more complex aromatic compounds, such as what constitutes kerogen.

The reaction of PAHs and alkanes is interesting because these compounds are suspected to have been abundant components of the organic inventory of the early Earth (28), as well as being observed in the interstellar medium (ISM) (29, 30). Photoreactions between these molecules may provide a facile mechanism for linking them to each other through the formation of new carbon-carbon bonds. The work we accomplished addressed three questions:

1. Does photochemistry between PAHs and alkanes yield new C-C bonds?
2. Were these reactions possible on the early Earth?
3. Could these reactions occur in the interstellar medium (ISM)?

In the first stage of our work, we exposed solutions of PAHs in alkanes to UV light (255-nm from a mercury lamp) and analyzed the resulting products using $\mu L^2 MS$. The PAHs phenanthrene, naphthalene, anthracene, 9-methylanthracene, pyrene, and fluoranthene were each reacted with hexadecane in solutions of 1:100 PAH:hexadecane. In each case, alkylated PAH products were observed that indicated the addition of the hexadecyl chain to the parent PAH. Peaks were also observed for dimethylated/ethylated products as well, but their peak intensities in the $\mu L^2 MS$ spectra were considerably weaker. In addition to the alkylated products, small amounts of oxidation products

8

appeared from the addition of one or two oxygen atoms or hydroxyl groups to the starting PAH. We also reacted phenanthrene with a series of alkanes, including n-nonane, n-decane, 4-methylnonane, cyclodecane, and 1,1'-(1,1,3-trimethyl-1,3-propanediyl)biscyclohexane. Again, alkylated PAHs were detected in each case. The fact that a wide variety of PAHs and alkanes reacted to give alkylated PAHs indicates that 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.

Next, we examined the photoreaction of PAHs and alkanes under model prebiotic conditions. On the early Earth, organics such as PAHs and alkanes could have been delivered by extraterrestrial material that entered the ocean and was released by hydrolytic processes over time, creating oil slicks at the surface of the ocean. We photoreacted PAH:alkane solutions in the form of both a thin film on the surface of simulated ocean water (0.5 M sodium chloride, 0.05 M magnesium chloride, 0.01 M calcium chloride, and 0.01 M ferrous chloride) and as a dispersion in this water. Both alkylated and oxidized aromatic products were observed, implying that some of the PAHs and alkanes present in an oil slick on the early ocean could have become linked to each other in the presence of UV radiation. The photochemical reaction would have yielded new carbon-carbon bonds between PAH and alkane molecules and may have been an important step in producing complex organics from simple precursors.

Finally, we analyzed the products formed upon UV irradiation of interstellar ice analogs consisting of PAHs and alkanes. The ices were prepared and irradiated at NASA Ames and were irradiated for a period of 30 minutes using a flowing-hydrogen discharge lamp (23). Again, both alkylated and oxidized aromatics were observed, indicating that the photochemical reactions of PAHs and alkanes under interstellar conditions may provide a plausible mechanism for forming C-C bonds between these molecules. Complex molecules can thus be built up from simpler ones, and perhaps contribute to the suite of organic molecules present in meteorites.

A paper based on our findings has been accepted for publication at *Origins of Life and Evolution of the Biosphere*(31). We have observed the formation of carbon-carbon bonds from photoreactions of PAHs and alkanes under conditions relevant to the early Earth and the ISM. We have not seen evidence of the extensive cross-linking that would be required for this reaction to form meteoritic kerogen, but we suggest that this photoalkylation process could play a role in the creation of more complex compounds from simpler ones under the conditions studied.

Appendix A: The μL^2MS 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 μL^2MS 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 (2, 32, 33, 34).

A detailed description of our technique has been presented elsewhere (35, 36), and is summarized here for convenience. The principle of μL^2MS is illustrated in Figure 1. 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.
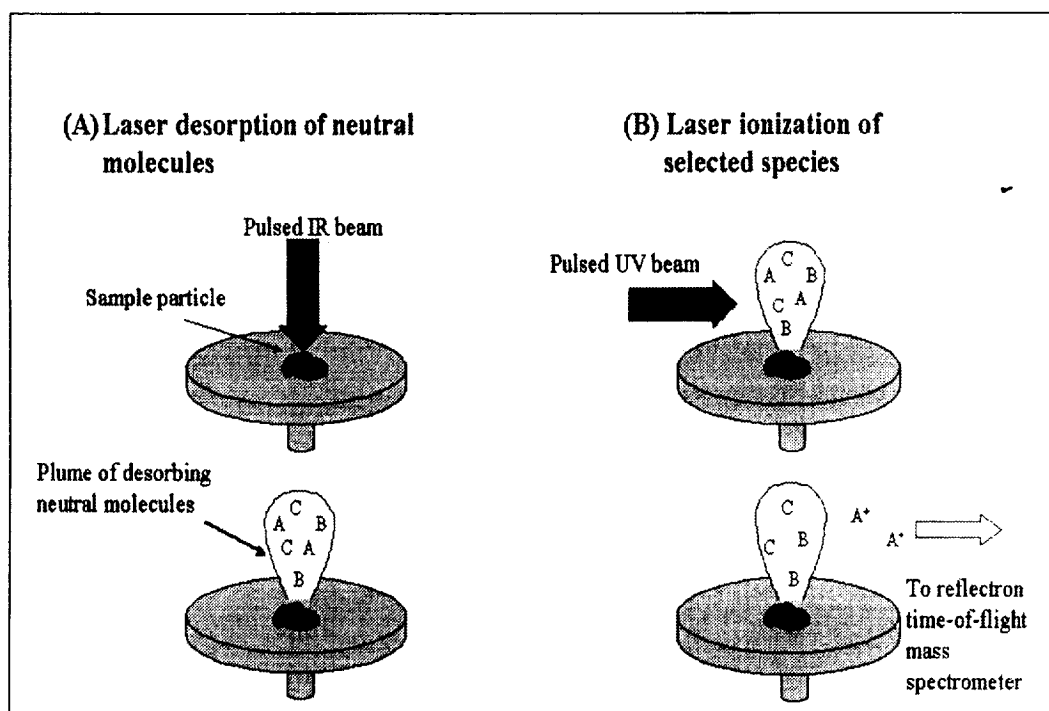

(A) Laser desorption of neutral molecules

Pulsed IR beam

Sample particle

Plume of desorbing neutral molecules

(B) Laser ionization of selected species

Pulsed UV beam

To reflectron time-of-flight mass spectrometer

FIGURE 1. The μL^2MS 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) (37). 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 (38, 39).

$\mu L^2 MS$ 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 40 μm in diameter.
- Desorption with minimal decomposition and ionization with minimal fragmentation, resulting in the production 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.

REFERENCES

1. A. E. Rubin, *Meteorit. Planet. Sci.* **32**, 231-247 (1997).
2. D. S. McKay, et al., *Science* **273**, 924-930 (1996).
3. J. R. Cronin, *Adv. Space Res.* **9**, 59-64 (1989).
4. J. L. Puget, A. Leger, *Ann. Rev. Astron. Astrophys.* **27**, 161-198 (1989).
5. L. J. Allamandola, A. G. G. M. Tielens, J. R. Barker, *Astrophys. J.* **71**, 733-775 (1989).
6. H. C. Connolly, B. D. Jones, R. H. Hewins, *Geochim. Cosmochim. Acta* **62** (1998).
7. G. J. MacPherson, D. A. Wark, in *Meteorites and the Early Solar System* J. F. Kerridge, M. S. Matthews, Eds. (University of Arizona Press, Tucson, 1988) pp. 748-807.
8. P. R. Buseck, X. Hua, *Annu. Rev. Earth Planet. Sci.* **21**, 255-305 (1993).
9. L. Grossman, *Ann. Rev. Earth Planet. Sci.* **8**, 559-608 (1980).
10. R. L. Levy, M. A. Grayson, C. J. Wolf, *Geochim. Cosmochim. Acta* **37**, 467-483 (1973).
11. J. F. Kerridge, S. Chang, R. Shipp, *Geochim. Cosmochim. Acta* **51**, 2527-2540 (1987).
12. J. R. Cronin, S. Chang, in *The Chemistry of Life's Origins* J. M. Greenberg, C. X. Mendoza, V. Pirronelle, Eds. (Kluwer Academic Publishers, Dordrecht, 1993), vol. 416, pp. 209-258.
13. F. L. Plows, J. E. Elsila, R. N. Zare, P. R. Buseck, *Geochim. Cosmochim. Acta* (in press).
14. F. Boulanger, et al., *Astron. Soc. Pac. Conf. Ser.* **132**, 15-23 (1998).
15. L. J. Allamandola, D. J. Hudgins, S. A. Sandford, *Astrophys. J.* **511**, L115-L119 (1999).
16. K. Sellgren, T. Y. Brooke, R. G. Smith, T. R. Geballe, *Astrophys. J.* **449**, L69-L72 (1995).
17. S. A. Sandford, *Meteoritics and Planetary Science* **31**, 449-476 (1996).
18. J. E. Chiar, et al., *Astrophys. J.* **537**, 749-762 (2000).
19. J. M. Greenberg, in *Comets* L. L. Wilkening, Ed. (University of Arizona Press, Tuscon, 1982) pp. 131-163.
20. W. A. Schutte, , Leiden (1988).
21. M. P. Bernstein, S. A. Sandford, L. J. Allamandola, S. Chang, M. A. Scharberg, *Astrophys. J.* **454**, 327-344 (1995).
22. G. Strazzulla, *Adv. Space Res.* **19**, 1077-1084 (1997).
23. M. P. Bernstein, et al., *Science* **283**, 1135-1138 (1999).
24. M. P. Bernstein, et al., *Ap. J.* **in press** (2002).
25. M. P. Bernstein, et al., *Astrophys. J.* **582**, L25-L29 (2003).
26. M. L. Sohn, *Org. Geochem.* **8**, 203-206 (1985).
27. R. Hayatsu, S. Matsuoka, R. G. Scott, M. Studier, E. Anders, *Geochim. Cosmochim. Acta* **41**, 1325-1339 (1977).
28. C. Chyba, C. Sagan, *Nature* **355**, 125-132 (1992).
29. J. Lacy, et al., *Astrophys. J.* **376**, 556-560 (1991).

30.   J. R. Cronin, S. Pizzarello, *Geochim. Cosmochim. Acta* **54**, 2859-2868 (1990).

31.   T. B. Mahajan, J. E. Elsila, D. W. Deamer, R. N. Zare, *Orig. Life Evol. Biosphere* (in press).

32.   S. J. Clemett, C. R. Maechling, R. N. Zare, P. D. Swan, R. M. Walker, *Science* **262**, 721-725 (1993).

33.   K. L. Thomas, et al., *Geochimica et Cosmochemica Acta* **59**, 2797-2815 (1995).

34.   S. J. Clemett, et al., *Meteoritics* **29**, 457 (1994).

35.   L. J. Kovalenko, et al., *Anal. Chem.* **64**, 682-690 (1992).

36.   S. J. Clemett, R. N. Zare, in *Molecules in Astrophysics: Probes and Processes* E. F. v. Dishoeck, Ed. (Kluwer Academic Publishers, Leiden, Netherlands, 1997) pp. 305-320.

37.   T. B. Mahajan, U. Ghosh, R. N. Zare, R. G. Luthy, *Int. J. Mass Spectrom.* **212**, 41-48 (2001).

38.   N. Winograd, J. P. Baxter, F. M. Kimock, *Chem. Phys. Lett.* **82**, 581 (1982).

39.   A. N. Shibanov, *Laser Analytical Spectrochemistry.* V. S. Letokhov, Ed. (Adam Hilger, Bristol, 1985).