

# MICROPROBE TWO-STEP LASER MASS SPECTROMETRY AS AN ANALYTICAL TOOL FOR METEORITIC SAMPLES

SIMON J. CLEMETT AND RICHARD N. ZARE

*Department of Chemistry*

*Stanford University*

*Stanford, CA 94305-5080 USA*

**Abstract.** Microprobe two-step laser mass spectrometry ( $\mu\text{L}^2\text{MS}$ ) is a new mass spectrometric method in which the two essential steps of any mass spectrometric analysis, vaporization and ionization, are carried out using two independent laser sources. In the first step, the output of a pulsed infrared laser is focused on the sample to cause rapid heating in the spot area illuminated, which is typically  $40\ \mu\text{m}$  by  $40\ \mu\text{m}$ . In the second step, the output of a pulsed ultraviolet laser causes (1+1) resonance-enhanced multiphoton ionization (REMPI) of those desorbed neutral molecules that (1) are able to absorb this UV wavelength and (2) whose ionization potential is less than the energy of two photons of this UV wavelength. The resulting ions are then mass analyzed in a reflectron time-of-flight apparatus. Under suitable conditions fragmentation can be avoided in both the vaporization and ionization steps so that  $\mu\text{L}^2\text{MS}$  can be applied to the analysis of a mixture of molecules. Applications of  $\mu\text{L}^2\text{MS}$  to meteorite samples are presented as a means of detecting trace amounts of certain organic molecules present in complex materials without prior sample preparation, extraction, purification, and separation steps. Moreover, this analysis can be carried out with micrometer spatial resolution so that in favorable cases the presence or absence of certain molecules can be correlated to mineralogical features of the sample.

## 1. Motivation

We have only just begun to take the first tentative steps toward interplanetary travel. To date, the only sample returns have been from our moon which is a mere 384,000 km away. It is expected that many generations

might go by before we explore the other planets in our Solar System, and it is not clear when we might develop the technology to allow travel between the stars within the timespan of a single person's life. Nevertheless, extraordinary and wondrous as it may seem, the possibility already exists for us to study, in the laboratory, fragments of the asteroid belt, the stuff from which comets are made, rocks from the surface of Mars, and perhaps most remarkably the dust out of which our own solar system condensed some 4.5 ga ago. These samples are brought to us in the form of meteorites and interplanetary dust particles that visit our planet. Our challenge is to find the means of analyzing these "extraterrestrial visitors" in a manner that gives confidence as to the chemical composition of these visitors while avoiding at the same time the confusion of terrestrial contamination and artifacts introduced by the analysis process.

The chemical analysis of meteorites and related material must overcome the problems that species of interest may only be present at trace levels of concentration, the samples are often extremely heterogeneous, the samples are often available in only limited quantities, and the species present are found in complex mixtures possibly containing hundreds of thousands of other molecular species. This review describes the design, development, and operating principles of one particular microanalytical instrument capable of analyzing some special classes of trace organic molecules with microscopic spatial resolution – the microprobe two-step laser mass spectrometer ( $\mu\text{L}^2\text{MS}$ ) – an instrument that has been evolving over the Ph.D. lifetimes of 4 graduate students: Jong Hoon Hahn (1988), Renato Zenobi (1990), Claude R. Maechling (1995), and Simon J. Clemett (1996). The development of this device has also benefited greatly from the contributions of several postdoctoral research associates including F. Engelke, J.-M. Phillipoz, L. J. Kovalenko, and X. D. F. Chillier. The detailed applications of this instrument to the study of meteoritic samples may be found elsewhere (Hahn et al. 1988; Zenobi et al. 1989, 1992; Kovalenko et al. 1991, 1992; Zenobi & Zare, 1991; Clemett et al. 1993; Thomas et al. 1995a; Maechling et al. 1995; McKay et al. 1996). In what follows we emphasize the capabilities of this analytic tool and its present limitations.

## 2. $\mu\text{L}^2\text{MS}$ : Methodology

Figure 1 illustrates the concept behind the instrument. The two-step laser mass spectrometry technique combines the advantages of laser desorption to volatilize intact neutral molecules from a solid sample with the molecular selectivity and sensitivity of resonance-enhanced multiphoton ionization (REMPI), and the high ion transmission, unlimited mass range, and multi-channel detection of a reflectron time-of-flight (RTOF) mass spectrometer.

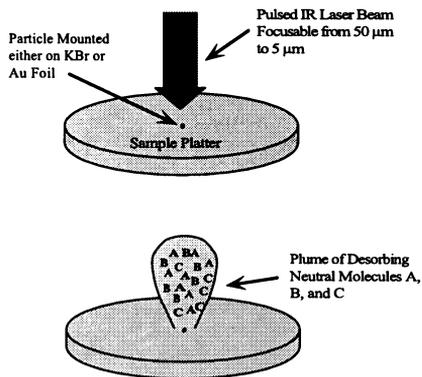
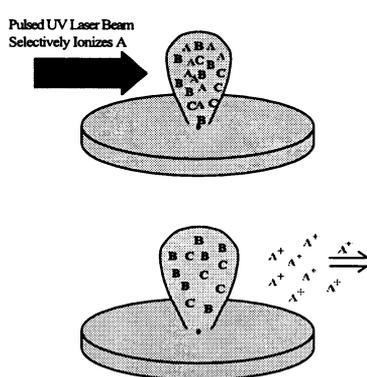
**(A) Laser Desorption of Neutral Molecules****(B) Laser Ionization**

Figure 1. Concept of the  $\mu\text{L}^2\text{MS}$  technique.

Constituent molecules of the sample are desorbed with a pulsed infrared (IR) laser beam focused to microscopic dimensions on the sample surface using a Cassegrainian microscope objective. The laser power is kept low to minimize decomposition, avoid plasma formation, and assure that only neutral species are desorbed. In the second step, some selected set of the desorbed molecules are ionized with a pulsed ultraviolet (UV) laser beam, and the resulting ions extracted into a RTOF mass spectrometer. Lighter ions travel faster than heavier ions so that by recording the arrival times at the detector the ions are weighed, i.e., their masses are determined.

Pulsed laser desorption can, in a very short time span, deposit large quantities of energy into a highly localized area, resulting in heating rates ranging from  $10^5$  to  $10^{11}$   $\text{K} \cdot \text{s}^{-1}$  (Cowin et al. 1978). Such processes provide a remarkably versatile method for introducing thermally labile and high molecular weight species intact into the gas phase. The mechanism of laser assisted thermal desorption has been extensively investigated by (Maechling 1995) as well as by Zenobi and coworkers (Voumard et al. 1994, 1995).

One of the main advantages of a photoionization process is that we can choose conditions that give rise to species-selective ionization. We presently use a (1+1) REMPI scheme, in which absorption of one photon causes a molecule to make a transition to an electronically excited state ( $S_0 \rightarrow S_1$ ) and absorption of a second photon causes ionization of the excited molecule, as illustrated in Fig. 2. Wavelength selectivity results from the photon en-

Selective ionization of the PAH chromophore is achieved using a 1+1 Resonance Enhanced Multiphoton Ionization scheme (1+1 REMPI)

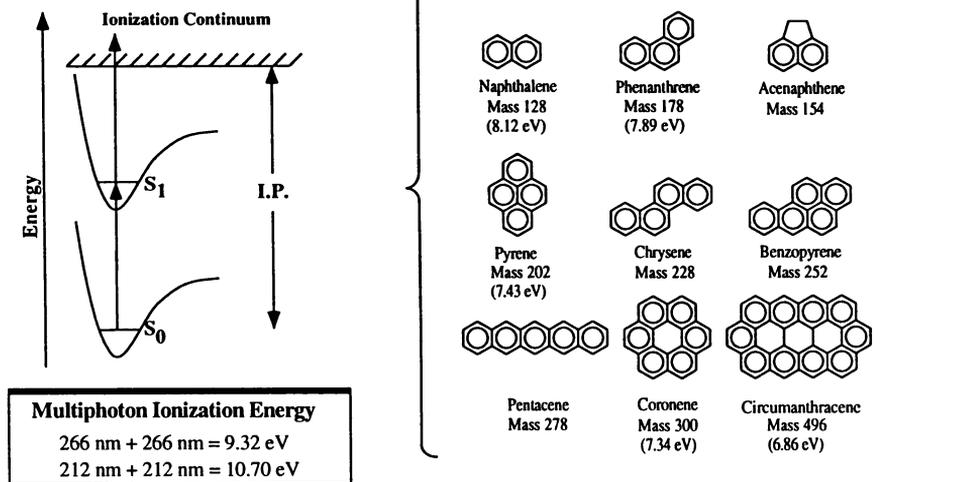


Figure 2. REMPI scheme used for species-selective photoionization.

ergy being resonant with a transition to an intermediate state. Because the ionization efficiency of a resonant mechanism is greater by many orders of magnitude than nonresonant multiphoton processes (Pappas et al. 1989), only those molecules with a transition in resonance with the laser photon are appreciably ionized, which allows us to achieve species-selective ionization. The chromophore we utilize is the benzene ring moiety that has a high absorption cross section at 266 nm associated with electronic excitation of the aromatic ring ( $\pi \rightarrow \pi^*$ ). This chromophore provides an ionization window on the class of compounds referred to as polycyclic aromatic hydrocarbons (PAHs), which are of fundamental cosmochemical interest. The real elegance of this ionization scheme lies not only in its selectivity, but also because it provides a very efficient “soft ionization” route (Winograd et al. 1982; Shibanov 1985); that is, ions are formed with very little internal excitation and consequently do not undergo any appreciable fragmentation.

### 3. $\mu\text{L}^2\text{MS}$ : Instrument configuration

Implementation of the  $\mu\text{L}^2\text{MS}$  principle has resulted in the instrument schematically represented in Fig. 3. The system may be divided into four sub-units:

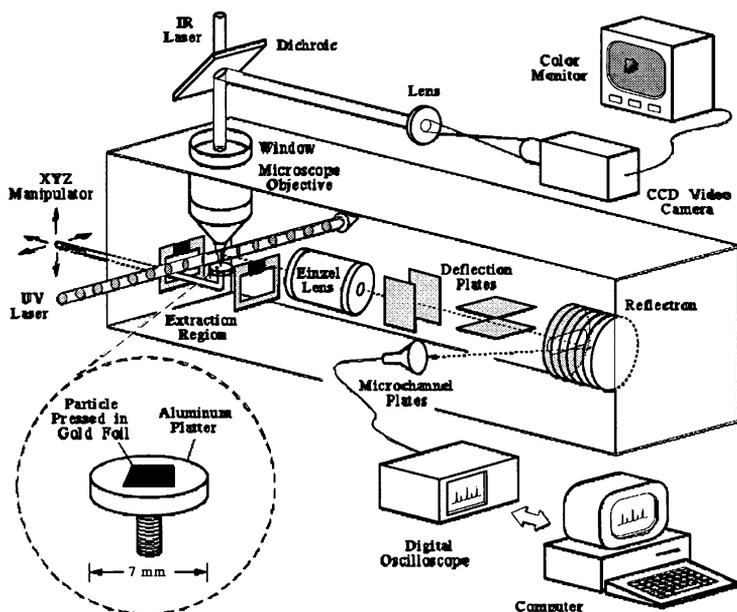


Figure 3. Schematic illustration of the  $\mu\text{L}^2\text{MS}$  instrument.

- IR and UV lasers; only entering beam paths shown.
- Main vacuum chamber, housing sample to be analyzed, sample introduction interlock (not shown), and RTOF mass spectrometer.
- Microscope and associated visualization / desorption optics, used to view the sample at micron resolution and to focus the desorbing laser that defines the size of the analysis area.
- Data collection and storage, consisting of a high-speed digitizing oscilloscope and dedicated computer.

#### 4. $\mu\text{L}^2\text{MS}$ : Operational parameters and examples

The spatial resolution of the  $\mu\text{L}^2\text{MS}$  instrument is determined by how tightly the IR laser beam can be focused onto the sample. This, in turn, depends primarily on the wavelength of the IR laser, its spatial beam properties, and the working distance of the microscope objective. The theoretical diffraction limit for the current  $\mu\text{L}^2\text{MS}$  configuration is estimated to be  $\sim 20 \mu\text{m}$ . Fig. 4 shows a cut surface of the Allende (CV3) meteorite with three laser burn spots. The spots were created by focusing the IR desorption laser onto the sample surface and raising the laser power until it began to melt the mineral matrix. When imaged in a scanning electron microscope the

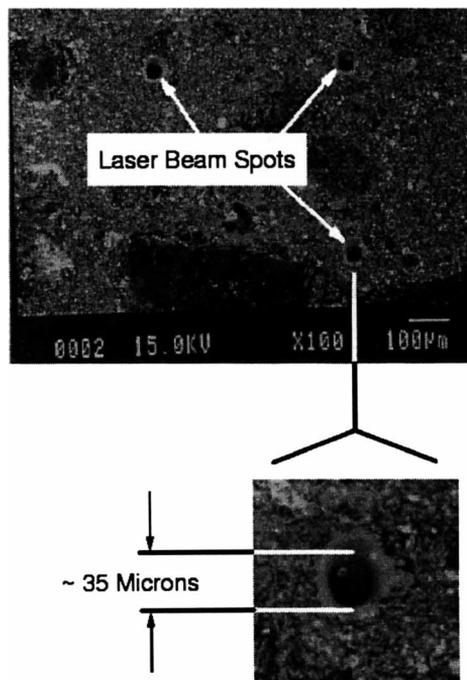


Figure 4. Cut surface of the Allende (CV3) meteorite with three laser burn spots.

burn spots are easily visualized and the analysis beam spot size is experimentally determined to be  $35 \pm 2 \mu\text{m}$ , which is several times the diffraction limit.

By translating the sample surface under the microscope objective, spatial distribution maps of PAHs on a surface can be generated. Because a complete mass spectrum can be obtained from a single analysis spot, spatial distribution maps for all masses are simultaneously acquired. The resolution of such maps is experimentally limited by the accuracy with which the surface can be translated and by the beam analysis spot size. Figure 5 shows the spatial distribution of the molecule chrysene ( $\text{C}_{18}\text{H}_{12}$ ) on a freshly fractured surface of the Martian (SNC) meteorite ALH84001 resolved to a resolution of 50 nm. Such maps have been used by us to prove the existence of indigenous “Martian PAHs” (McKay et al. 1996). Furthermore, we have been able to demonstrate specific correlations between the observed PAHs and mineralogical features as determined by scanning electron microscopy (Thomas et al. 1995b). In this figure chrysene peaks at the location of a carbonate globule.

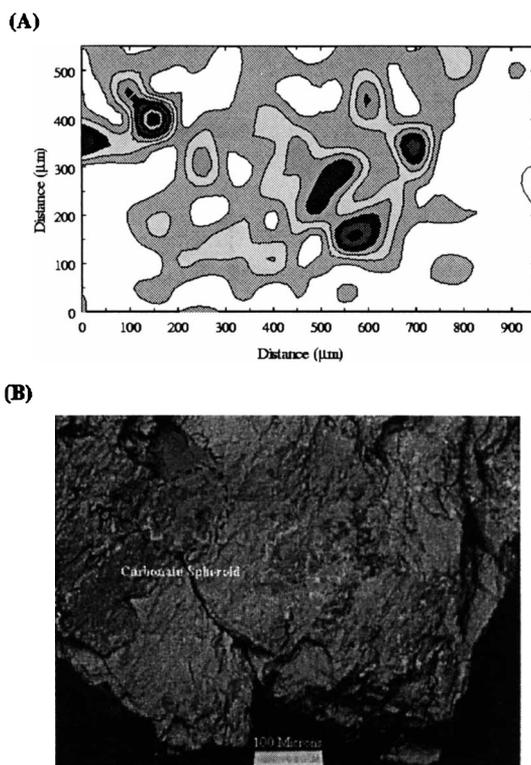


Figure 5. Spatial distribution of chrysene on a freshly fractured surface of the Martian meteorite ALH84001.

#### 4.1. “SOFT” IONIZATION

Resonant laser ionization allows aromatic molecules to be ionized with virtually no fragmentation. Figure 6 shows the analysis of a mixture of the sex hormone  $\beta$ -estradiol ( $C_{18}H_{24}O_2$ ) and a protophyrin IX ester ( $C_{36}H_{38}N_4O_4$ ) dissolved at the part per million concentration level in toluene ( $C_6H_5CH_3$ ). The  $\mu L^2MS$  spectrum isotopically resolves each of these molecules almost exclusively as their parent ion with little to no fragmentation.

In certain circumstances, molecular fragmentation can provide useful information for structure elucidation. By increasing the power of the ionization laser, molecular fragmentation can be deliberately “turned on.” Figure 7 shows the  $\mu L^2MS$  spectrum of toluene under typical laser ionization powers which yields a fragmentation-free parent ion spectrum, and at high powers which causes fragmentation to occur all the way down to  $C^+$ .

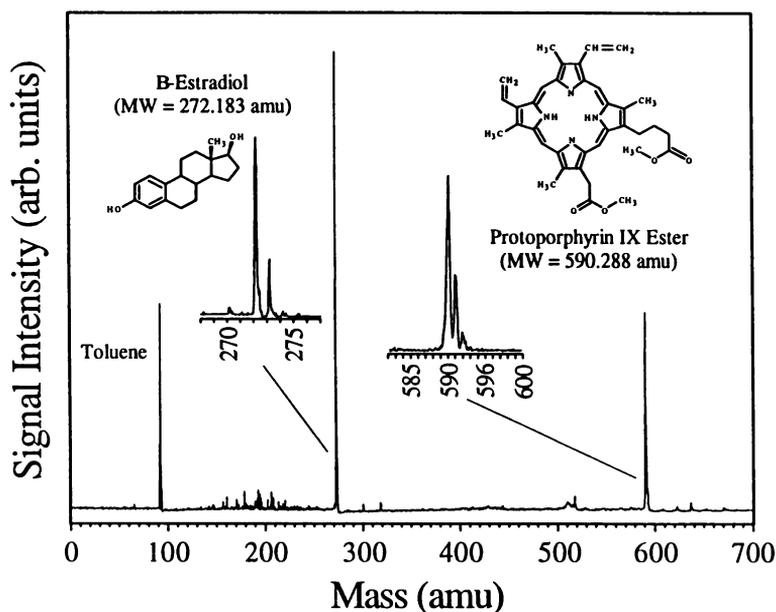


Figure 6. Mass spectroscopic analysis of  $\beta$ Estradiol and Protoporphyrin IX Ester following resonant laser ionization.

#### 4.2. PHOTOIONIZATION SELECTIVITY

The analysis of a complex mixture of PAHs and other organic/inorganic species by  $\mu\text{L}^2\text{MS}$  is illustrated in Fig. 8. Fifteen PAHs, classified by the U. S. Environmental Protection Agency as priority pollutants, ranging from 2- to 7-ring species, were dissolved in methylene chloride at the ppm concentration level. This solution was evaporated onto a finely powdered KBr – basalt matrix and analyzed directly by  $\mu\text{L}^2\text{MS}$ . A parent ion spectrum of only the fifteen PAH species was observed, with no fragmentation or polymerization, even though they represented only a trace component of the desorbed matrix. This result illustrates the sensitivity and specificity of the technique of microprobe two-step laser mass spectrometry.

By varying the laser ionization wavelength the  $\mu\text{L}^2\text{MS}$  instrument can be “tuned” to analyze other types of molecular species. Under high photoionization powers and suitable conditions nonaromatic organic species can be analyzed through nonresonant photoionization, which provides a window on a wide range of organic and inorganic species at the cost, however, of potentially severe fragmentation.

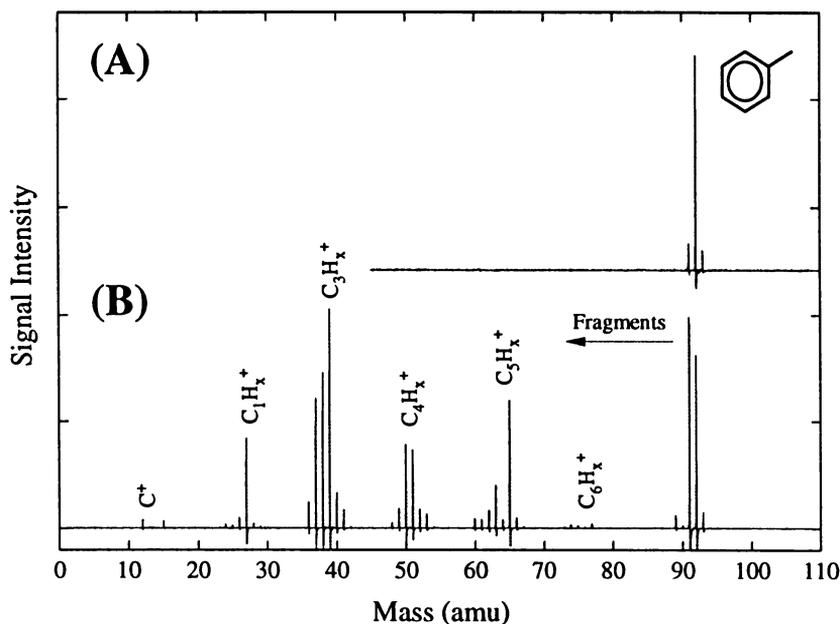


Figure 7.  $\mu\text{L}^2\text{MS}$  spectrum of toluene at typical laser ionization powers (A) and high powers (B).

#### 4.3. MASS RESOLUTION

The mass resolution of a TOF mass spectrometer is defined in terms of the flight time ( $t$ ) of a given mass peak to its FWHM ( $\Delta t$ ):

$$\text{Mass Resolution} = \frac{t}{2\Delta t} \quad (1)$$

This number represents the mass at which mass peaks differing in weight by only 1 amu will overlap at their FWHM. Alternatively, if this number is divided by 3, it represents the mass at which two masses separated by 1 amu will be approximately baseline-resolved. For linear TOF mass spectrometers the mass resolution is typically in the range of 100–400. The use of a reflectron can significantly improve this resolution. Figure 9 illustrates a gas-phase toluene TOF spectrum acquired by the  $\mu\text{L}^2\text{MS}$  instrument; the mass resolution is measured to be 2000. Under typical operating conditions the instrument is operated at a mass resolution of  $\sim 1800$ .

#### 4.4. DETECTION SENSITIVITY

Early measurements of the detection sensitivity of the  $\mu\text{L}^2\text{MS}$  instrument were made using coronene ( $\text{C}_{24}\text{H}_{10}$ ; 300 amu) standards. A 50 Å thick

## EPA Priority Pollutants (Supelco 4-8905M)

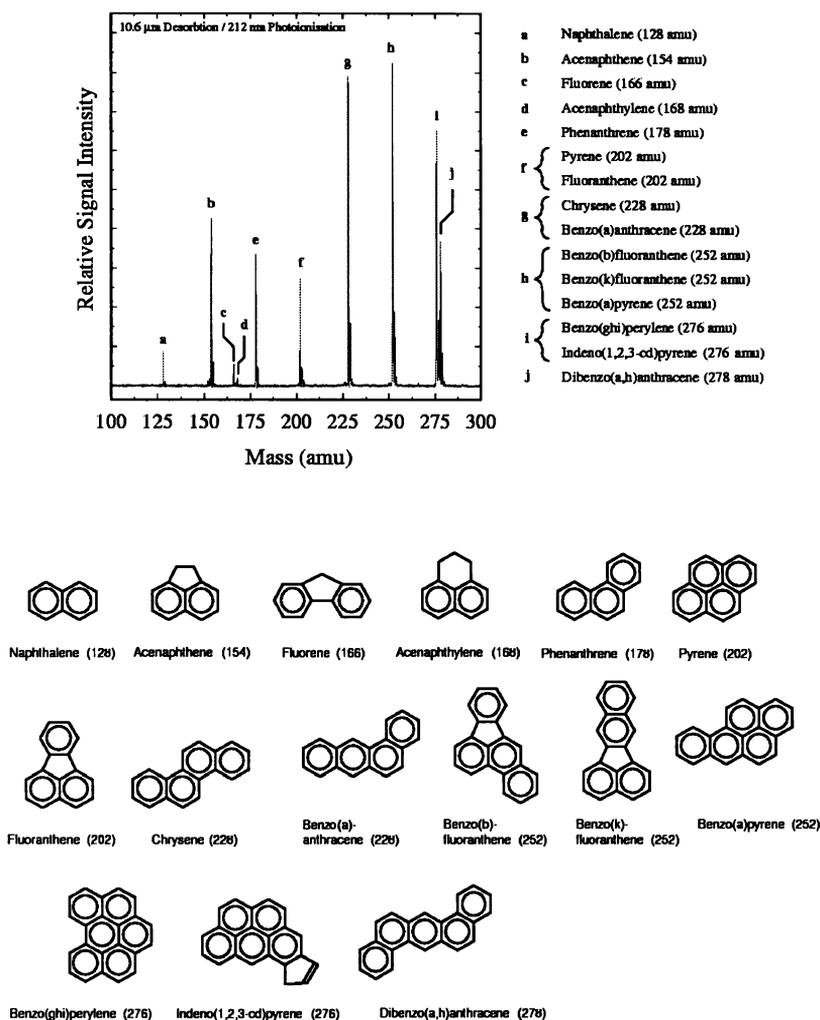


Figure 8.  $\mu\text{L}^2\text{MS}$  analysis of a complex mixture of PAHs and other species.

layer of coronene was vapor deposited onto a glass substrate and analyzed with a 40  $\mu\text{m}$  desorption spot, defining an analysis volume containing 30 femtomoles of coronene. The layer was removed in eight laser shots which corresponds to  $\sim 4$  femtomoles per laser shot. This removed rate determines an upper limit to the ultimate detection sensitivity of  $\sim 6$  attomoles for the molecule coronene or 0.15 attomoles for the molecule phenanthrene ( $\text{C}_{14}\text{H}_{10}$ ; 178 amu) when the higher photoionization cross-section of phenan-

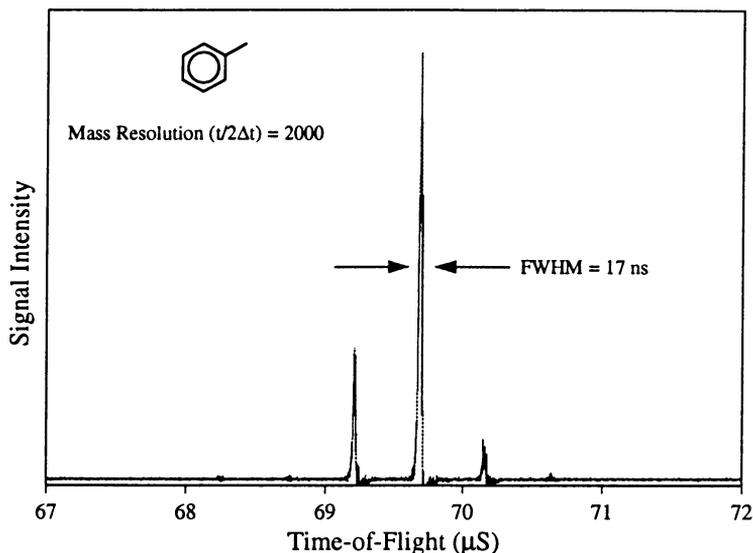


Figure 9.  $\mu\text{L}^2\text{MS}$  spectrum of toluene, illustrating the high mass resolution of 2000.

threne (Zenobi & Zare 1991) is taken into account. Subsequent to these studies, the ion extraction region was reconstructed several times and a new large-area detector assembly added. These sensitivity experiments have not since been repeated, but micron-sized fragments of both the Murchison (CM2) and Allende (CV3) meteorites yield well-resolved, single-shot spectra of PAHs. The total concentration of extractable PAHs in these meteorites is estimated to be in the 15 to 28 ppm range (Pering & Ponnamperuma 1971) and this suggests that the sensitivity of the instrument is now subattomole for most PAH species.

#### 4.5. MOLECULE-SPECIFIC CARBON ISOTOPE RATIOS

The carbon isotope ratio  $R$  is defined in the astrophysical literature as the ratio of the C-12 to C-13 stable isotope concentrations of carbon, namely  $R = [^{12}\text{C}]/[^{13}\text{C}]$ . The variation in  $R$  both on Earth and within our Solar System is small and ranges from 88 to 93 with the mean solar value of 89. For interstellar grain material, however,  $R$  ranges from 2 to 2000 and is associated with different nucleosynthetic pathways and hence different stellar sources for the grains. Clearly, such large isotope variations provide an unambiguous means to differentiate solar material from extrasolar material (although it must be recognized that extrasolar material may also have carbon  $R$  values that are in the range of solar material). The  $\mu\text{L}^2\text{MS}$  instrument is capable of providing such molecule-specific carbon isotope

information. It should be stressed that the  $\mu\text{L}^2\text{MS}$  instrument does not have the mass resolution to distinguish  $^{12}\text{C-D}$  from  $^{13}\text{C-H}$ , but the  $[\text{H}]/[\text{D}]$  isotope ratio is so large that the D contribution to peaks associated with C-13 can be neglected.

Consider a molecule having  $n$  carbon atoms of which  $i$  are C-13 and  $n - i$  are C-12; then the probability of finding an isotopomer with  $i$  C-13 atoms is given by  $\binom{n}{i} a^{n-i} b^i$  where  $\binom{n}{i} = n!/[i!(n-i)!]$  represents the number of ways of taking  $n$  objects  $i$  at a time,  $a$  is the fraction of carbon that is C-12 and  $b$  is C-13. Hence  $R = a/b$  and the area under the isotopomer peak of pure C-12 with mass  $M$  to that containing one C-13 atom with mass  $M + 1$  is given by

$$(\text{Area})_M/(\text{Area})_{M+1} = \binom{n}{0} a^n b^0 / \binom{n}{1} a^{n-1} b = Rn \quad (2)$$

Hence a measurement of the peak area of the pure C-12 isotopomer to that containing one C-13 atom allows the value of  $R$  to be determined from a knowledge of  $n$ , i.e., a knowledge of the organic detected. The precision to which the  $R$  value can be measured by  $\mu\text{L}^2\text{MS}$  compares poorly to that of an isotope ratio mass spectrometer (Maechling et al. 1995), but it is sufficient to distinguish PAHs that are associated with extrasolar grains from those that are solar. Figure 10 shows evidence for four C-13 depleted PAHs associated with C-13 depleted interstellar grains extracted from a sample of the Murchison meteorite. Evidence has also been found for C-13 enriched PAHs associated with C-13 enriched grains in the same meteorite sample (Clemett et al. 1993).

## 5. $\mu\text{L}^2\text{MS}$ : Experimental procedure

The sample selected to be analyzed is attached to an aluminum or brass sample platter, and is introduced into the chamber through a vacuum interlock and is pumped down to  $\sim 1 \times 10^{-3}$  torr in about two minutes. After introduction into the main chamber, samples are left to outgas for about 15 minutes or until the pressure in the main chamber returns to the original base pressure of less than  $5 \times 10^{-8}$  torr.

The sample platter is positioned just below the extraction region and brought into focus using an x-y-z manipulator. For sample viewing, a macro zoom lens and field lens are used in a telescope mode, so that an image of the sample is projected onto a CCD video camera. To couple the video camera to the microscope objective a 2 mm thick Ge flat is used, which reflects visible light used for sample viewing but transmits the IR light of the desorption laser. The sample is illuminated exterior to the vacuum

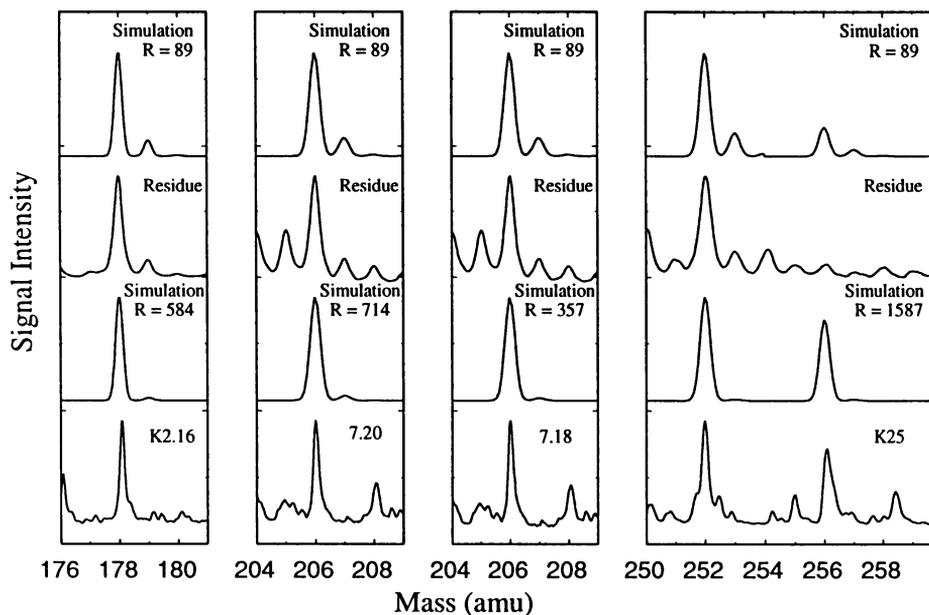


Figure 10. Evidence for high isotopic ratios  $R$  (i.e., C-13 depletion) in PAHs extracted from the Murchison meteorite.

chamber, through a side viewport, with a focused quartz halogen lamp, which is incident at a glancing angle (not shown in Fig. 3).

Infrared light from a pulsed CO<sub>2</sub> laser (Alltec AL. 853; 10.6 μm, 120 ns FWHM with a 4 μs tail) is attenuated and beam shaped using a variable high-power (Venetian blind / spatial filter) attenuator similar to that described by Bialkowski (1987). The beam is then collimated and clipped prior to entrance into the vacuum chamber with two irises opened to a diameter equal to that of the microscope “spider” mirror (5 mm) and then focused with the reflecting microscope objective (Ealing x36) to a 40 μm diameter spot on the sample. The laser pulse energy is chosen to maximize the desorption yield without producing appreciable fragmentation or ionization. A typical pulse energy is measured to be 22 μJ; we estimate 5.2 μJ is contained in the initial spike, and 16.8 μJ in the tail. (The pulse shape depends on the CO<sub>2</sub> laser gas mixture. Often we use a gas mixture containing 68.6% He, 18% N<sub>2</sub>, 9% CO<sub>2</sub>, 4% CO and 0.4% H<sub>2</sub> that provides the most stable operation; shot-to-shot fluctuations in the peak intensity of the laser profile are less than 10%. Removal of the N<sub>2</sub> from the gas mixture eliminates the 4 μs tail but results in greater shot-to-shot power fluctuations). For effective desorption of PAHs from the Allende (CV3) matrix, the IR laser power density is estimated to be  $2.5 \times 10^6 \text{ W cm}^{-2}$ .

After an appropriate time delay (25  $\mu\text{s}$ ), the fourth harmonic of a pulsed Nd:YAG laser (Spectra Physics DCR11; 266 nm, 2.5 ns FWHM - fast pulse mode; Gaussian mode output coupler) is attenuated with a halfwave plate - calcite polarizer combination, apertured to a 1 mm diameter with an iris, and directed between the center electrodes of the modified Wiley-McLaren (1955) ion extraction region. The ionization laser pulse energy is chosen to maximize parent ion signal intensities produced by (1+1) REMPI with minimal fragmentation; a typical pulse energy is  $\sim 2 \mu\text{mJ}$ . We estimate the UV laser power density to be  $1.25 \times 10^6 \text{ W cm}^{-2}$ .

A pulse generator with an adjustable delay is used to trigger both lasers. The Nd:YAG laser is triggered at its optimal rate, 10 Hz. Because we want to take single desorption shots, the trigger pulses for the  $\text{CO}_2$  laser first passes through a pulse-repressor/pulse synchronizer box which allows the trigger to continue to the  $\text{CO}_2$  laser only after a pushbutton has been activated. The Nd:YAG trigger pulses serve as the master system clock so that the  $\text{CO}_2$  laser pulse arrives 25  $\mu\text{s}$  ahead of the Nd:YAG laser pulse.

The ions produced from the UV laser are extracted from the source using a spectrometer with a modified Wiley-McLaren geometry, and brought to a primary space focus just outside of the extraction region. As the ions travel down the flight tube they begin to disperse longitudinally along the flight axis until they reach the reflectron. The reflectron acts as an ion mirror reflecting the ions back down the flight tube and refocusing the spreading ions to a secondary focus on the detector which is in the same plane as the primary focus. The reflectron geometry significantly improves the mass resolution. To minimize the effect of sample platter position on the electric fields in the extraction region, the sample platter is floated to a voltage approximately equal to that of the midfield of the extraction region, as is the microscope objective. The x-y-z manipulator arm is composed of nonconducting materials, Teflon and Plexiglas. In addition, care is taken to fix the sample near the center of the platter.

To enhance ion transmission to the detector, the ion trajectories are controlled with an Einzel lens and two sets of deflection plates before injection into the reflectron. The total flight path length is 3 m. A 20-cm active area dual microchannel plate detector with an oversized anode (Galileo TOF-4000) is used in a Chevron configuration to detect the ions; the output passes through a fast preamplifier (LeCroy VV100BTB; 500 MHz bandwidth) and a timing filter (Ortec 474 timing/filter amp.), and is displayed on a 350 MHz digital oscilloscope (LeCroy 9450). For data processing and storage, the oscilloscope is connected via a general-purpose interface bus to a dedicated computer.

As an internal reference, a metered leak valve is used to introduce a constant background of toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ) as a reference gas. The presence

of toluene enables periodic optimization of the ion collection optics and aids in mass calibration.

Space limitations prevent a discussion of the uses of the  $\mu\text{L}^2\text{MS}$  instrument in the analysis of meteoritic samples, but highlights include the detection of PAHs in freshly fractured meteorite samples (Hahn et al. 1988; Zenobi et al. 1989) including those believed to have originated from Mars (McKay et al. 1996), PAHs in meteoritic acid residues, in interplanetary dust particles (Clemett et al. 1993), and associated with graphite grains that are believed to be interstellar in origin (Clemett 1996). It is hoped that the present  $\mu\text{L}^2\text{MS}$  device and its improved successors will become another powerful instrument in the arsenal that astrochemists have for exploring and understanding what is out there.

## References

- Bialkowski, S.E. 1987, *Rev. Sci. Instrum.* 58, 2338.
- Clemett, S. J. 1996, Ph.D. thesis, Stanford University, Stanford, CA.
- Clemett, S.J., Maechling, C.R., Zare, R.N., Swan, P.D., Walker, R.M. 1993, *Science* 262, 721-725.
- Cowin, J.P., Auerbacj, Becker, C., and Wharton, L. 1978, *Surface Science* 78, 69-92.
- Hahn, J. H. 1988, Ph.D. thesis, Stanford University, Stanford, CA.
- Hahn, J. H., Zenobi, R., Bada, J. L., Zare, R. N. 1988, *Science* 239, 1523-1525.
- Kovalenko, L.J., Philippoz, J.M., Bucenell, J.R., Zenobi, R., Zare, R.N. 1991, *Space Science Reviews* 56, 191-195.
- Kovalenko, L.J., Maechling, C.R., Clemett, S.J., Philippoz, J.M. Zare, R.N., Alexander, C. M. O'D. 1992, *Anal. Chem.* 64, 682-690.
- McKay, D.S., Gibson, Jr., E.K., Thomas-Keptrta, K.L., Vali, H., Romanek, C.S., Clemett, S.J., Chillier, X.D.F., Maechling, C.R., and Zare, R.N. 1996, *Science* 273 924-930.
- Maechling, C. R. 1995, Ph.D. thesis, Stanford University, Stanford, CA.
- Maechling, C.R., Clemett, S. J., Zare, R.N. 1995, *Chem. Phys. Lett.* 241, 301-310.
- Maechling, C.R., Clemett, S.J., Engelke, F., Zare, R.N. 1996, *J. Chem. Phys.* 104 8768-8776.
- Nettesheim, S., Zenobi, R. 1996, *Chem. Phys. Lett.* 255, 39-44 and references therein.
- Pappas, D.L., Hrubowchak, D.M., Ervin, M.H., Winograd, N. 1989, *Science* 243, 64-66 (1989).
- Pering, K.L., Ponnampereuma, C. 1971, *Science* 173, 237-239.
- Shibanov, A.N. 1985, *Laser Analytical Spectrochemistry* V.S. Letokhov, Ed. (Adam Hilger, Bristol).
- Thomas, K.L., et al. 1995b, *Lunar and Planetary Science XXVI*, 1409-1410.
- Thomas, K.L., Blanford, G.E., Clemett, S.J., Flynn, G. J., Keller, L.P., Klock, W., Maechling, C.R., McKay, D.S., Messenger, S., Nier, A.O., Schlutter, D.J., Sutton, S.R., Warren, J.L. and Zare, R.N. 1995a, *Geochimica et Cosmochimica Acta* 59, 2797-2815.
- Voumard, P., Zenobi, R., Zhu, Q. 1994, *Surf. Sci.* 360, 307-309.
- Voumard, P., Zenobi, R., Zhu, Q. 1995, *J. Phys. Chem.* 99 11722.
- Wiley, W.C., McLaren, I.H. 1955, *Rev. Sci. Instrum.* 26, 1150-1157.
- Winograd, N., Baxter, J.P., Kimock, F.M. 1982, *Chem. Phys. Lett.* 82, 581.
- Zenobi, R. 1990, Ph.D. thesis, Stanford University, Stanford, CA.
- Zenobi, R., Philippoz, J.M., Buseck, P.R., Zare, R.N. 1989, *Science* 246, 1026-1029.
- Zenobi, R., Zare, R.N. 1991, in *Advances in Multi-Photon Processes and Spectroscopy*,

*Vol. 7 (World Scientific Publishing), pp. 1-167.*

Zenobi, R., Philippoz, J.M., Zare, R.N., Wing M.R., Bada, J.L., Marti, K. 1992, *Geochimica et Cosmochimica Acta* 56, 2899- 2905.

## Discussion

**Scappini:** You mentioned amino acids in meteorites. Can you study them with your mass spectrometer technique? If so, what kind of amino acids have you found?

**Zare:** We are currently working on a method to reveal the presence of amino acids (AA) in meteorites. The method involves an "in situ" derivation followed by  $\mu\text{L}^2\text{MS}$  analysis. The goal is not to redo what has already been done by classical methods (solvent extraction/GC/MS) but to significantly scale down the analysis of AA in meteorites so as to detect AA in  $\leq 1$  mg meteorite chunks. For a simulated 'meteorite rock' we use  $\text{SiO}_2$  powder in which we add some AA standards at approximately the concentration we expect to find in meteorites.

**Scappini:** What about terrestrial contamination in the core of amino acids in meteorites? I know that this is a much debated issue.

**Zare:** For extraterrestrial (abiotic) AAs, we expect that the concentration will decrease from glycine and alaline to higher mass aliphatic AAs. Moreover, some of them are not terrestrial biogenic AAs. Our method might also allow us to detect (and even perhaps differentiate) primary  $\alpha$  AAs from primary  $\beta$ ,  $\gamma$  AAs, etc.

**Mauersberger:** Recently, Newsweek quoted Professor Lew Snyder saying that a large fraction of organic compounds on Earth may be of extraterrestrial origin. In view of your results, would you agree?

**Zare:** I have not seen the remarks by Professor Snyder, so I cannot comment directly on whatever Newsweek reported him saying. The idea that interplanetary dust particles may represent an important source for providing organic carbon to early Earth, however, is not new. I believe it was proposed by Professor Ed Anders and others some time ago, and I also believe it needs to be taken seriously, particularly in light of the possibility that the accretion rate that S.G. Love and D.E. Brownlee report in *Science* 262, 550 (1993) of  $(40 \pm 20) \times 10^6$  kg/year might have been significantly higher for early Earth.

**d'Hendecourt:** PAHs in interstellar environments seem to be larger ( $\geq 600$  amu) than the ones observed in meteorites. How genuinely interstellar are the meteoritic PAHs? Can they be transformed to smaller molecules within the meteorites over long lifetimes in the solar system?

**Zare:** The transformation of PAHs to larger and smaller entities either through polymerization processes or decomposition processes requires much additional study. In this area I am aware of exciting unpublished work by Dr. Christine Joblin showing that pyrene can undergo thermally induced dimerization. I respectfully suggest that we also do not know enough about the size distribution of PAHs in the interstellar medium to be confident in making comparisons with meteoritic PAH distributions. I also wish to point out that our results are biased toward those PAHs with relatively larger vapor pressures so that they can be desorbed by the infrared laser pulse we use. One of the consequences of this situation is, that we do not study the so-called kerogen component found in carbonaceous chondrites.