

ORGANIC CHEMICAL ANALYSIS ON A MICROSCOPIC SCALE USING TWO-STEP LASER DESORPTION/ LASER IONIZATION MASS SPECTROMETRY

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Abstract. The distribution of polycyclic aromatic hydrocarbons (PAHs) in the Allende meteorite has been measured using two-step laser desorption/laser multiphoton ionization mass spectrometry. This method enables in situ analysis with a spatial resolution of 1 millimeter or better of selected organic molecules. We present results showing that PAH concentrations are locally high compared to the average concentration found by analysis of pulverized samples, and are found primarily in the fine grained matrix; no PAHs were detected in the interiors of individual chondrules at our detection limit of about 0.05 parts per million. We have recently extended the spatial resolution of this instrument to 40 microns.

1. Introduction

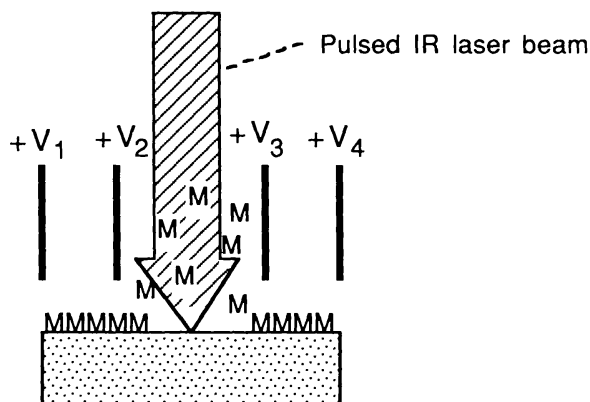
We are developing a microanalytical instrument to analyze the molecular composition of particulates and inhomogeneous samples with a spatial resolution of approximately 40 μm . A particularly interesting application is to determine the organic constituents of interplanetary dust particles (IDPs).

In the first step of our method, as shown in Figure 1, constituent molecules of the sample are desorbed intact with a pulsed infrared (IR) laser. In the second step, the desorbed molecules are ionized with a pulsed ultraviolet (UV) laser. The resulting ions are extracted into a reflectron time-of-flight mass spectrometer (RETOFMS).

Two *soft ionization* schemes (i.e., ionization schemes that cause little or no fragmentation) are shown in Figure 2. In 1 + 1 resonance enhanced multiphoton ionization (1 + 1 REMPI), the UV laser is tuned to be in resonance with an excited state of the molecule of interest; absorption of a second photon ionizes the molecule (Figure 2a). Since the ionization efficiency of 1 + 1 REMPI exceeds that of non-resonant multiphoton ionization by orders of magnitude, the laser power can be chosen low enough so that only the molecules with a resonant state will be appreciably ionized, simplifying the interpretation of mass spectra from complex mixtures. A second soft ionization process, one-photon vacuum ultraviolet (VUV) ionization, is shown in Figure 2b, where the laser wavelength is tuned so that its energy exceeds the ionization potential of the molecule of interest. In this scheme, all molecules with ionization potentials less than the photon energy will be ionized. Both these ionization methods produce primarily parent ions and are highly efficient, even when compared with electron impact, which has the added disadvantage of causing fragmentation. In

the work described here, we have chosen to focus on the 1 + 1 REMPI method, at a wavelength (266 nm) that ionizes polycyclic aromatic hydrocarbons (PAHs), a class of compounds found in extraterrestrial matter (Cronin *et al.*, 1988).

Step 1) Laser Induced Desorption



Step 2) Laser Ionization

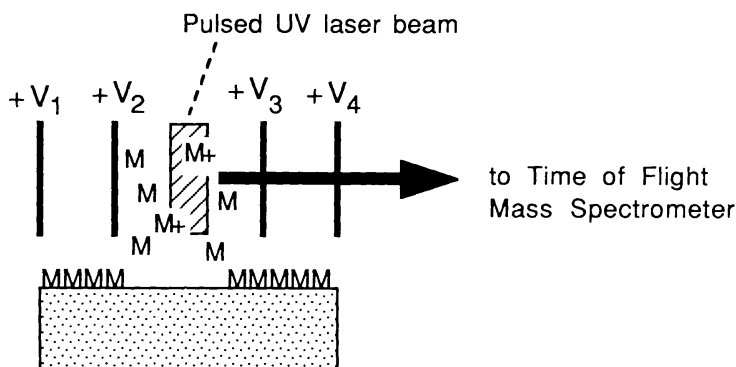


Fig. 1. Two-Step Laser Desorption/Laser Ionization Mass Spectrometry. In the first step, molecules (M) are desorbed intact with a pulsed IR laser; in the second step, the desorbed molecules are ionized with a pulsed UV laser. These ions are then extracted into a time-of-flight mass spectrometer.

The key attributes of our instrument are as follows:

1. Samples are analyzed *in situ*, minimizing the possibility of contamination and chemical alteration, and the amount of sample required.
2. In the first step, the desorption occurs without decomposition, while in the second step the desorbed molecules are ionized softly, resulting in mass spectra consisting primarily of parent ion peaks.

3. When 1 + 1 REMPI is used as the ionization method, only molecules with an excited state in resonance with the photon energy are ionized, enabling selective detection of a chosen class of compounds, PAHs in the present case.
4. The desorption and ionization steps are separated both in space and in time, avoiding complex matrix effects found in single-step methods such as secondary ionization mass spectrometry (SIMS) and laser microprobe mass analysis (LAMMA).

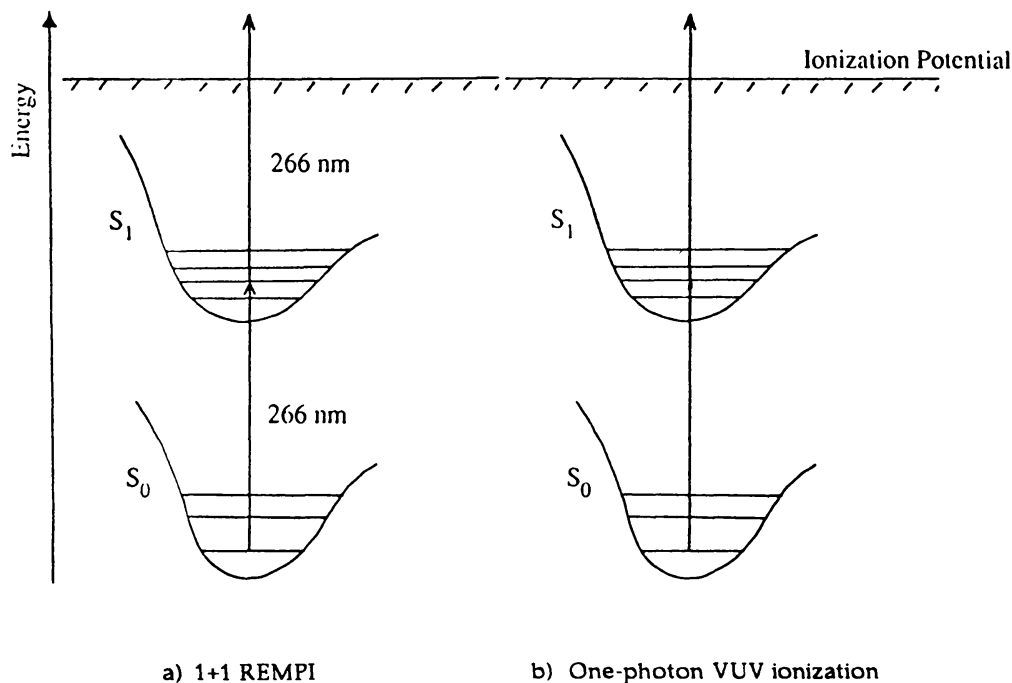


Fig. 2. Two ionization schemes: a) REMPI, b) one-photon VUV ionization. S_0 is the ground electronic state of the molecule of interest, while S_1 is an excited electronic state.

2. Present Capabilities

We recently investigated (Zenobi *et al.*, 1988) the distribution of PAHs in a sample of the Allende meteorite, which is a carbonaceous (CV3) chondrite that fell in Mexico in 1969. To obtain fresh meteorite surfaces, we either cleaved off chunks with a rock splitter or ground down the sample with a diamond drill. Our investigation revealed that the Allende meteorite matrix material contains the largest concentration of PAHs, while chondrules, which are millimeter-sized spherical objects composed of silicates and glass and believed to have been molten drops, are devoid of PAHs at the detection limit of our instrument (0.05 ppm by weight). Moreover, by analyzing several nearby chips of matrix material, we found that the matrix material is inhomogeneous on a millimeter scale, the limit of the instrument's spatial resolution at that time.

The parent ion peak intensity depends not only on the concentration of the compound in the sample but also on the absorption cross section of that compound at the UV laser

wavelength. Therefore, in order to quantify the PAH signals, we calibrated our instrument by fabricating artificial meteorites from glass powder, charcoal, and known concentrations of pure PAHs. We then measured the parent ion signal intensity as a function of concentration. (We previously showed that parent ion peak heights are linear with concentration over a range of five orders of magnitude; Hahn *et al.*, 1988). From these plots, we obtained detection limits ranging from 0.04 ppm (by weight) for phenanthrene to 2.6 ppm for 2-tertbutylantracene.

3. Future Capabilities

We have recently extended the spatial resolution of our instrument from 1 millimeter to approximately 40 microns by incorporating a microscope objective to focus the IR desorption laser beam. A schematic of the experimental apparatus is shown in Figure 3. The sample to be analyzed is placed on a non-conducting substrate whose position

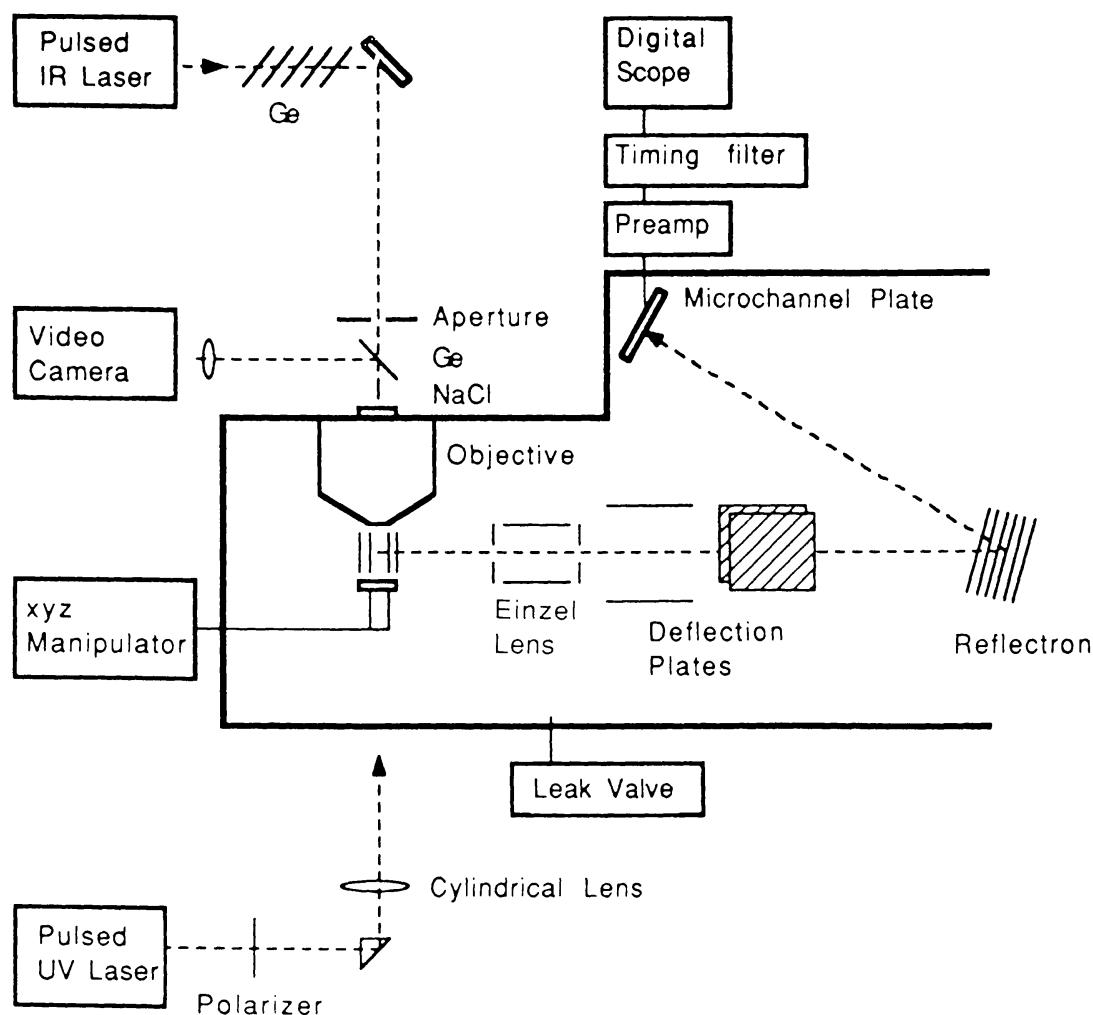


Fig. 3. Schematic of microanalytical instrument.

with respect to the objective is controlled with an x-y-z manipulator. Infrared light from a pulsed CO₂ laser is attenuated with Ge flats and then focused with the microscope objective onto the sample. Since the same microscope objective also views the sample, Cassegrainian optics are used, which are achromatic. After an appropriate time delay, light from a pulsed UV laser is attenuated with a polarizer and focused with a cylindrical lens; it passes between the inner two extraction electrodes where it selectively ionizes the desorbed molecules. The resulting ions are then extracted into a RETOFMS using a modified Wiley-McLaren geometry.

To enhance mass resolution, the ion trajectory is controlled with an *einzel*-lens and two sets of deflection plates before injection into the reflectron. A microchannel plate is used to detect the ions, and the resulting signal intensity as a function of arrival time (or mass) is displayed on a digital oscilloscope.

Preliminary measurements indicate that the sensitivity of the new instrument is comparable to that of the previous one; we can detect the same absolute amount of compound exposed to the desorption laser (for example, for coronene the detection limit is 8 fmol). However, since the desorption laser spot size is so much smaller (40 microns rather than 1 millimeter), the sample concentration must be greater. The detection limit of our new instrument in ppm is therefore poorer than the previous instrument by a factor of 400 (the ratio of the spot areas). One strategy to overcome this limitation is to analyze more concentrated samples, such as acid residues. Also, since meteorites have been shown to be inhomogeneous, perhaps local concentrations will be high enough to detect. Finally, some IDPs have been shown to be highly carbonaceous and so may have high concentrations of detectable organics, though the form of the carbon is not yet known.

Acknowledgement

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