



Supporting Online Material for
**Comment on “Organics Captured
from Comet 81P/Wild 2 by the Stardust Spacecraft”**

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Supporting Online Material

Materials and Methods

Complete reports on this work, including other impact heating experiments using both borosilicate glass bead and polycyclic aromatic hydrocarbon (PAH) containing impactors into Stardust-type aerogel, are in preparation for publication.

Microprobe laser-desorption laser-ionization mass spectrometry ($\mu\text{L}^2\text{MS}$) is a highly sensitive technique capable of spatially resolving distributions 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 $\mu\text{L}^2\text{MS}$ 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 (1-4).

A detailed description of our technique has been presented elsewhere (5, 6) and is summarized here for convenience. Constituent neutral molecules of the sample are first desorbed with a pulsed infrared laser beam focused down to a diffraction limited spot, presently adjustable at 10 or 40 μm using either an Er:YAG or CO_2 laser, respectively (Fig. 1S). The laser power density is maintained 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 (Nd:YAG fourth harmonic, 266 nm; 4 mJ pulse energy; 10^6 W/cm^2 power density). 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.

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 (7). 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

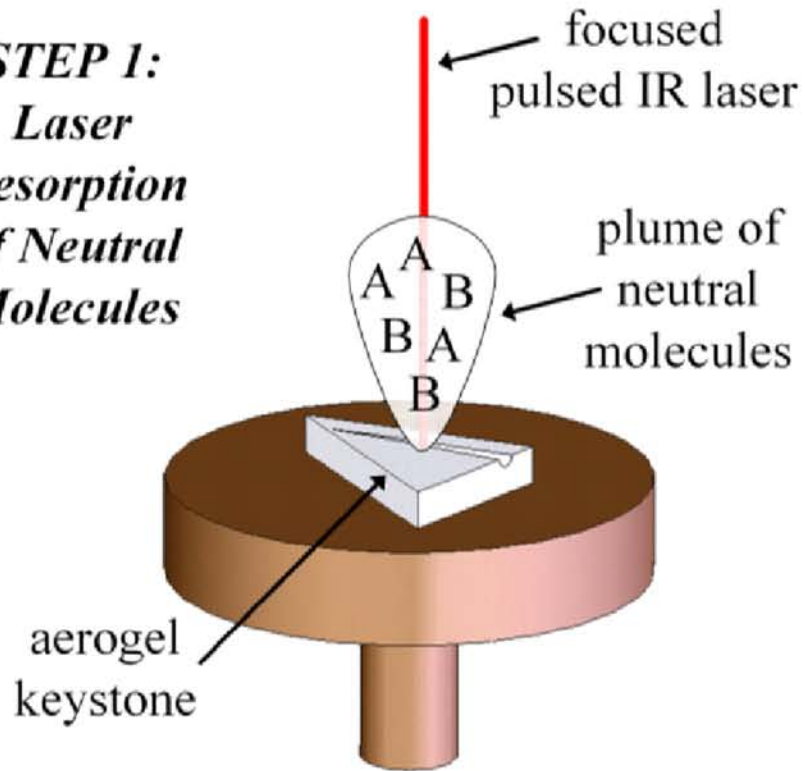
fragmentation (8, 9).

The $\mu\text{L}^2\text{MS}$ technique 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 (Table S1).

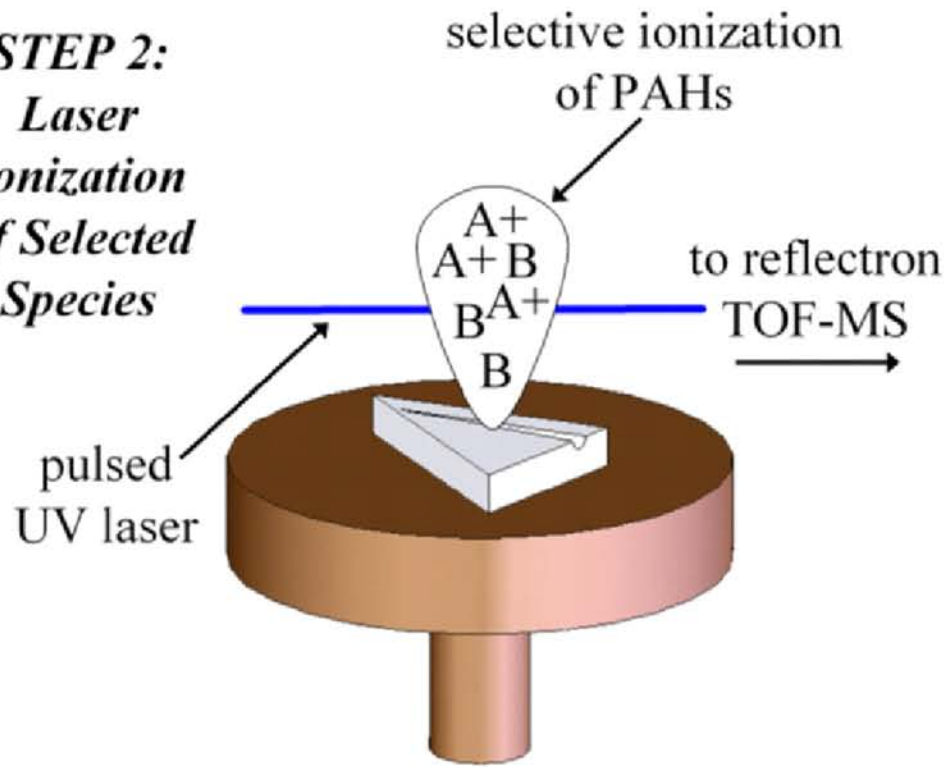
References and Notes

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STEP 1:
*Laser
Desorption
of Neutral
Molecules*



STEP 2:
*Laser
Ionization
of Selected
Species*



- i. High spatial resolution and mapping capabilities down to 10 μm resolution
- ii. Low power desorption, resulting in simple spectra consisting of primarily parent ions
- iii. Selective ionization of PAHs, simplifying the spectra of complex mixtures
- iv. High sensitivity, with PAH detection limits down to the subattomole level
- v. *In situ* analysis, requiring minimal handling and reducing contamination possibilities