

## Spatially Resolved Organic Analysis of the Allende Meteorite

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The distribution of polycyclic aromatic hydrocarbons (PAHs) in the Allende meteorite has been probed with two-step laser desorption/laser multiphoton ionization mass spectrometry. This method allows direct *in situ* analysis with a spatial resolution of 1 square millimeter or better of selected organic molecules. Spectra from freshly fractured interior surfaces of the meteorite show that PAH concentrations are locally high compared to the average concentrations found by wet chemical analysis of pulverized samples. The data suggest that the PAHs are primarily associated with the fine-grained matrix, where the organic polymer occurs. In addition, highly substituted PAH skeletons were observed. Interiors of individual chondrules were devoid of PAHs at our detection limit (about 0.05 parts per million).

**M**ETEORITES ARE HIGHLY HETEROGENEOUS mineralogically and chemically, even on a submillimeter scale. Techniques for elemental analysis are well established for the investigation of microgram amounts of solids and the investigation of surfaces with micrometer-scale resolution (1–6). In contrast, analysis of organic molecules has been impossible even in a few milligrams of carbonaceous chondrites, the meteorite group with the highest carbon content. Among the reasons are (i) the low concentrations of organic compounds in such materials (parts-per-million range or below) and (ii) the rich variety of organics in these meteorites. Generally, multiple extraction and purification steps are required before analysis. These steps are time-consuming and introduce the risk of contamination.

We have analyzed the spatial distribution of various organic molecules in millimeter-sized regions of the Allende meteorite, a CV3 carbonaceous chondrite, by using laser desorption/laser multiphoton ionization mass spectrometry (L<sup>2</sup>MS). In contrast, all earlier analyses have been done on homogenized pulverized samples (7–11). We focused our study on polycyclic aromatic hydrocarbons (PAHs), which have also been proposed to play an important role in interstellar chemistry (12). Our goal was to determine which PAHs are present in Allende

and whether they are uniformly distributed and, if not, to identify the specific regions and phases containing the PAHs. Because of their wide range of volatilities, thermal stabilities, and reactivities, PAHs can serve as chemical markers; determination of their spatial distribution can potentially provide a wealth of detailed information about meteorites.

Carbonaceous chondrites contain a number of easily identifiable components, many of which formed roughly 4.5 billion years ago in the solar nebula (13). A major constituent is a fine-grained mixture of minerals and amorphous material that is collectively known as matrix; it is typically composed of anhydrous ferromagnesium silicates and lesser amounts of hydrous silicates, oxides,

sulfides, and carbonaceous phases (14). Visually, the most striking features in chondritic meteorites are millimeter-sized spherical objects called chondrules that are mainly composed of silicate minerals and glass. It is now widely accepted that chondrules were once either fully or partially molten droplets (15). Many chondrules are surrounded by dark halos or rims that seem to have developed in dusty regions of the solar nebula before the accretion of the meteorite parent body (15).

Probably the most thoroughly studied meteorite is the Allende (CV3) carbonaceous chondrite. However, analyses of organic matter in the Allende meteorite are sparse (7–11), in part because it contains only sub-parts-per-million amounts of extractable organic carbon (9). Most of Allende's organic matter is contained in the so-called organic polymer, a kerogen-like material whose properties are not well understood (10). In contrast, the organic constituents of CM and CI carbonaceous chondrites are generally quite well known from gas chromatography–mass spectroscopy studies of extracted pulverized samples (16), but significant discrepancies concerning the concentrations of specific compounds have been reported (17). Although contamination and analytical errors cannot be excluded, a likely explanation for these discrepancies is the heterogeneity of meteorite samples. Organic analyses with greater spatial resolution than is possible with wet chemical analysis are necessary for characterizing the distribution of organic matter.

In the L<sup>2</sup>MS technique (11, 18), the pulsed output of a CO<sub>2</sub> laser (10.6 μm; 10 mJ per pulse; 10-μs pulse width) is focused onto the surface of a freshly fractured or ground sample. The infrared (IR) radiation is absorbed by the sample, and intact neutral

**Table 1.** Relative sensitivity and detection limits for various PAHs. Boiling points are indicated as a measure of the volatility of the compounds (27). The detection limit was set at a 5-mV signal level with a generously estimated chemical background of ~2 mV; this value corresponds to a signal-to-noise ratio of 2.5.

Compound	Mass (amu)	Boiling point (°C)	Sensitivity (mV/ppm)	Detection limit (ppm)
Naphthalene	128	218	86	0.06
2-Methylnaphthalene	142	245	80	0.06
2,3-Dimethylnaphthalene	156	268	44	0.11
Phenanthrene	178	340	130	0.04
Anthracene	178	340	6.8	0.7
2-Methylanthracene	192	NA*	3.2	1.6
9-Methylanthracene	192	196	3.4	1.5
2-Tertbutylanthracene	234	NA*	1.9	2.6
Fluorene	166	249	65	0.08
Fluoranthene	202	375	4.3	1.2
Pyrene	202	393	99	0.05
Perylene	252	350 to 400†	4.4	1.1
Coronene	300	525	3.2	1.6

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\*Not available. †Sublimation point.

molecules are released from its surface by rapid laser-induced thermal desorption. Even nonvolatile and thermally labile compounds with high molecular weight (over 1000 atomic mass units [amu]) are readily desorbed (18). After approximately 40  $\mu$ s, the fourth harmonic of a Nd:YAG laser (266 nm; 0.2 mJ per pulse; 10-ns pulse width) is used to induce 1 + 1 resonance-enhanced multiphoton ionization (REMPI) of the desorbed molecules 2 mm above the surface. Compared to substances that do not resonantly absorb this wavelength, the ionization efficiency for aromatic compounds is larger by orders of magnitude. The ions are mass selected in a reflectron time-of-flight mass spectrometer and detected by a microchannel plate. Improvements in the ion optics of the instrument provide an order-of-magnitude gain in detection sensitivity over that previously reported (11). A complete mass spectrum is obtained for each sequence of laser pulses. Unit mass resolution above 600 amu can be achieved at the most sensitive instrument settings. When desorption of intact neutrals is combined with the soft ionization characteristics of REMPI, parent molecular ion signals dominate the mass spectra. This allows interpretation of spectra from complex mixtures, and therefore complicated sample preparation procedures can be circumvented.

The IR laser pulse desorbs material from about 1 mm<sup>2</sup> of the sample surface. This spatial resolution is only limited by the focusing optics and divergence of the IR laser beam. Data can be obtained from sample regions much smaller than 1 mm<sup>2</sup> by partial overlap of consecutive laser shots.

Great care was taken to avoid sample contamination (19). We obtained fresh sample surfaces by cleaving chunks of meteorite material (20) with a rock splitter. A piece of Allende (~15 cm in diameter) that had never been exposed to solvents or cutting fluid was used for some experiments. Material both directly below the fusion crust and several centimeters below the surface was examined. The meteorite was fractured, and the splits were collected in aluminum foil. Chondrules were liberated from adhering material with stainless steel instruments. Without further treatment, samples were then mounted with a thermoplastic polymer (21) onto substrates that could be directly introduced into the source region of the laser mass spectrometer. After investigation of their exteriors, chondrules were machined by slowly grinding them with a diamond tool while they were spun on their substrate by a hand drill (22). Other chondrule interiors were exposed by simple mechanical splitting.

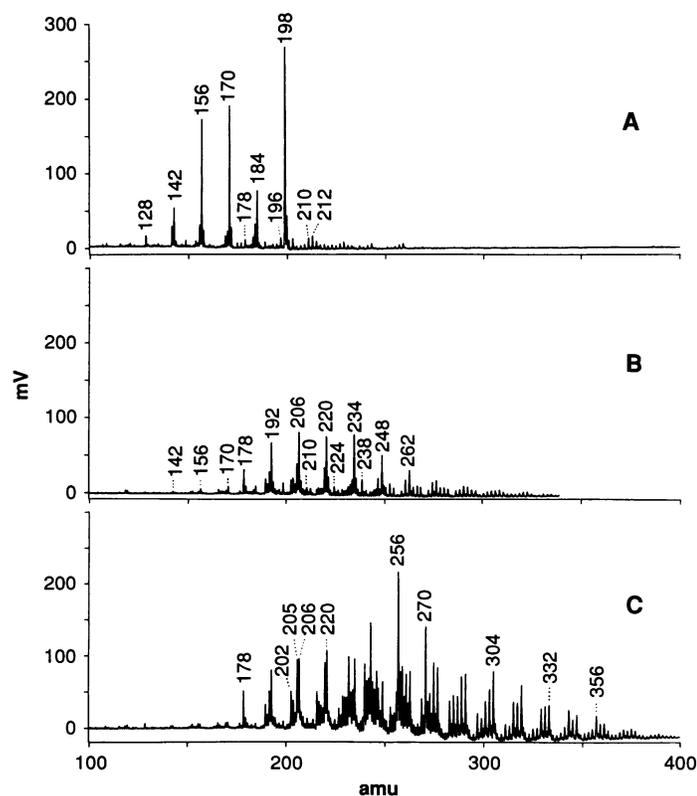
Because different PAH structures have

varied cross sections for REMPI, quantification of the observed mass signals is not trivial. For this purpose, an "artificial meteorite matrix" (50 mg of glass powder per 50 mg of pulverized activated charcoal) was spiked with  $5 \times 10^{-10}$  moles each of various pure PAHs (23) and analyzed with L<sup>2</sup>MS (Table 1). Although there is considerable variation in volatility among the PAHs, the main effect leading to different signal intensities is their ultraviolet absorption profile and therefore their REMPI cross section. Different PAH skeletons showed large variations in intensity, whereas PAHs that differed only by the substitution of a given ring structure showed only small variations. For example, the sensitivities of phenanthrene and pyrene were enhanced by an order of magnitude compared to their isomers anthracene and fluoranthene. The bulk sensitivity can be inferred from these measurements, and detection limits were calculated (Table 1). These experiments also confirmed that fragmentation of the PAHs listed in Table 1 did not occur under our experimental conditions.

The mass spectra of 1-mm<sup>2</sup> spots on two nearby chips from Allende (Fig. 1, A and B) indicate that the meteorite contains PAHs with extensively alkylated rings. We chose chips that macroscopically were free of observable mineral fractures or other types of

inclusions and therefore, by inference, were rich in matrix. Assignments of the main mass peaks are easily made: they correspond to naphthalene (128 amu) and alkyl-substituted naphthalenes (142, 156, 170, 184, 198, . . . amu), as well as phenanthrene/anthracene (178 amu) and alkyl-substituted phenanthrenes/anthracenes (192, 206, 220, 234, 248, . . . amu). Masses 182, 196, 210, 224, and 238 amu are most likely members of another homologous series, possibly starting with the biphenyl or acenaphthene skeleton (154 amu); other spectra show a series (106, 120, 134, . . . amu) that probably represents alkyl-substituted benzenes. Extraction and pyrolysis studies (7, 9, 10) have shown that alkylbenzenes and alkyl-naphthalenes are present in Allende, but higher PAHs have not been reported. The high degree of substitution of the PAHs also contrasts with earlier data we obtained with L<sup>2</sup>MS from pulverized samples (11); the PAHs in these samples may have been diluted through homogenization.

Pyrene (202 amu), fluorene (166 amu), and their alkyl homologs are also ionized with high efficiency (see Table 1). In some spectra, mass 202 amu was present as a minor peak (for example, Fig. 2A) whereas alkylated pyrenes, fluorene, and alkylated fluorenes have not been detected in the samples we investigated. At masses greater



**Fig. 1.** Mass spectra of Allende samples (L<sup>2</sup>MS, 50-shot averages). Spectra (A) and (B) are from two nearby interior chips and (C) is from a sample just below the fusion crust. Mass labels above 260 amu in (C) are given to guide the eye.

than about 260 amu, there are peaks at almost every even mass number (see, for example, Fig. 1B). The presence of  $-C=C-$  double bonds in longer alkyl substituents reduces the molecular weight by an even number of mass units. In the higher mass range, a large variety of alkyl- and alkenyl-substituted PAHs apparently occur together. Perhaps these species are the precursors of larger aromatic structures or even of polymeric sheets.

Except for peaks at mass  $[M - 1]^+$  accompanying some of the most intense signals, there is an almost complete absence of prominent odd-mass peaks in the samples from the interior of Allende (Fig. 1, A and B). This lack indicates that nitrogen-containing aromatic compounds only occur at concentrations below their detection limit. In contrast a sample from directly below the fusion crust (Fig. 1C) shows a distinctively richer spectrum that also includes a number of moderately strong odd-mass peaks. We tentatively attribute these peaks to compounds introduced by terrestrial contamination of the near-surface layer. Such contamination has previously been found in a study of amino acids in Allende (8).

Other striking features in our data are the marked differences in mass distribution and intensity from spectrum to spectrum (compare Fig. 1, A and B) and the local enrichment of the PAHs with respect to their average concentrations as determined from wet chemical analysis of pulverized samples (24). Although it is problematic to infer bulk concentrations directly from laser desorption, comparison with the spiking experiments shows that several parts per million of naphthalene and phenanthrene occur

in Allende within the sampling depth of the desorption laser (a few micrometers). The PAHs appear to be concentrated in regions associated with the matrix and the organic polymer, its main carbonaceous phase. We can rule out production of PAHs by degradation of the organic polymer during analysis because the observed mass pattern for a selected sample is independent of the desorption laser fluence, below the onset of plasma formation. The porosity of the structures where PAH are preferentially detected could have allowed enrichment of organic molecules by transport processes. The inferred distribution of the PAHs is consistent with that of elemental carbon in Allende, as obtained with deuteron beam mapping (25). Whether a similar distribution is also present for other classes of organic compounds is an open question.

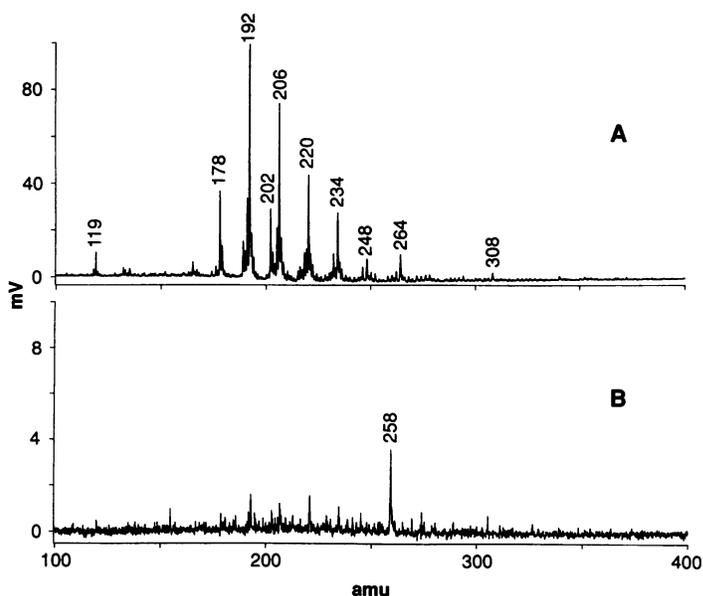
Figure 2 shows a comparison between the exterior and the interior of a 2-mm-diameter chondrule from Allende. The exterior, untreated and partially covered with adhering rim material, had an intense spectrum of PAHs (Fig. 2A), consisting mainly of alkyl-homologs of the compounds at 178 amu (phenanthrene/anthracene) together with other minor signals. In the spectrum from the interior of the same chondrule (plotted on an expanded scale in Fig. 2B), the signals were at or below the level of the chemical background except for the peak at 258 amu, a common but unassigned contamination signal. Similar spectra were obtained for a number of chondrules (26), and we conclude that PAHs are absent in chondrules at the detection limits given in Table 1.

Our study demonstrates that PAH are heterogeneously distributed in the Allende

meteorite and display a rich variety of side chains. Chondrules have been shown to be free of PAHs, whereas other regions are enriched compared to the average PAH concentration. Similar studies with yet higher spatial resolution, a goal that is now within reach, will open the way for determining possible correlations of organics with various mineralogical phases and inclusions, information that will provide fundamental data regarding the formation and history of meteorites.

## REFERENCES AND NOTES

1. J. I. Goldstein *et al.*, *Scanning Electron Microscopy and X-ray Microanalysis* (Plenum, New York, 1981); K. F. J. Heinrich, *Electron Beam X-ray Microanalysis* (Van Nostrand, New York, 1981).
2. O. L. Krivanek, in *High-Resolution Transmission Electron Microscopy*, P. R. Buseck, J. M. Cowley, L. Eyring, Eds. (Oxford Univ. Press, London, 1988), pp. 519–567.
3. S. J. B. Reed, *Mineral. Mag.* **53**, 3 (1989); A. Benninghoven, A. M. Huber, H. W. Werner, Eds., *International Conference on Secondary Ion Mass Spectrometry VI* (Wiley, New York, 1988).
4. S. Amiel, Ed., *Nondestructive Activation Analysis* (Elsevier, Amsterdam, 1981); V. Valkovic, *Nuclear Microanalysis* (Garland, New York, 1977).
5. J. Cezeux, *J. Microsc.* **145**, 257 (1987); M. Thompson, M. D. Bauer, A. Christie, J. F. Tysan, *Auger Electron Spectroscopy* (Wiley, New York, 1985).
6. N. Nakamura *et al.*, *Anal. Chem.* **61**, 755 (1989).
7. R. L. Levy *et al.*, *Nature* **227**, 148 (1970).
8. K. Harada and P. E. Hare, in *Biogeochemistry of Amino Acids*, P. E. Hare, T. C. Hoering, K. King, Jr., Eds. (Wiley, New York, 1980), pp. 169–181.
9. J. Han *et al.*, *Nature* **222**, 364 (1969).
10. J. Oró and E. Gelpi, *Meteoritics* **4**, 287 (abstr.) (1969); P. G. Simmonds, A. J. Bauman, E. M. Bollin, E. Gelpi, J. Oró, *Proc. Natl. Acad. Sci. U.S.A.* **64**, 1027 (1969).
11. J. H. Hahn, R. Zenobi, J. L. Bada, R. N. Zare, *Science* **239**, 1523 (1988).
12. A. Léger, L. d'Hendecourt, N. Boccard, Eds., *Poly-cyclic Aromatic Hydrocarbons and Astrophysics* (vol. 191 of NATO-ASI Ser., Reidel, Dordrecht, 1986).
13. G. R. Tilton, in *Meteorites and the Early Solar System*, J. F. Kerridge and M. S. Matthews, Eds. (Univ. of Arizona, Tucson, 1988), pp. 249–275, and references therein.
14. E. R. D. Scott, D. J. Barber, C. M. Alexander, R. Hutchison, J. A. Peck, in *ibid.*, pp. 718–745; K. Tomeoka and P. R. Buseck, *Geochim. Cosmochim. Acta* **52**, 1627 (1988).
15. E. A. King, Ed., *Chondrules and Their Origins* (Lunar and Planetary Institute, Houston, 1983).
16. For recent reviews, see F. Mullie and J. Reisse, *Top. Curr. Chem.* **139**, 85 (1987); J. R. Cronin, S. Pizzarello, D. P. Cruikshank, in *Meteorites and the Early Solar System*, J. F. Kerridge and M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, 1988), pp. 819–857; also E. Anders and R. Hayatsu, *Top. Curr. Chem.* **99**, 1 (1981).
17. For PAHs in the Murchison meteorite, see for example K. L. Pering and C. Ponnampurama, *Science* **173**, 237 (1971); B. P. Basile, B. S. Middle-ditch, J. Oró, *Org. Geochem.* **5**, 211 (1984); M. H. Studier, R. Hayatsu, E. Anders, *Geochim. Cosmochim. Acta* **36**, 189 (1972).
18. J. H. Hahn, R. Zenobi, R. N. Zare, *J. Am. Chem. Soc.* **109**, 2842 (1987); R. N. Zare, J. H. Hahn, R. Zenobi, *Bull. Chem. Soc. Jpn.* **61**, 87 (1988).
19. The main vacuum chamber was evacuated with turbomolecular pumps, which are essentially oil-free. The chamber was baked every night before measurements were done. All roughing vacuum lines of the instrument were fitted with molecular sieve traps. Background signals were routinely monitored by exposure of clean materials (glass, charcoal, ceramics, and a few chips of Allende that were



**Fig. 2.** Mass spectra of (A) the exterior and (B) interior (intensity scale expanded by a factor of 10) of a chondrule from Allende ( $L^2MS$ , 50-shot averages).

baked at 300°C overnight) for varied amounts of time to the atmosphere of different working areas. Exposures of the test materials for short times (30 min or less) to the lab atmosphere and to a nitrogen-flushed glove box for sample preparation only gave rise to chemical background about a factor of 2 larger than the electronic noise. However, laboratory air was found to cover surfaces slowly (within many hours) with contaminants, some of which are believed to be PAHs originating from oil vapors or car exhaust entering the lab through the ventilation system.

20. Samples were from the meteorite collection at Arizona State University.
21. Crystalbond 509, Armeco Products, Inc., Ossining, NY.
22. Small glass balls dipped into a solution of coronene served as blanks for the chondrule machining. No coronene signal was detected after the glass balls were ground by the same method as described above

and their interiors were analyzed; other contamination peaks were also negligible. These data indicate that material was not transferred from the outside by the grinding process. The thermoplastic polymer used for specimen mounting gave no background interferences.

23. Obtained from ChemService, West Chester, PA.
24. Benzene-methanol extractions of interior samples of Allende only gave about 0.002 ppm of aromatic hydrocarbons (9). This low concentration was speculated to result from organic material being trapped in the meteorite matrix (7, 10). In pyrolysis studies, up to 70 ppm of total organics were released (7), and aromatic compounds accounted for more than 75% of the total (10). One of the few PAHs reported is naphthalene, which had concentrations between 0.055 ppm (10) and 2 ppm (7).
25. C. C. A. H. Van der Stap, D. Heymann, R. D. Vis, H. Verheul, *J. Geophys. Res.* **91**, D373 (1986).
26. Some chondrules were mechanically split rather than

ground, and in these too the signal was only at or below the chemical background level. These data support the contention that organics were not removed during the grinding process.

27. R. C. Weast, Ed., *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, ed. 68, 1987).
28. We thank K. Marti who provided us with some cleaned chondrules, C. B. Moore for samples, and B. C. Hintzman for assistance in computer interfacing this experiment. J.M.P. is grateful to the Swiss National Science Foundation for a postdoctoral fellowship. This work was supported by the National Science Foundation (NSF) Materials Research Laboratory program (grant NSF DMR 87-21735) through the Center for Materials Research at Stanford University (to R.N.Z.) and by National Aeronautics and Space Administration grant NAG9-59 (to P.R.B.).

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## Covariance Mapping: A Correlation Method Applied to Multiphoton Multiple Ionization

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In some cases there are hidden correlations in a highly fluctuating signal, but these are lost in a conventional averaging procedure. Covariance mapping allows these correlations to be revealed unambiguously. As an example of the applicability of this technique, the dynamics of fragmentation of molecules ionized by an intense picosecond laser are analyzed.

IN AN INTERESTING APPLICATION OF the covariance approach, Hanbury Brown and Twiss used intensity interferometry to determine the angular diameter of stars (1). In their experiment the covariance between the signals from two independent telescopes was obtained as a function of telescope separation. We describe here an experiment in which the covariance concept is used to analyze the fragmentation pattern of molecules after multiple ionization by an intense subpicosecond laser (2, 3). In this experiment, the covariance is displayed in the form of a two- or three-dimensional map of competing fragmentation channels with axes given by ion time of flight (TOF).

When a molecule is rapidly ionized by the laser, a Coulomb explosion produces ion fragments with considerable kinetic energy and the fragment momentum vectors carry structural information about the parent molecule. To this extent such experiments are similar to those in which molecular ions are stripped of electrons by beam-foil techniques and in which TOF mass spectrometry is combined with an area detector to allow the stereochemical structure of the molecular ion to be inferred (4).

At each laser pulse only a few tens of ions are recorded, and this results in large pulse-

to-pulse variations in the TOF spectra. These large variations can be overcome by averaging over many laser pulses. Even so, the analysis of the resulting TOF spectrum is often quite difficult because the fragment ion peaks of differing masses, charge states, and kinetic energies can overlap substantially. More importantly, the one-dimensional TOF spectrum suffers from two specific shortcomings. The first is that it is impossible to differentiate, for example, the process  $[\text{CO}^{2+}] \rightarrow \text{C}^+ + \text{O}^+$  from the processes

$[\text{CO}^+] \rightarrow \text{C}^+ + \text{O}$  and  $[\text{CO}^+] \rightarrow \text{C} + \text{O}^+$ , where undetected neutral particles are produced (brackets denote a transient molecular ion). Moreover, it is difficult to separate the process  $[\text{CO}^{2+}] \rightarrow \text{C}^+ + \text{O}^+$  from the process  $[\text{CO}^{3+}] \rightarrow \text{C}^{2+} + \text{O}^+$  if the  $\text{O}^+$  ions have identical kinetic energies. [The problems associated with homonuclear molecules such as  $\text{N}_2$  are even more severe (3).]

Covariance mapping allows the different fragmentation channels involving charged fragments to be identified conclusively. Consider a particular fragmentation channel of CO, namely,  $\text{CO} \rightarrow [\text{CO}^{3+}] \rightarrow \text{C}^{2+} + \text{O}^+$ , depicted in Fig. 1. Let us suppose that for a given laser pulse an  $\text{O}^+$  fragment is detected. If it results from the above process, there is an enhanced probability of detecting a  $\text{C}^{2+}$  fragment. This probability is less than 100%, reflecting the detector efficiency. (The TOF system is designed to provide almost 100% collection efficiency.) When one calculates, over many laser pulses, the covariance between the two TOF points at which the fragments were detected, one

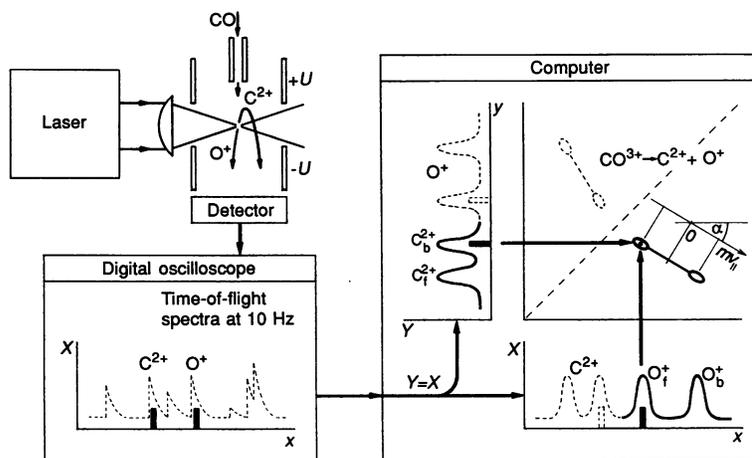


Fig. 1. The covariance mapping principle illustrated for a particular ionization and fragmentation channel of carbon monoxide, CO. One can identify the molecular parent ion by correlating the atomic daughter ions. The subscripts f and b denote forward and backward fragment ejection as seen by the detector.

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