

Ultrafast laser analysis of nitro-PAHs using laser desorption/femtosecond ionization mass spectrometry

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Abstract

Analytical interest in nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) is related to their high mutagenicity and potential presence in a variety of environmental media such as diesel exhaust and urban air particulate matter. Furthermore, fundamental interest in these molecular systems stems from the photophysics of the labile NO₂ functional group, which has been investigated using mass spectrometry. The nitro-PAHs, 1-nitronaphthalene, 9-nitroanthracene, and 1-nitropyrene, have been studied using both femtosecond ($\lambda = 395$ and 790 nm) and nanosecond ($\lambda = 266$ nm) lasers coupled to a reflectron time of flight mass spectrometer. Analysis of mass spectra taken over a range of intensities (10^{14} – 10^{15} W/cm²) has demonstrated that structurally specific ions can be observed for each molecule, with little or no fragmentation at lower intensities. It has also been found that an intact parent ion can be detected using femtosecond ionization at 395 nm in each case. This work demonstrates the potential use of laser desorption/femtosecond laser mass spectrometry (LD/FLMS) as an analytical technique for the detection of nitro-PAHs and other environmental pollutants and as a means of studying the photodynamics of labile molecular systems.

1. INTRODUCTION

The rapidly developing field of ultrafast laser–molecule interactions has highlighted new areas of physics and chemistry and is becoming an important tool for atomic and molecular analysis. From a mass spectrometry perspective, the generation of molecular or structurally characteristic ions is a key feature in the technique's analytical ability. In addition to studies of elemental, inorganic, and biomolecular materials, the potential of using femtosecond laser mass spectrometry (FLMS) for the detection of environmentally hazardous materials is considerable.

Polycyclic aromatic hydrocarbons, a group of molecules consisting of a number of fused benzene rings, are major environmental contaminants. They are formed during the incomplete combustion of fuel and it is now well established that they have carcinogenic and teratogenic effects on humans (I.A.R.C., 1985). Reactions between PAHs and other environmental chemicals can produce molecules with a significantly greater toxicity than the original PAH.

Nitro-PAHs, one class of highly polar PAH derivatives, are formed when PAHs react with oxides of nitrogen (Pitts *et al.*, 1978). It has been found that some nitro-PAHs have high mutagenicity and, along with PAHs and oxy-PAHs, can be present in a variety of atmospheric pollutants such as diesel exhaust (Hankin *et al.*, 1999) and urban air particulates (Noyes Dotter *et al.*, 1996). Due to the quantity of nitro-PAHs present in the urban atmosphere, exposure to these potentially dangerous particles is becoming increasingly unavoidable. Recent reports (UK DoH, 1995; US EPA, 1999; W.H.O., 1999) have shown that a deterioration in cardiovascular health, which has been observed through increasing cases of asthma and heart disease, is related to the inhalation of particulates in atmospheric pollution. In addition to this, it has been observed that the human diet may be a source of exposure to PAHs and nitro-PAHs in foods such as herbs (Spitzer, 2000) and seafood (Notar, 2000).

One method of detecting PAHs in environmental samples which allows the sensitivity and selectivity required is two-step laser desorption/ionization mass spectrometry. This technique offers several advantages over conventional chromatographic methods of analysis. Firstly, since the desorption and ionization steps are separated, it is possible to gain an optimum performance for the system by adjusting the

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laser conditions for each step individually. The use of intense (10^{14} – 10^{15} W/cm²), ultrafast ($\tau = 50$ fs) laser pulses is also an important feature in the technique's analytical ability as the pulse duration of the ionizing laser may be shorter than the vibrational, rotational, and dissociative time scales of molecules.

Until recently, the majority of work studying nitrated-PAHs using laser mass spectrometry has been carried out using nanosecond laser pulses. Noyes Dotter *et al.* (1996) have looked at four nitro-PAH standards and concluded that competing photofragmentation pathways were able to produce the NO⁺ ion. A prominent parent ion, however, was not always observed. Unfortunately, laser pulses of nanosecond duration are not always able to analyze nitro-PAHs due to the rapid dissociation of the molecules before they can be detected. The intense, short pulses of a femtosecond laser, however, are able to ionize the nitro-PAHs, thus reducing the probability of the molecules dissociating before being detected in a mass spectrometer (Ledingham *et al.*, 1997). The process as a whole is assisted by the fact that, theoretically, the time-of-flight instrument has no mass limit, which makes it an ideal partner with soft ionization techniques.

The aim of the present work is to apply laser desorption/femtosecond laser mass spectrometry (LD/FLMS) to the detection of nitro-PAHs with a view to analyzing real-world environmental samples.

2. EXPERIMENTAL SECTION

The nitro-PAHs studied were 1-nitronaphthalene ($m = 173$ a.m.u.), 9-nitroanthracene ($m = 223$ a.m.u.), and 1-nitropyrene ($m = 247$ a.m.u.). Their molecular structures are shown in Figure 1.

The reflectron time-of-flight (ToF) mass spectrometer used in this work has been described previously (Borthwick, 1993). Briefly, the source chamber and flight tube are pumped using rotary-backed turbomolecular pumps to a base pressure of 10^{-9} Torr. The sample for analysis is deposited on a stainless steel stub and transferred to the source chamber by means of a load-lock. Laser desorption of the solid samples was achieved using the fourth harmonic output (266 nm) from a nanosecond Nd:YAG laser (Minilite I, Continuum) focused onto the sample stub using a 27-cm focal length lens. The ASTRA femtosecond laser system (Langley *et al.*, 1998) at the Rutherford Appleton Laboratory was used for postionization of the desorbed molecules

and nanosecond ionization was achieved using a Nd:YAG laser (Minilite I, Continuum). The delay between desorption and ionization was variable from 0 to 37 μ s using a delay generator (SRS, DG535). The ions, extracted from the source using purpose-designed ion optics, were guided into the reflectron in order to correct the energy dispersion of the ions leaving the source. After this, they were detected by a multichannel plate (Galileo). The signal output from the detector was coupled to a digital oscilloscope (LeCroy, 9344C) for single-shot and averaged-data collection. A PC installed with GRAMS/32 software (Galactic) was connected to the oscilloscope through a GPIB interface and was used for data acquisition and analysis.

3. RESULTS AND DISCUSSION

Femtosecond ionization mass spectra were obtained for 1-nitronaphthalene, 9-nitroanthracene, and 1-nitropyrene over a range of ionization laser intensities (1.74 – 8.4×10^{14} W/cm² at 395 nm and 2.2 – 4.5×10^{15} W/cm² at 790 nm). All spectra contained an abundance of fragmentation at high intensities and each of the molecules displayed a similar contrast in the mass spectra between 395 and 790 nm.

To illustrate the general behavior observed, Figure 2 shows the mass spectra of 1-nitropyrene at both 395 and 790 nm. Each spectrum displays structurally characteristic ions although there are considerably more high mass ions in the 395 nm case. This is particularly evident through the observation of a large parent peak ($m/z = 247$) in the 395 nm spectrum; the parent was not observed at 790 nm.

In the 395 nm mass spectrum, the next discernible peaks of lower mass correspond to the [M-O]⁺ fragment ion at $m/z = 231$ followed by the [M-NO]⁺ fragment at $m/z = 217$. It can be seen that, while the 790 nm spectrum displays far more low mass fragmentation, including a large NO⁺ ion at $m/z = 30$, it does not contain the three high mass ions, including the large parent peak, that were observed at 395 nm. The other significant high-mass peaks in both spectra are the [M-NO₂]⁺ and [M-NO-CO]⁺ fragments.

The greater abundance of high-mass ions at 395 nm could be due to the fact that at the lower intensity used at this shorter wavelength, multiphoton processes cannot be ruled out. It is certainly apparent that high-mass ions can be detected at considerably lower laser intensities using 395 nm compared to 790 nm. Thus, for nitro compounds, changing the ionizing radiation to shorter wavelengths leads to an increased efficiency for production of high-mass fragments.

The features observed in Figure 2 are very similar to those found in the ToF mass spectra of 9-nitroanthracene and 1-nitronaphthalene. Structurally significant ions were observed in both cases and an intact parent ion was found at 395 nm for each molecule. As with 1-nitropyrene, the mass spectra for these molecules also displayed peaks at high mass corresponding to the [M-NO]⁺ fragment at $m/z = 143$ for 1-nitronaphthalene and $m/z = 193$ for 9-nitroanthracene.

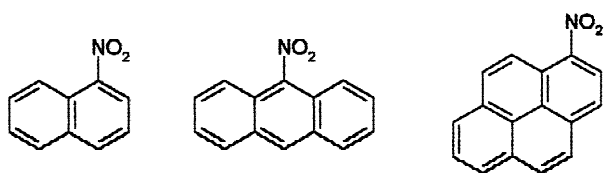


Fig. 1. Nitro-PAHs: 1-nitronaphthalene, 9-nitroanthracene, and 1-nitropyrene.

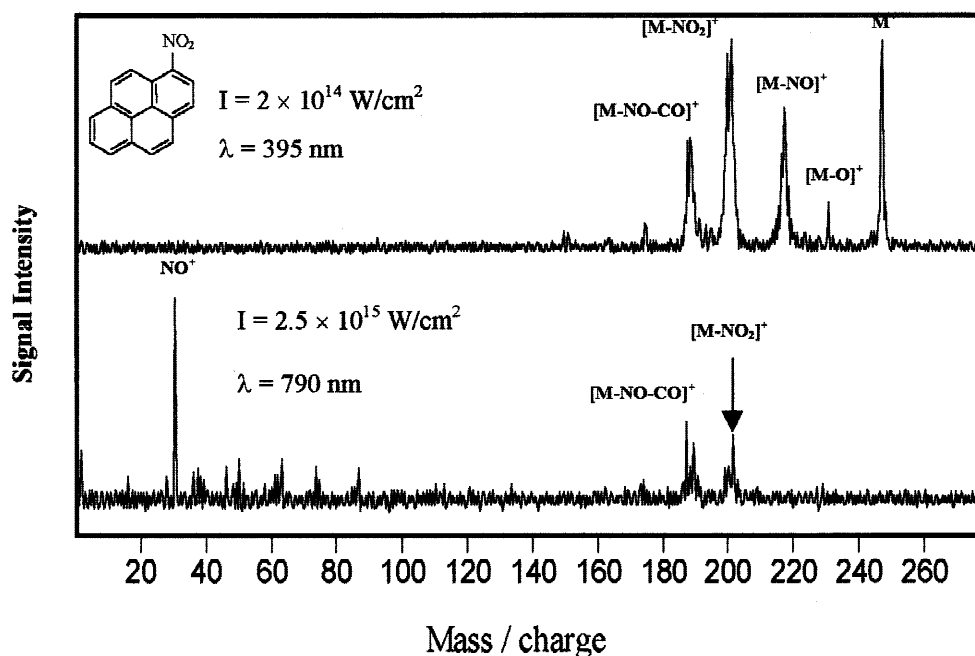


Fig. 2. Mass spectra of 1-nitropyrene.

The other observable peaks at high mass once again corresponded to the $[M-NO_2]^+$ and $[M-NO-CO]^+$ ions.

The spectra observed for the three nitro-PAHs used in this study imply that the major mechanism for the decomposition of these molecules involves the dissociation of the parent to yield an $[M-NO]^+$ (Galloway *et al.*, 1993; Kilic *et al.*, 1997) fragment along with the $[M-NO_2]^+$, $[M-NO-CO]^+$ and NO^+ ions.

Figure 3 shows mass spectra for 1-nitronaphthalene recorded at three different intensities. At the highest intensity level, the mass spectrum shows considerable fragmentation and an abundance of carbon clusters (a), as was also the case with the other nitro-PAHs. It can be seen that as the intensity

of the ionizing beam is lowered ($4.98 \times 10^{14} \text{ W/cm}^2 \rightarrow 1.74 \times 10^{14} \text{ W/cm}^2$), the degree of fragmentation decreases significantly until there is virtually no low-mass ions (d). Lowering the intensity leads to a situation where there is not enough energy available to ionize the carbon clusters that are formed after any photorearrangement or dissociation of the molecule.

To demonstrate the potential analytical advantages provided by the use of a femtosecond laser beam, the molecules 1-nitronaphthalene, 9-nitroanthracene, and 1-nitropyrene were studied using a nanosecond laser pulse to ionize the samples. As with the mass spectra obtained using femtosecond ionization, structurally significant ions were observed in each case. However, due to the rapid dissociation

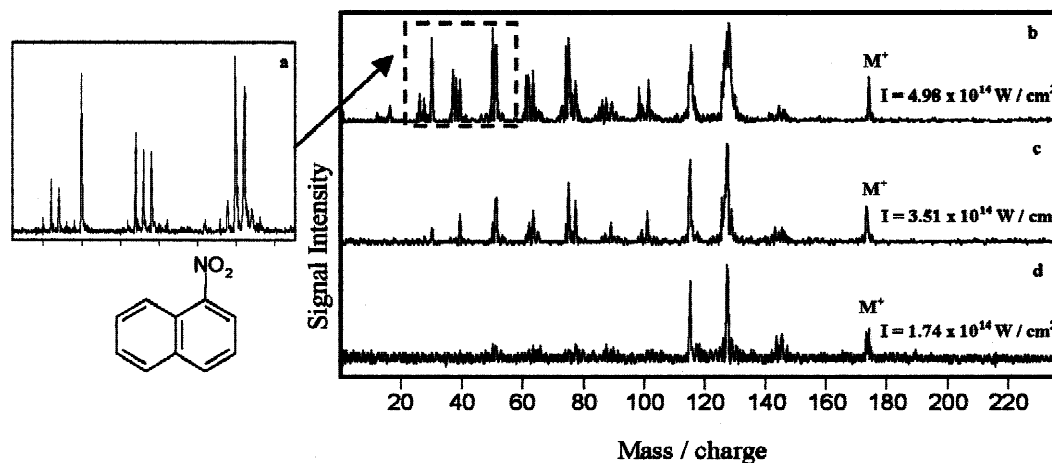


Fig. 3. Mass spectra of 1-nitronaphthalene at 395 nm.

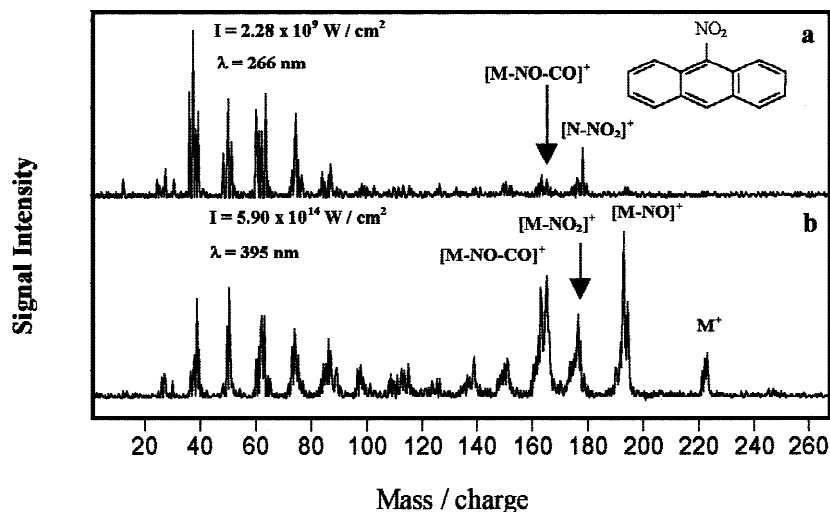


Fig. 4. Mass spectra of 9-nitroanthracene using nanosecond (a) and femtosecond (b) ionization.

of the molecules, intact parent ions were not observed for any of the nitro-PAHs studied.

The mass spectra of ion yield versus mass-to-charge ratio (m/z) for 9-nitroanthracene using both nanosecond and femtosecond ionization ($\lambda = 395$ nm) is shown in Figure 4. It can be seen that the ultrafast pulses were able to produce a parent ion at $m/z = 223$ and a strong $[M-NO]^+$ ion at $m/z = 193$. In contrast to this, when a nanosecond Nd:YAG laser was used for ionization, neither of the two highest mass peaks that were found in the femtosecond case were detected in the mass spectra due to dissociation of the molecule. A similar contrast between nanosecond and femtosecond ionization mass spectra was also observed for 1-nitropyrene and 1-nitronaphthalene.

4. CONCLUSIONS

Laser-desorbed nitro-PAHs 1-nitronaphthalene, 9-nitroanthracene, and 1-nitropyrene have been studied using both femtosecond ($\lambda = 395$ and 790 nm) and nanosecond ($\lambda = 266$ nm) lasers coupled to a ToF mass spectrometer. Analysis of mass spectra taken over a range of laser intensities has demonstrated that structurally significant ions can be observed for each molecule. It was also found that an intact parent ion can be detected at 395 nm (femtosecond) in each case. The greater abundance of high mass ions at 395 nm may be due to multiphoton processes taking place during ionization.

There is evidence, as is the case under nanosecond conditions, that the predominant mechanism for femtosecond laser-induced fragmentation of these nitro-PAHs involves the dissociation of the parent to produce $[M-NO]^+$, $[M-NO_2]^+$, and $[M-NO-CO]^+$ ions. It was also found that, as the intensity of the ionizing laser beam was reduced, the degree of fragmentation decreased, yielding parent ion-dominated mass spectra.

This work demonstrates the potential use of LD/FLMS as a tool for the detection of labile nitro-PAHs. Other labile environmental pollutant molecules including pesticides and PCBs have also been successfully analyzed using this technique.

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REFERENCES

- BORTHWICK, I.S. (1993). Ph.D. Thesis University of Glasgow, Glasgow, United Kingdom.
- GALLOWAY, D.B. *et al.* (1993). *J. Chem. Phys.* **98**, 2107.
- HANKIN, S.M. *et al.* (1999). *Anal. Chem.* **71**, 1100.
- KILIC, H.S. *et al.* (1997). *J. Phys. Chem.* **101**, 817.
- I.A.R.C. (1985). *Int. Agency for Res. On Cancer Monographs on the Eval. Of Carcinogenic Risks to Humans* (Lyon France).
- LANGLEY, A.J. *et al.* (1997–1998). *CLF RAL Annual Report* (RAL-TR-1999-062), 187.
- LEDINGHAM, K.W.D. *et al.* (1997) *Int. J. Mass Spectrom.* **163**, 149.
- NOYES DOTTER, R. *et al.* (1996). *Anal. Chem.* **68**, 2319.
- NOTAR, M. (2000). *Fresenius Environ. Bull.* **9**, 247.
- PITTS, J.N. *et al.* (1978). *G. B. Science* **202**, 515.
- SPITZER, B. (2000). *Journ. Chromatogra. A* **113**, 880.
- UK DEPARTMENT OF HEALTH, (1995). Committee on the Medical Effects of Air Pollution <http://www.doh.gov.uk/comeap/state.htm>.
- US ENVIRONMENTAL PROTECTION AGENCY, (1999). *Health Assessment Documents for Diesel Emissions* <http://www.epa.gov/nceawww1/diesel.htm>.
- WORLD HEALTH ORGANIZATION, (1999). *World Health Organization Report Summary* <http://www.who.dk/cpa/pb9904e.htm>.