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Femtosecond ionization and dissociation of laser desorbed nitro-PAHs

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Abstract

Mass spectra of six nitro-PAHs, 5-nitroacenaphthene, 9-nitroanthracene, 1-nitropyrene, 3-nitrofluoranthene, 6-nitrochrysene, and 3-nitrobenzanthrone, have been investigated using laser desorption/femtosecond laser mass spectrometry (LD/FLMS). A prominent parent ion was observed for each molecule along with the structurally-characteristic $[M-NO]^+$ and $[M-NO_2]^+$ fragments. The consistent observation of the $[M-NO]^+$ and $[M-NO-CO]^+$ ions, in the mass spectra of all the nitro-PAHs, along with the presence of certain doubly charged fragments, is thought to be indicative of a molecular rearrangement. Although this photorearrangement may be occurring within the pulse duration (<80 fs), it is thought that it is more likely to be taking place within the low intensity regions of the laser pulse. In addition to this, an abundance of doubly charged polyatomic ions were observed for the first time in the mass spectra of these molecules under laser irradiation. It was found that only the two smallest molecules (5-nitroacenaphthene and 9-nitroanthracene) were able to generate an observable dication, with the highest-mass doubly charged species corresponding to the $[M-NO_2]^{2+}$ fragment in the remaining molecules. An investigation has also been conducted into the effect of varying the molecular structure of the analyte and the position of the focussed beam. It was found that variation of molecular structure had little effect on the observed fragmentation pathways. However, movement of the focussed beam was found to exert a considerable influence over the observed mass spectra.

Keywords: Nitro-PAHs; Femtosecond ionization; Laser desorption; Multiple ionization

1. Introduction

It has recently been shown [1] that femtosecond laser irradiation of gas-phase nitrobenzene and 3-nitrotoluene can generate several multiply charged polyatomic species. Moreover, at high intensities ($>10^{15}$ W cm^{-2}) the observation in the mass spectra of the $NO_2{}^+$ ion was found to be of importance in understanding the dissociation mechanics of these nitroaromatic molecules. The present paper aims to extend this study to include a wider range of nitroaromatic molecules and to examine the effects of varying

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the molecular structure and the spatial position of the ionizing laser beam.

From an analytical perspective, laser desorption/femtosecond laser mass spectrometry (LD/FLMS) has been found to be an important technique in terms of the generation of intact molecular ions [2–6]. However, the presence of labile molecular substituents is a complicating factor. The rapid dissociation of molecules containing these labile groups can often lead to an ambiguous identification of the analyte due to a lack of structurally-specific ions in the mass spectra. In particular, the addition of an NO_2 group to aromatic molecules has a particularly destabilising effect. The nitro substituent tends to weaken the π ring system, as it is electron-deficient compared to the parent aromatic, and this is thought to have repercussions on the ionization and fragmentation of these molecules.

Nitro-PAHs are one group of aromatic molecules that exhibit photo-labile properties. It is well documented that these molecules have been found to be major environmental contaminants [7] and are formed when PAHs react with oxides of nitrogen [8] in the atmosphere. The study of these molecules is of increasing relevance due to their sustained presence in the atmosphere [7,9] and it is now well established that they have carcinogenic, teratogenic and mutagenic effects on humans and animals [10]. Recent reports [11–13] have linked cases of asthma, heart disease and a general deterioration in cardio-vascular health to the inhalation of nitro-PAHs that have condensed on particulate matter in the atmosphere. Moreover, it is thought that even the human diet, through foods such as herbs [14] and seafood [15], may be a source of exposure to PAHs and nitro-PAHs. Of the molecules included in this study, 3-nitrobenzanthrone has been described as the most strongly carcinogenic compound ever analysed [16]. With an estimated 60,000 deaths in the US each year occurring from the inhalation of these and other carcinogens present on the surface of airborne particulates [16], the need to examine the metabolic and dissociative properties of these species is greater than ever.

The study of these molecules using ultrafast lasers is a relatively new area of research. In general, the analysis of laser-induced dissociation and ionization has been limited to nitrobenzene and its derivatives. The Glasgow/Ioannina collaboration has conducted several experiments designed to examine the photodynamics of NO_2 loss and NO^+ production from these molecules [1,17–20] and much of this work may have a relevance to the larger molecules in this study. Dotter et al. [21] were among the first to study the interaction of nanosecond laser pulses with a group of nitro-PAHs. On this occasion the authors observed strong $[M - NO]^+$ and NO^+ peaks in the mass spectra although a prominent parent ion was not always detected due to the rapid dissociation of the molecule. More recently, Tasker et al. [5] have demonstrated that the ultrafast pulses of a femtosecond laser are able to largely defeat the fragmentation pathways associated with nanosecond irradiation of these molecules, thereby enabling the generation of an intact molecular ion. The high mass resolution of the present data allows for a more in-depth analysis of the multiple ionization and fragmentation pathways associated with femtosecond irradiation of nitro-PAHs. Moreover, the present paper is a companion piece to a previous publication from this group on the ionization and fragmentation of laser desorbed PAHs [22].

2. Experimental

The reflectron time-of-flight (ToF) mass spectrometer used in this work has been described previously [23]. The system comprised a sample load-lock, stainless steel source chamber, and a flight tube of length 1.5 m. 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 dissolved in volatile solvent such as methanol. Once dry, the stub is then transferred to the source chamber by means of the load-lock. Laser desorption of the solid samples is achieved using the fourth harmonic output (266 nm) from a nanosecond Nd:YAG laser (Minilite I, Continuum) focussed onto the sample stub using a 27 cm focal length lens. The delay between desorption and ionization was variable from 1 to 20 µs using a delay generator (SRS, DG535), and the intensity of the desorption laser was consistently below the ionization threshold. The ions, extracted from the source using purpose-designed ion optics, were guided into the reflectron in order to correct any initial spatial energy dispersion. Ion extraction is achieved by applying an electrostatic potential of +3 kV to the sample stage +2.5 kV to the first and second ion optic plates, respectively. Following this the ions are detected by a multi-channel plate detector (Galileo) maintained at a voltage of −2.1 kV. The signal output from the detector was coupled to a digital oscilloscope (LeCroy, 9344C) for averaged-data collection, typically over 10,000 shots.

The TOPS femtosecond laser system [24] is used for ionization of the gas-phase molecules. A Ti:Sapphire oscillator is optically pumped to produce pulses of 500 mW at a pulse duration of 20 fs. These pulses are then stretched to 200 ps before passing through a regenerative amplifier, a two-pass amplifier and an eight-pass amplifier, all pumped by Nd:YAG lasers. The beam is then passed through a compressor and pulses of around 10 mJ are produced with a duration of 80 fs, a wavelength of 800 nm and a repetition rate of 10 Hz. Attenuation of the beam was achieved by using a set of neutral density filters and the pulse duration was measured using a second order autocorrelator (MC2). After focusing through a 27 cm focal length lens intensities of the laser were determined from the thresholds for Xe^{n+} ionization [25], and from calculation using the known pulse parameters and the following equation:

$$I = \frac{E}{\tau A}$$

where I is the intensity (W cm^{-2}), E the pulse energy (J), and A is the area of focussed spot (cm^2).

In order to quantify any possible non-linear effects in the laser beam, a value for the B integral was calculated according to the following equation:

$$B = \frac{2\pi n_2}{\lambda} \int_0^z I(t, z)\, \mathrm{d}z$$

where n_2 is the non-linear refractive index of a material, λ the wavelength and $I(t, z)$ is the intensity of the laser pulse in the medium under consideration. The B integral is a deleterious effect occurring when a high intensity laser beam propagates through a medium (e.g., optics) where the index of refraction

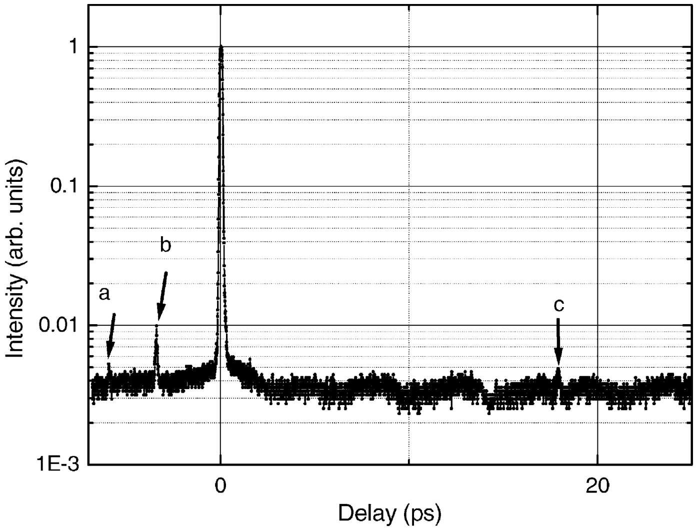

Fig. 1. Cross correlation of 800 nm laser pulse containing the following features: (a) pre-pulse at the rate of −5.97 ps; (b) reflection from SHG crystal at the rate of −3.39 ps; (c) post-pule at the rate of 17.9 ps.

changes non-linearly with intensity. A high *B* value can affect molecular fragmentation and should therefore be calculated to allow comparisons between different groups. It is thought that significant distortion of the beam can occur when *B* is greater than 5. The value $B \approx 3$ in this experiment suggests that beam is not dramatically distorted. It is also worth noting that a cross correlation of the pulse at 800 nm (Fig. 1) reveals that a small pre-pulse is present. However, this is not thought contribute significantly to the present data.

3. Results and discussion

In a recent publication [1], the production of multiply charged polyatomic ions has been reported for nitrobenzene and nitrotoluene. The present paper extends this study to examine a wider range of nitroaromatic molecules. All molecules were ionized using 800 nm radiation and multiply charged ions were observed in each case.

In the case of nitrobenzene it has been previously reported [26,27] that the NO_2 loss occurs through dissociation processes within excited electronic states of the ionic structure. However, for NO loss to occur in nitro-containing molecules, it has been postulated that the parent structure must undergo a nitro-nitrite rearrangement [21,28]. Any such photorearrangement proceeding in this manner would require isomerisation from an NO_2 to an –ONO structure, and this has recently been identified as being a necessary prerequisite of the NO loss dissociation channel in nitrobenzene and nitrotoluene [27]. Moreover, it has been proposed by Dotter et al. [21] that this rearrangement may be an inherent feature of the dissociation and fragmentation of nitro-PAHs. In the case of 9-nitroanthracene, this would similarly proceed in a manner depicted in Fig. 2.

As shown in Fig. 2, there are thought to be a number of competing fragmentation pathways for the nitro-PAHs in this study. The $[M - NO_2]$ structure may be reached either through a direct cleavage of the C–N bond or through a dissociation of the C–O bond following rearrangement. Once this has occurred, fragmentation proceeds through the loss of various C_xH_y fragments. Similarly, once photorearrangement of the parent structure has taken place, the

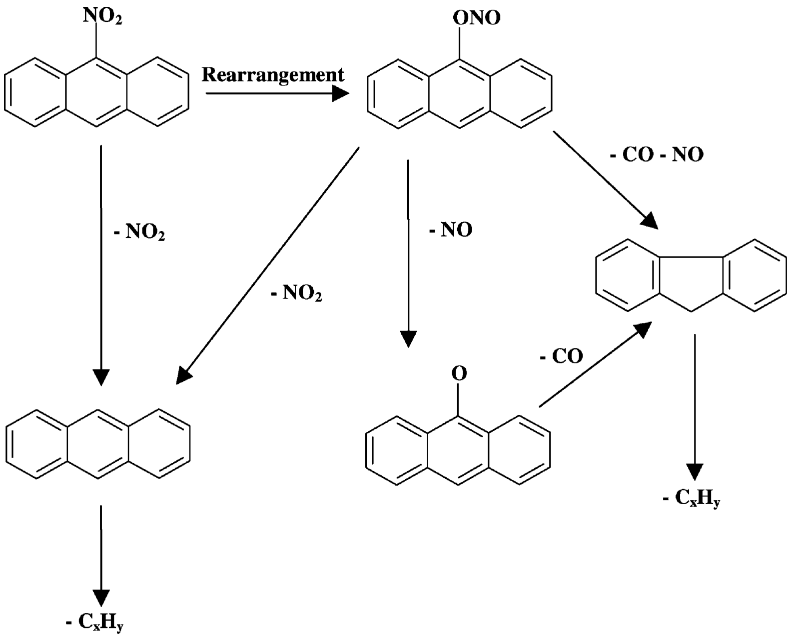

Fig. 2. Competing fragmentation pathways for 9-nitroanthracene.

$[M - NO - CO]^+$ species may be produced either through stepwise losses of NO and CO or through direct loss of CNO_2. This dissociation channel would also conclude through the loss of C_xH_y fragments.

After consideration of the possible dissociation channels of these molecules, it is apparent that the $[M - NO]^+$, $[M - O]^+$ and $[M - NO - CO]^+$ ions, which are present in the mass spectra of all six nitro-PAHs, are clearly not arising from a simple cleavage of the C–N bond. The appearance of these species therefore seems to be indicative of the proposed C–ONO rearrangement. Moreover, the observation of the $[M - NO]^{2+}$ and $[M - O]^{2+}$ ions in the case of 9-nitroanthracene (Fig. 3), and the appearance of the $[M - NO - CO]^{2+}$ ion in the mass spectra of the other nitro-PAHs, suggests that this molecular rearrangement may be taking place within the pulse duration, i.e., on a time-scale of 80 fs. Unfortunately, however, it is not currently possible to say whether 80 fs is long enough to allow for both molecular rearrangement and double ionization. An alternative proposal may therefore be that the molecular photorearrangement takes place either within the low intensity wings of the laser pulse, or as a result of the small pre-pulse (see Fig. 1). This explanation would allow a greater amount of time for the necessary isomerisation before the species undergoes double ionization in a higher intensity part of the laser pulse. This proposal would be consistent with the observation of Dotter et al. [21] who have previously observed similar singly-charged high-mass ions as a result of nanosecond ionization. It is certainly apparent that further study is required to establish the exact nature and time-scale of the rearrangement taking place within these molecules, in addition to the fragmentation time scales, since fragmentation on the ps (or even μs) time frame cannot be excluded.

3.1. High resolution mass spectra

Femtosecond laser mass spectra of all the nitro-PAHs studied are presented in Figs. 3–8 along with enlargements of certain local regions. Several structurally-characteristic peaks were observed in all spectra at high-mass corresponding to the parent, $[M - O]^+$, $[M - NO]^+$ ions and the $[M - NO_2]^+$ envelope. The consistent observation of these features demonstrates the generality of femtosecond laser mass spectrometry (FLMS) over this range of molecules. It is also noteworthy that the mass spectra in this study share several features with those recorded by Dotter et al. [21] using UV pulses of 8 ns duration.

In addition to the $[M - O]^{2+}$, $[M - NO]^{2+}$ and $[M - NO - CO]^{2+}$ ions, which have been previously discussed, the mass spectrum of 9-nitroanthracene displays several other doubly charged molecular species. Most significantly, peaks are visible at $m/z = 111.5$, 88.5, 87.5 and 81.5 which correspond to the M^{2+}, $[M - NO_2]^{2+}$, $[M - NO_2 - 2H]^{2+}$ and $[M - NO - CO - 2H]^{2+}$ ions. These peaks can be unambiguously identified as they fall at half m/z values. Double ionization of this nature has never previously been observed for nitro-PAHs under laser irradiation and a doubly charged parent ion has not previously been reported for any nitroaromatic molecule under these conditions. It is also noteworthy that several of the doubly charged molecular peaks, most prominently in the $[M - NO]^{2+}$ envelope of 9-nitroanthracene, display a more narrow profile than their neighbouring singly charged ions. This difference in profile is thought to arise principally from the kinetic energy released in the fragmentation process of singly charged ions [29].

A comparison with EI mass spectra of nitroanthracene [30] reveals that both EI ionization and the current femtosecond laser ionization are able to yield singly charged $C_{14}H_n$ fragments. It therefore seems likely that the doubly charged $C_{14}H_n$ ($[M - NO_2 - nH]^{2+}$) ions are produced through fragmentation pathways within the doubly charged parent that are similar to those observed for the singly charged molecular ion. However, it is interesting to note that while a doubly charged parent was observed for 9-nitroanthracene, this was not the case for many of the other nitro-PAHs. Indeed, the only other molecule to generate an M^{2+} ion was 5-nitroacenaphthene (Fig. 4). The remaining molecules bore a closer resemblance to the previous study [1] with the highest mass doubly charged fragments corresponding to the

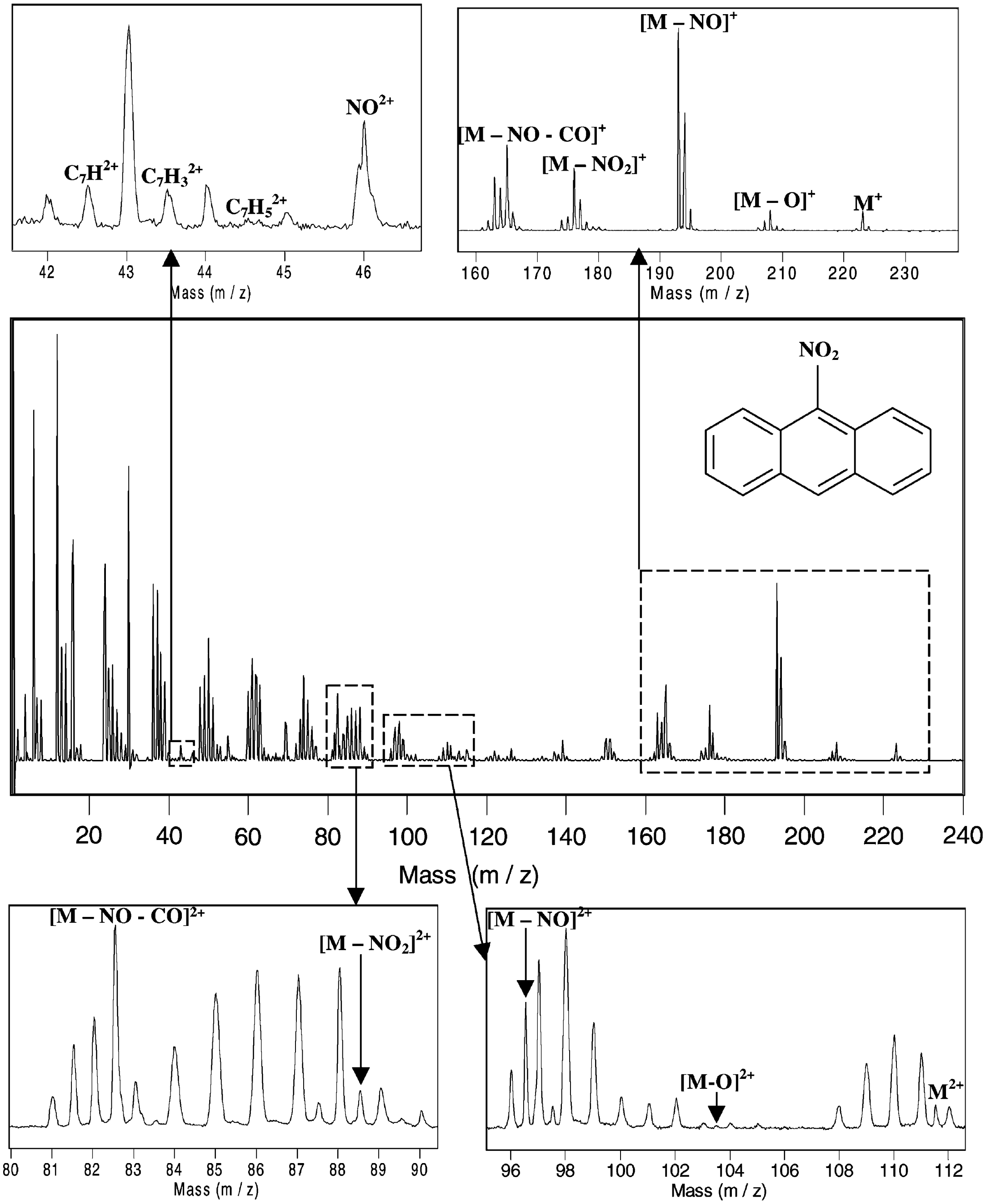

Fig. 3. Femtosecond mass spectrum of 9-nitroanthracene; $\lambda = 800\,\text{nm}$, $I = 2.5 \times 10^{15}\,\text{W}\,\text{cm}^{-2}$.

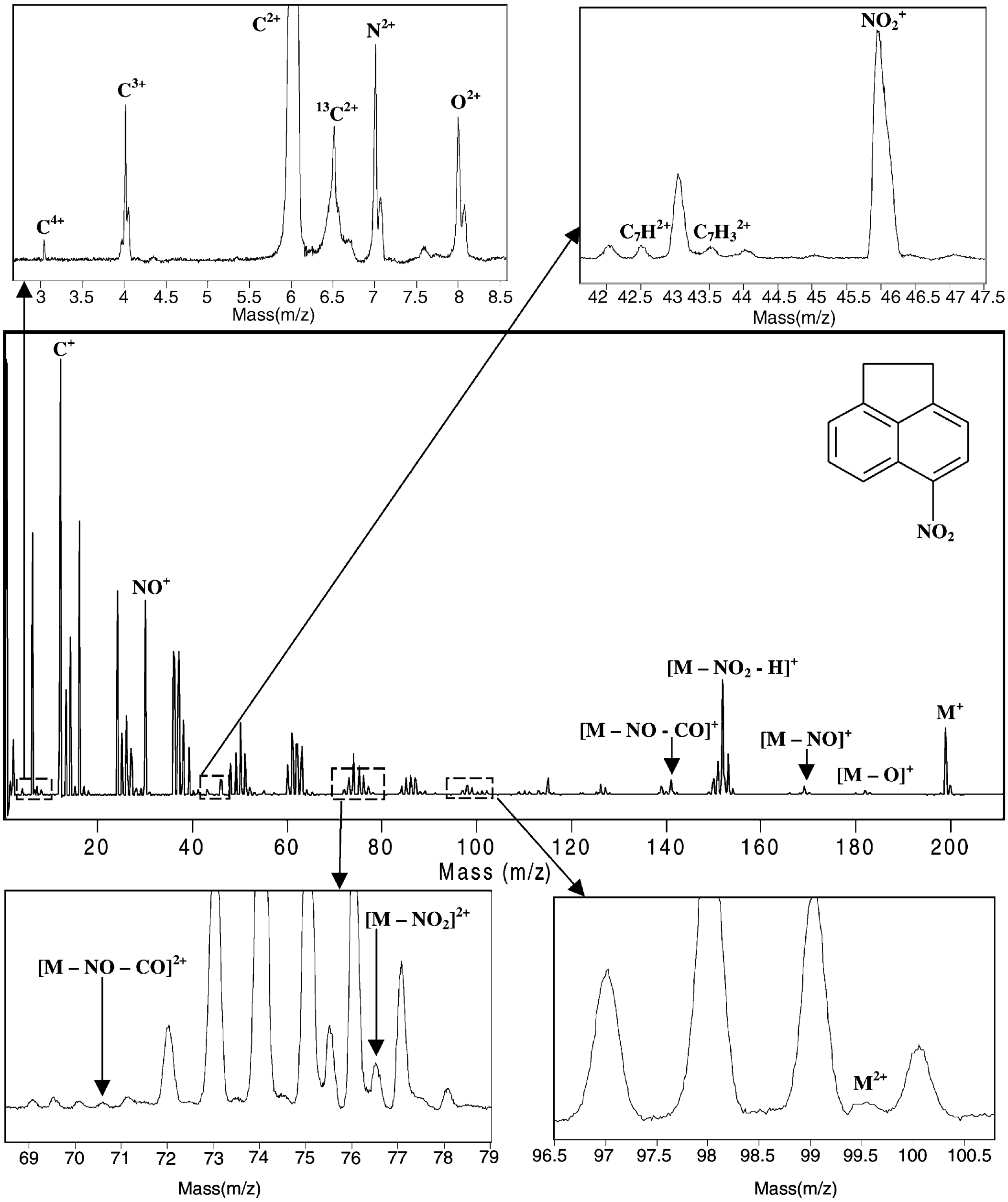

Fig. 4. Femtosecond mass spectrum of 5-nitroacenaphthene; $\lambda = 800\,\text{nm}$, $I = 1.3 \times 10^{16}\,\text{W}\,\text{cm}^{-2}$.

$[M - NO_2]^{2+}$ envelope. This may well suggest that a doubly charged parent ion is generated for all of the nitro-aromatic molecules studied, although the varying lifetimes of the dications determines whether it is detected or not.

In a recent paper [1] from this group a study was conducted between small gas-phase nitroaromatic molecules and their corresponding aromatic. On this occasion the authors observed no M^{2+} for the nitrated molecules and attributed this to the instability

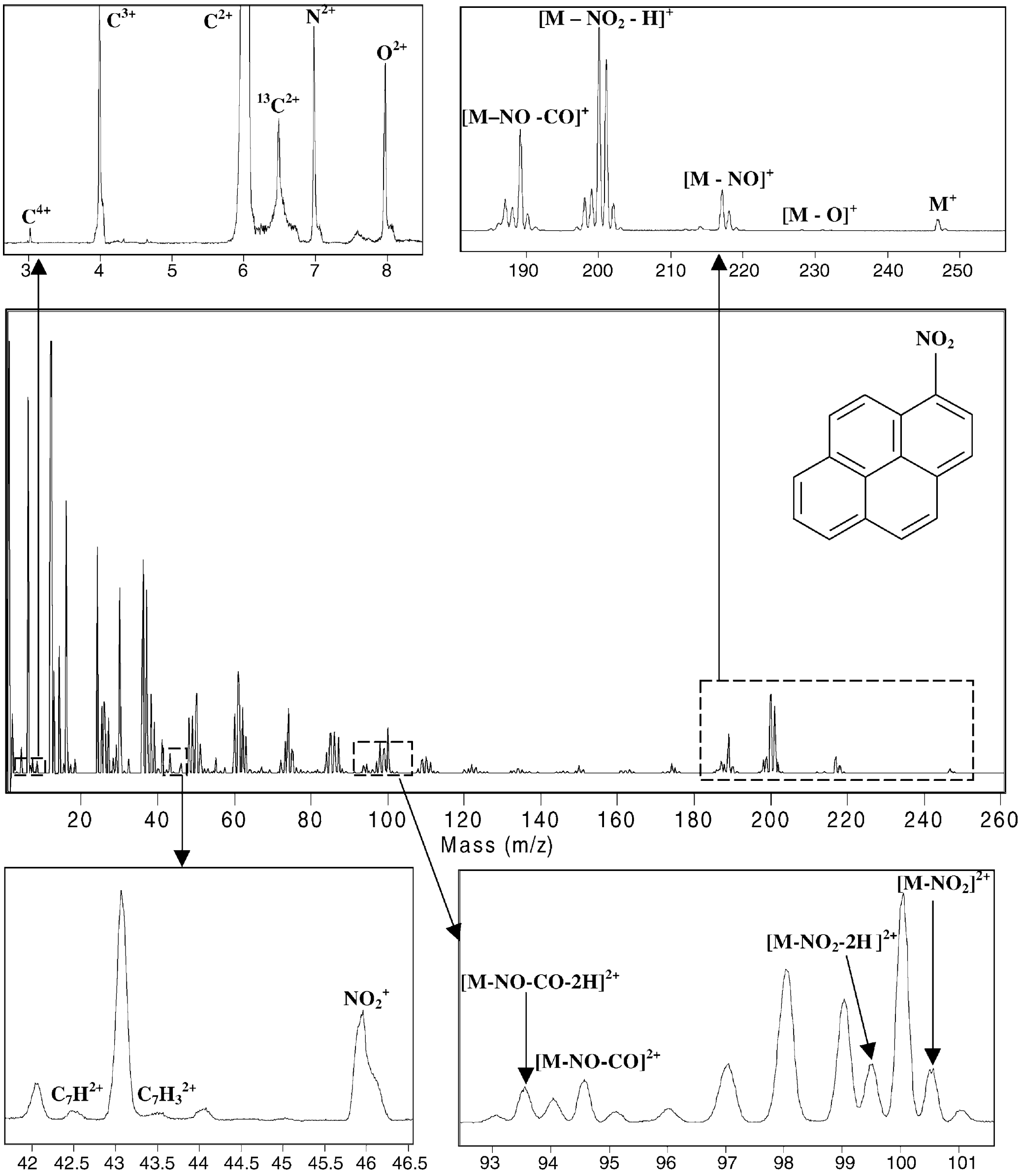

Fig. 5. Femtosecond mass spectrum of 1-nitropyrene; $\lambda = 800\,\mathrm{nm}$, $I = 6.8 \times 10^{15}\,\mathrm{W\,cm^{-2}}$.

caused by the coulombic repulsion between charges localised in the aromatic ring and the nitro group. In principle, the same effect may well be taking place here, thus accounting for the lack of doubly ionized parent molecules in some nitro-PAHs and the relatively small abundance of M^{2+} in others. However, this does not explain why the dication is observed only for certain molecules. It may well be that the addition of the desorption step influences the production and survival of the doubly charged species. In addition, it appears that molecular structure may play an important role in dication production. The fact that

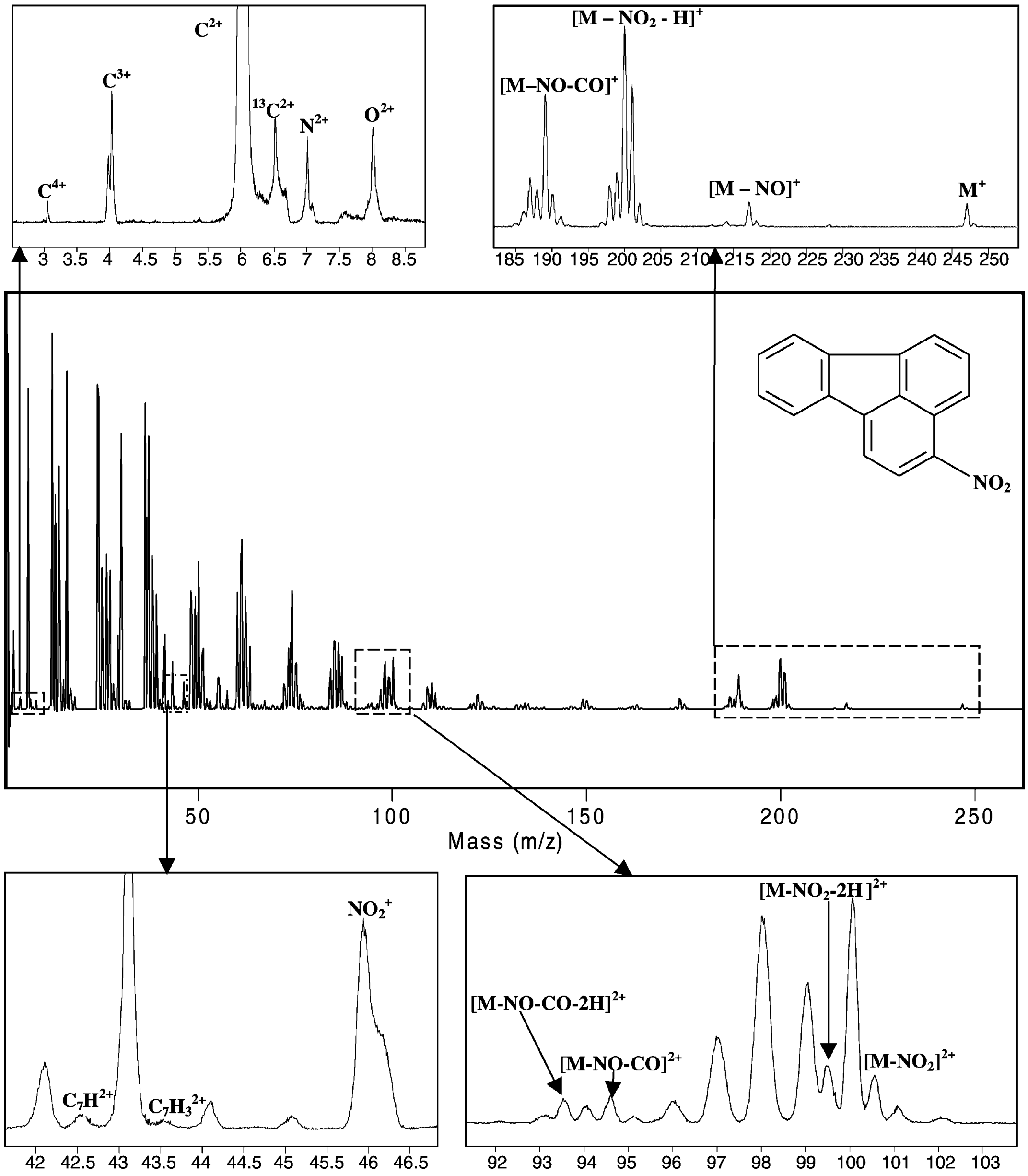

Fig. 6. Femtosecond mass spectrum of 3-nitrofluoranthene; $\lambda = 800\,\text{nm}$, $I = 1.0 \times 10^{16}\,\text{W cm}^{-2}$.

the nitro-PAHs in the present study were desorbed from the solid-phase may differentiate them energetically from any gas-phase molecules undergoing laser ionization. It is possible that this is the reason why no doubly charged molecular ions were reported in the previous paper [1]. However, as the desorption conditions are generally optimised to produce a neutral plume of gas-phase species, this explanation is thought to be unlikely. Nevertheless, in the present study it does seem apparent that only the smaller

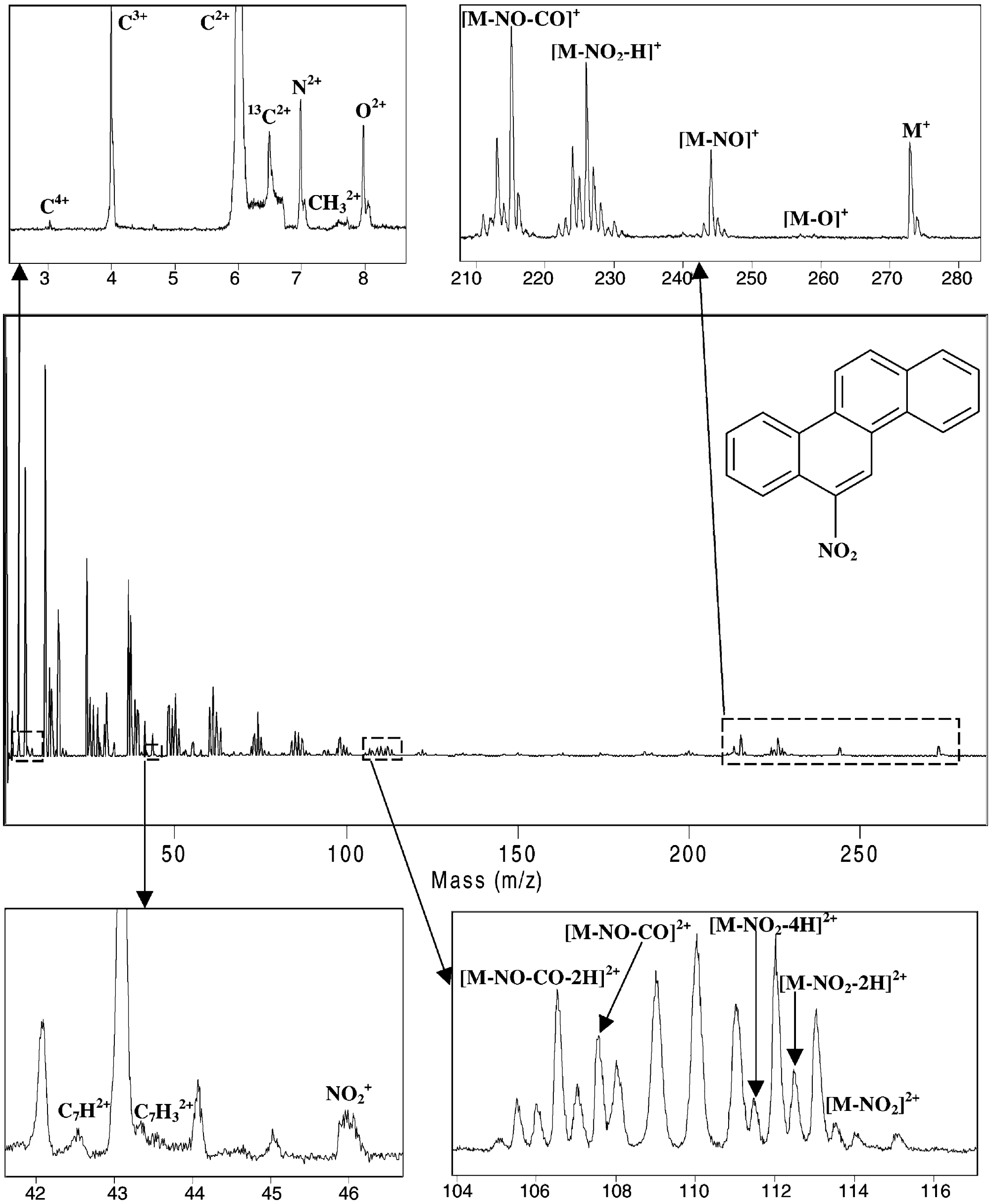

Fig. 7. Femtosecond mass spectrum of 6-nitrochrysene; $\lambda = 800\,\text{nm}$, $I = 1.1 \times 10^{16}\,\text{W cm}^{-2}$.

molecules are able to generate M^{2+}, with the four largest samples, 1-nitropyrene, 3-nitrofluoranthene, 6-nitrochrysene, and 3-nitrobenzanthrone all unable to produce this ion.

The appearance of the NO_2 ion in the mass spectra may provide useful information as to how the multiply charged transient ion undergoes fragmentation. This ion appears very weakly, if at all, in the electron impact mass spectra [30] of the nitro-PAHs studied and is generally considered to be a good example of Stevenson's rule [31], i.e., when a single ion dissociates to produce two fragments the charge resides

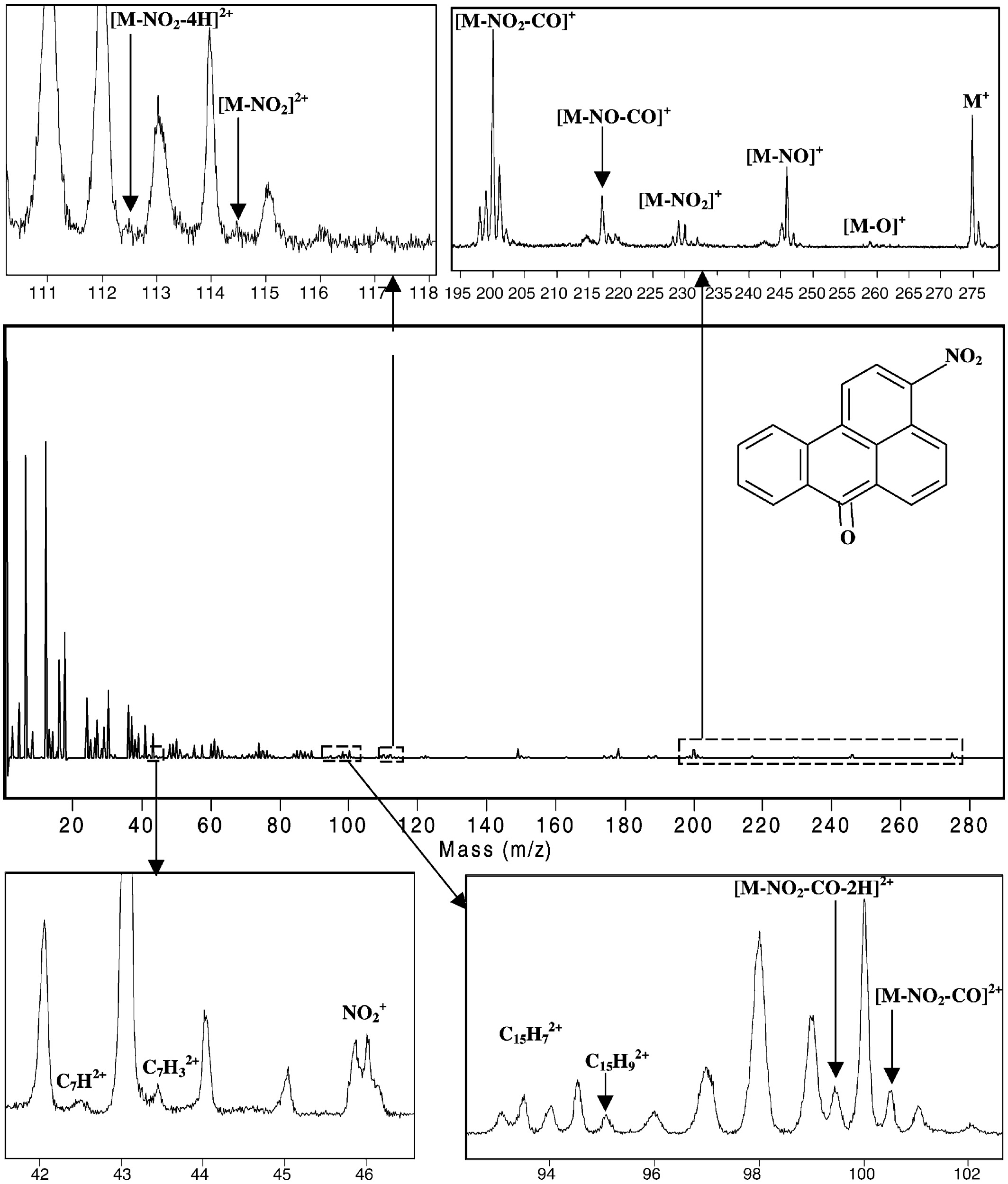

Fig. 8. Femtosecond mass spectrum of 3-nitrobenzanthrone; λ = 800 nm, $I = 1.3 \times 10^{16}\,\mathrm{W\,cm^{-2}}$.

on the fragment with the lower ionization potential. In two recent publications, NO_2^+ has been observed for the first time in mass spectra of nitrobenzene under both synchrotron [32] and femtosecond laser [1] irradiation. In both papers, the authors attribute the appearance of this ion to a charge separation process occurring within the doubly charged parent ion. This explanation is consistent with the observation of the asymmetric peak profile of the NO_2 ion in the mass spectra of the nitro-PAHs in this study. In the case of

9-nitroanthracene such a process could proceed in the following manner:

$$[C_{14}H_9NO_2]^{2+} \rightarrow C_{14}H_9{}^+ + NO_2{}^+$$

Naturally, since the multiply charged transient may be able to reach higher charged states than 2+, it is possible that the NO_2 ion may be generated through the dissociation of these species. For example:

$$[C_{14}H_9NO_2]^{3+} \rightarrow C_{14}H_9{}^{2+} + NO_2{}^+$$

However, as the relative abundance of $NO_2{}^+$ is higher than that of the $[M - NO_2]^{2+}$ ($C_{14}H_9{}^{2+}$) ion, it is unlikely that this channel is a major contributor to the $NO_2{}^+$ ion yield. Moreover, since charge separation is more likely to occur within the doubly charged parent, it is thought that the two ejected electrons would be localised in one C–C bond. This would inevitably lead to ring opening [33] and the formation of an isomerised structure. Therefore, as was recently reported for nitrobenzene and nitrotoluene [1], the possibility that laser irradiation of these nitro-PAHs results in a linear formation cannot be ruled out.

At the high intensities used (10^{15} to 10^{16} W cm^{-2}) the mass spectra presented here show many features synonymous with the occurrence of a Coulomb explosion [34]. In the presence of the intense electric field of the laser the binding forces experienced by the valence electrons of the molecule may be superseded by the external perturbation. This situation may lead to the production of highly charged transient species which in turn can explode into multiply charged atomic fragments. This is demonstrated in Fig. 4 where it can be seen that the Coulomb explosion of 5-nitroacenaphthene yields up to C^{4+}, O^{2+} and N^{2+}. These observations indicate that the transient reaches a charge of at least 4+ before any explosion. However, it has been postulated that this manner of fragmentation may favour charge symmetry [35,36], which would imply the formation of at least an M^{8+} species. The split profile of the peaks corresponding to these atomic ions, arising from the difference in flight times of ions ejected in the forward and backwards directions, provides further evidence of the fact that these ions are the product of Coulomb explosion events [34]. Moreover, when it is considered that a reflectron is employed in the experimental arrangement to correct for energy dispersion within the interaction region, then the observation of these split peaks implies that there are large kinetic energies associated with these species. In other words, it is thought that these ions are generated from explosion within highly charged transient species whereas the formation of the heavier molecular fragments is considered to have taken place in the (spatial and temporal) wings of the pulse.

3.2. Molecular structure

In order to further the understanding of the ionization and dissociation of nitro-PAHs it is important to study the influence of molecular structure on these physical processes. Presented in Fig. 9 is a comparison of mass spectra of 1-nitropyrene and 3-nitrofluoranthene taken at the same ionizing intensity. Each molecule has a mass of 247 Da although their molecular structures differ markedly. At first glance it appears that the nitrofluoranthene spectrum contains a greater abundance of the parent ion as well as certain lower mass carbon clusters. The presence of the slightly inferior signal-to-noise in this trace, however, indicates that this is largely due to the higher desorption energy. It is apparent though that 3-nitrofluoranthene is able to generate a slightly larger yield of the molecular ion in comparison to the $[M - O]^+$ and $[M - NO_2]^+$ envelopes. This would suggest that this molecule is able to preserve the parent ion structure to a greater extent than nitropyrene. Other than this one discrepancy, the two spectra are remarkably similar. In terms of the structurally-characteristic peaks present and also the relative abundance of these peaks compared to one another, the two traces are almost identical. This is also the case in the doubly ionized regions where, once again, there is little difference in the size and profile of the doubly charged peaks. Moreover, the observation of C^{4+} in the mass spectra implies that the molecules reach the same charged states before

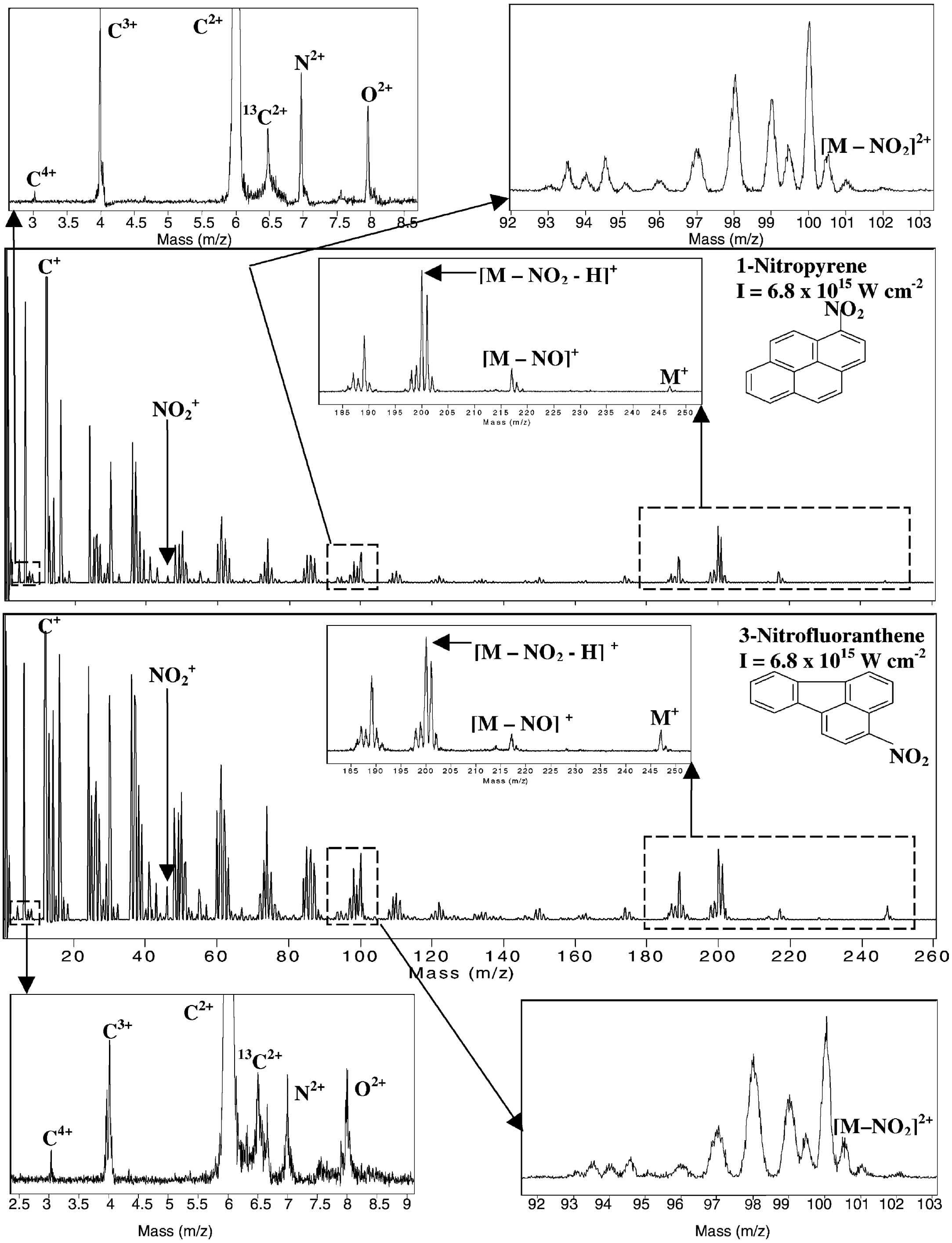

Fig. 9. A comparison of femtosecond mass spectra of 1-nitropyrene and 3-nitrofluoranthene. Both molecules have a mass of 247 Da but their structures differ significantly.

subsequent Coulomb explosion, thereby indicating that they couple with the laser field to a similar extent.

Since it has already been established that one of the main dissociation pathways for these molecules may involve the cleavage of the C–N bond [26], it may not be entirely unexpected that the mass spectra are so similar at high-mass. However, it has been well documented for nitrotoluene isomers [37,38], among others, that the position of the NO_2 group on the aromatic ring greatly influences the dissociation mechanics of the molecule. Furthermore, with the

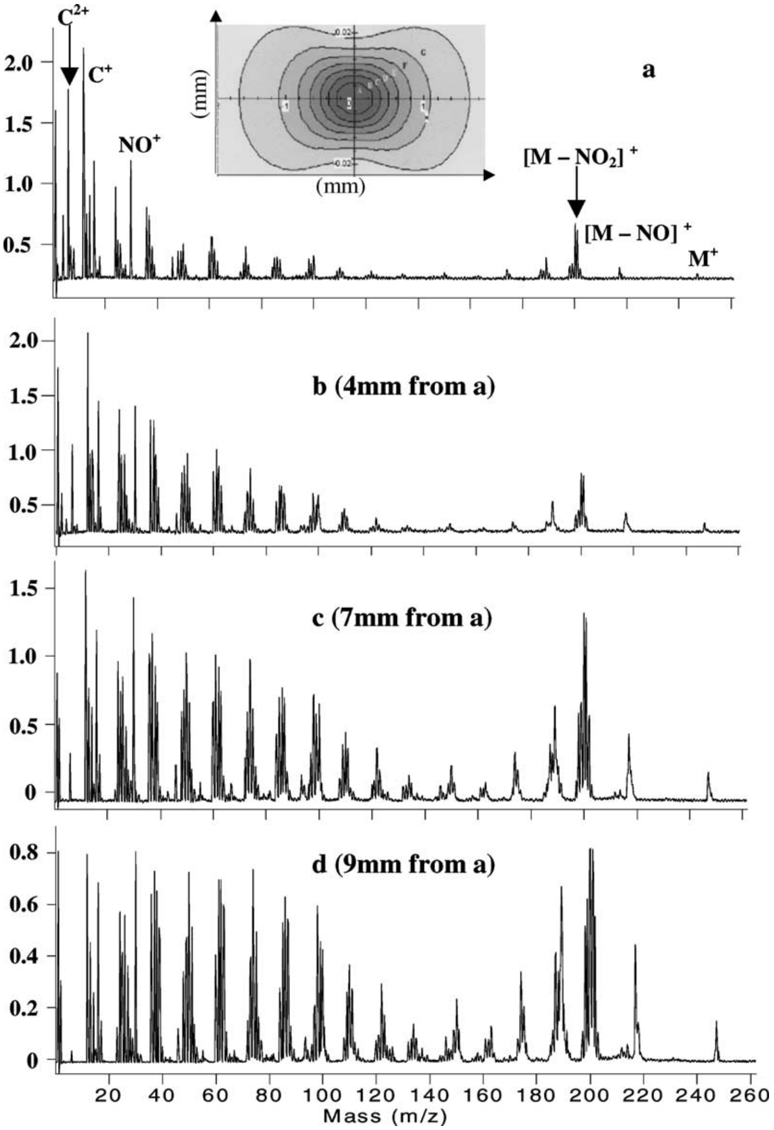

Fig. 10. Mass spectra of 1-nitropyrene recorded at an intensity of 4×10^{15} W cm^{-2}. The spectra were taken using varying positions of the focussed beam (in the plane of propagation of the beam). The inset shows the typical intensity contours for a focused Gaussian pulse of varying intensities.

obvious differences in the aromatic structures, it seems surprising that the relative abundances of the various C_nH_m groups should be so alike. Evidently, further comparisons are required to explore the influence of molecular structure on the ionization/dissociation of these molecules.

3.3. Variation of focus position

During the course of the present study it was observed that the mass spectra were affected by varying the position of the laser focal point with respect to the ion optics. A thorough report on the effects and

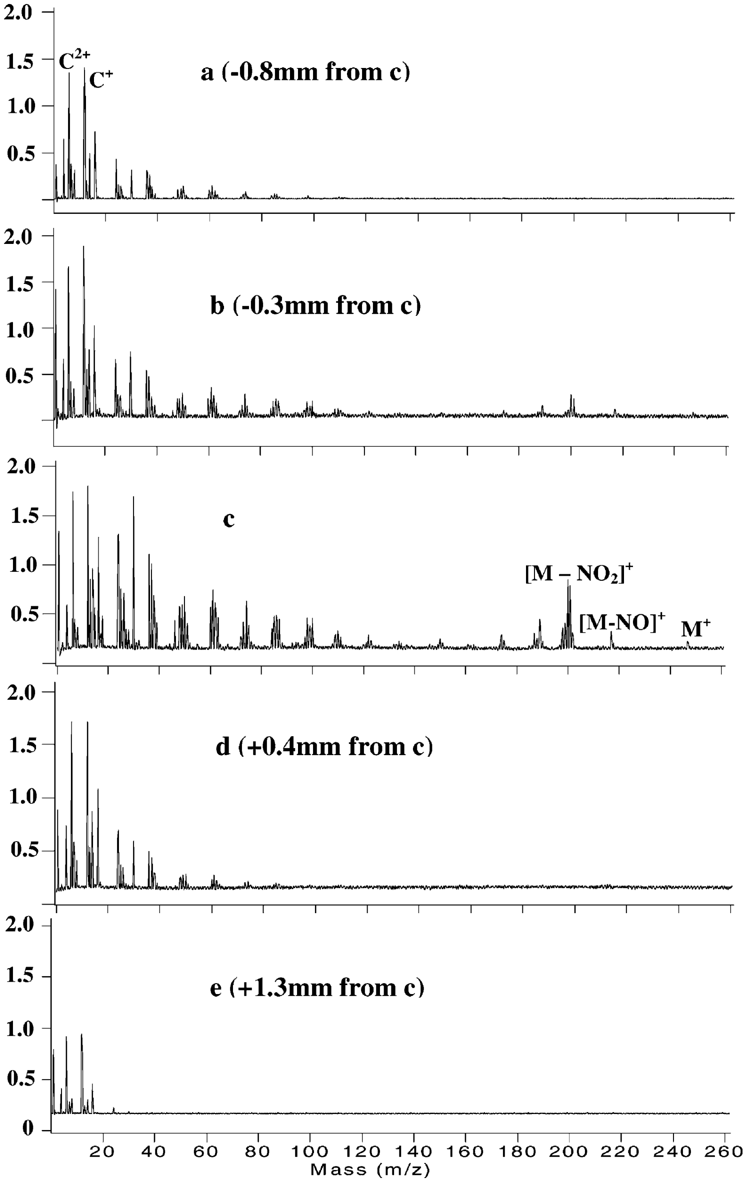

Fig. 11. Mass spectra of 1-nitropyrene recorded using varying positions of the focussed beam in the y-axis (i.e., perpendicular to the time-of-flight axis and the plane of propagation of the beam). $I = 4 \times 10^{15}\,W\,cm^{-2}$.

implications of this study will be forthcoming from this group but it was thought to be very important to present the initial results at this time. These are presented in Figs. 10 and 11.

It is evident from Fig. 10 that movement of the focal point along the direction of propagation of the beam exerts a considerable influence on the observed fragmentation pattern. It was felt that the spectrum displayed in Fig. 10a corresponds to the position at which the most intense part of the laser focus is in the optimum position in relation to the first optic for the collection of ions. This conclusion was reached in light of the fact that this position appeared to yield the greatest abundance of multiply charged atomic ions that are synonymous with high intensity processes. It may be seen that as the focus is moved away from this position the overall signal size begins to decrease. In particular, low-mass ions such as C^+ and C^{2+} reduce dramatically until eventually the high-mass, structurally-characteristic ions such as $[M - NO_2]^+$ are of a comparable size to the lower mass fragmentation. At present it is not possible to manoeuvre the focus point more than 9 mm from the perceived “optimum position”. Nevertheless, it would appear that the effect of moving the focal point in this manner produces effects similar to those expected from simply reducing the intensity of the ionizing laser—a suppression of low-mass fragmentation and a comparatively greater yield of high-mass ions. It is noteworthy that this observation would be consistent with the ‘dog-bone’ shaped intensity contours contained within a focussed Gaussian laser pulse [39], an example of which is shown in the inset of Fig. 10a. The maximum peak intensity (contained at the centre) corresponds to a relatively small geometrical volume in comparison to the lower intensities contained at the peripherals. It is apparent that by scanning the laser focus in the direction of propagation, various intensities are accessed with different geometrical volumes. A detailed description of the spatially-dependent ionization of nitro-PAHs, similar to that carried out by El-Zein et al. [39] and Hansch et al. [40] for Xenon, is out with the scope of this paper and will be presented in a future publication.

This initial investigation has also been extended to a variation of the height of the focussed spot. It is apparent from the spectra presented in Fig. 11 that movement of the beam in this plane is considerably more critical for the observation of ions than was the case for beam variation along the plane of propagation of the beam. It is interesting to note, however, that while there seems to be only a very small region that enables the observation of the parent ion, the observation of the C^+ and C^{2+} ions was facilitated over a much larger range of beam movement. As with Fig. 10, it is likely that many of the features observed in Fig. 11 may be explained by invoking the pattern of intensity contours within the focussed spot [39]. Nevertheless, the full implications of the relationship between the position of the focussed beam and the observed fragmentation patterns have not, as yet, been fully investigated. This will be the subject of a more thorough examination in the future.

4. Conclusions

Femtosecond mass spectra have been recorded for a group of laser desorbed nitroaromatic molecules using pulses of $\lambda = 800$ nm and $\tau = 80$ fs. An observable molecular ion was generated in each case along with other structurally-significant species. The consistent observation of the $[M - NO]^+$ and $[M - NO - CO]^+$ ions, in the mass spectra of all the nitro-PAHs, along with the presence of certain doubly charged fragments, is thought to be indicative of a molecular rearrangement. Although this photorearrangement may be occurring within the pulse duration (<80 fs), it is thought that it is more likely to be taking place within the pre-pulse or low intensity regions of the laser pulse. Furthermore, an abundance of doubly charged polyatomic ions was also present in the mass spectra of all six nitro-PAHs. It was found, however, that only 5-nitroacenaphthene and 9-nitroanthracene were able to produce an intact M^{2+} ion, with the remaining molecules generating the $[M - NO_2]^{2+}$ fragment. This observation seems to indicate that the dication is generated in the interaction volume for all the molecules although the smaller species are more stable. Further investigation is required, however, to fully establish the exact nature of this physical process.

A study of varying molecular structure has also been undertaken. A comparison of femtosecond mass spectra of 1-nitropyrene and 3-nitrofluoranthene (both with a mass of 247 Da) has revealed a similar fragmentation pattern for each. The obvious differences in the structure of these molecules renders this a surprising observation. Clearly more work is required to further investigate the influence of molecular structure on the dissociation mechanics of nitroaromatic molecules.

Initial investigations have been carried out in order to examine the effect of the position of the focussed beam on the observed mass spectra. As may be expected, the position of the focussed spot has a considerable influence over the observed mass spectra. In particular, movement along the direction of propagation of the beam resulted in an effect similar to reducing the intensity of the ionizing laser—a suppression of low-mass fragments compared with a comparatively superior yield of high-mass ions. Moreover, it was found that for movement of the beam perpendicular to both the time-of-flight axis and the beam propagation axis was critical for the observation of a molecular ion. The appearance of the parent ion in the mass spectra was facilitated over a very small region in this plane compared to the C^+ and C^{2+} ions, which were observed over a much larger range of beam movement. This work requires considerable further study and will be the subject of a more thorough analysis in the future.

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