

A High Mass Resolution Study of the Interaction of Aromatic and Nitro-Aromatic Molecules with Intense Laser Fields

A. D. Tasker,[†] L. Robson,[†] K. W. D. Ledingham,^{*,†,||} T. McCanny,[†] S. M. Hankin,[†]
P. McKenna,[†] C. Kosmidis,[‡] D. A. Jaroszynski,[§] and D. R. Jones[§]

Department of Physics and Astronomy, University of Glasgow, Glasgow G12 8QQ Scotland, United Kingdom,
Department of Physics, University of Ioannina, GR-45110, Ioannina, Greece, TOPS Laser Facility,
Department of Physics and Applied Physics, University of Strathclyde G4 ONG, Scotland, United Kingdom,
and AWE plc., Aldermaston, Reading RG7 4PR, United Kingdom

Received: October 16, 2001; In Final Form: February 14, 2002

The technique of femtosecond laser mass spectrometry has been applied to benzene, nitrobenzene, toluene and nitrotoluene using pulses of 80 fs and $\lambda = 800$ nm ($10^{14} - 10^{16}$ W cm⁻²). The ultrafast laser pulses used were able to largely defeat the dissociation pathways associated with nanosecond ionization and produce a molecular ion for both the aromatics and the two photounstable nitro-aromatics. The high mass resolution ($m/\Delta m = 800$) permitted, for the first time, the observation of various doubly charged species and allowed a study of the effect of the substituent NO₂ group on the multiple ionization process. It was found that the femtosecond laser irradiation of benzene and toluene enabled the production of a doubly charged cation envelope in each case along with an additional doubly ionized contribution from certain lower mass fragments. Doubly ionized species were also observed for the nitro-aromatics including, most notably the **loss of NO₂ doubly charged ion** ($[M-NO_2]^{2+}$) although a doubly charged parent was not observed. In addition, an NO₂⁺ ion was detected for both nitro-aromatics which was thought to be evidence of a “charge-separation” process involving a transient doubly charged molecular ion.

Introduction

The development of high-power lasers with pulse durations in the femtosecond regime has opened up new avenues of research in both physics and chemistry. The interaction of atoms and molecules with the intense electric field of a laser ($10^{12} - 10^{17}$ W cm⁻²) has been the subject of much discussion in recent years. Many of the experiments carried out have been instrumental in developing a deeper understanding of the molecular dynamics involved in the ionization and dissociation of organic matter in a laser field. This work has enabled the observation of many novel physical processes such as the “Coulomb explosion” of molecules.

It has been well documented¹ that when UV, visible, and infrared intense laser radiation interacts with polyatomic molecules, ionization can occur. This will take place through either a multiphoton (MPI) or field ionization mechanism, depending on the intensity, wavelength and pulse duration of the ionizing radiation. Molecular size and structure are also thought to influence the ionization process.² It has been demonstrated that molecular dissociation can compete with ionization, leading to a degree of fragmentation.¹ In the case of multiphoton absorption,^{3–7} the molecule can fragment either through a ladder switching mechanism, where dissociation is followed by ionization, or through ladder climbing, where an ionization state is reached before dissociation occurs. The

ultrafast pulses of a femtosecond laser make the latter of these processes the more likely.

When the electric field of the ionizing laser is sufficiently intense that it is able to distort the Coulomb potential of the molecule,⁸ electrons are able to escape either through or over the barrier and field ionization becomes the dominant mechanism. A qualitative interpretation of this process is defined by the Keldysh adiabaticity parameter, γ ⁹

$$\gamma = (IP/(1.87 \times 10^{-13}) I \lambda^2)^{1/2}$$

where IP is the ionization potential in eV, I is the ionizing laser intensity in W cm⁻², and λ is the laser wavelength in μ m. Ilkov et al.¹⁰ have demonstrated that field ionization will prevail for an adiabaticity value of less than 0.5. However, while this parameter is appropriate for the study of atoms, Levis and co-workers^{2,11} have shown that the molecular case may be somewhat different owing to the extended molecular orbitals.

In recent years, several studies^{12–25} have been carried out, providing valuable information on the ionization mechanisms and fragmentation pathways of aromatic and nitroaromatic molecules. In particular, the Glasgow/Ioannina collaboration^{12,20,22–24,26} has reported on the multiple ionization and Coulomb explosion of benzene, toluene, and other cyclic species in addition to studies carried out on the photodissociation of some nitrated molecules.

The aim of the present paper is to extend this experimental program by using infrared femtosecond laser mass spectrometry (FLMS), coupled with an improved resolution in mass spectra, due to a reflectron ToF spectrometer, to present a more detailed analysis of the ionization and subsequent fragmentation of the molecules presented in Figure 1. In particular, the effect of the

* To whom correspondence should be addressed. E-mail: K.Ledingham@physics.gla.ac.uk. Fax: +44 (0)141 330 5881.

[†] Department of Physics and Astronomy, University of Glasgow.

[‡] Department of Physics, University of Ioannina.

[§] TOPS Laser Facility, Department of Physics and Applied Physics, University of Strathclyde.

^{||} AWE plc., Aldermaston.

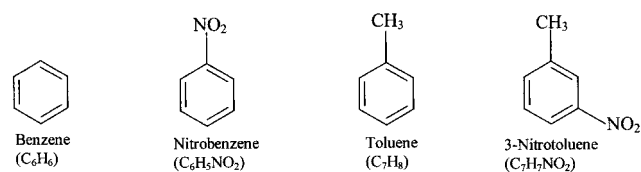


Figure 1. Molecular structures of benzene, nitrobenzene, toluene, and 3-nitrotoluene.

labile NO₂ group on the multiple ionization of the two nitroaromatics is examined and compared to benzene and toluene. It is well-known that the nitro substituent exhibits a negative inductive behavior, which has an effect on photophysical and photochemical properties (i.e., increase of the molecular ionization potential, the stability of the aromatic ring, etc). Nevertheless, the repercussions in the multiple ionization and fragmentation processes induced by strong laser fields have not previously been explored.

Experimental Section

The reflectron time-of-flight (ToF) mass spectrometer used in this work (see Figure 2) has been described in detail elsewhere.²⁷ Briefly, the spectrometer comprised a stainless steel source chamber and a 1.5 m flight tube, both pumped by rotary-backed turbomolecular pumps to a base pressure of 10⁻⁹ Torr. Liquid-phase samples were contained in glass phials coupled to a bleeder valve on the spectrometer and the vapors were effusively admitted to the source chamber via a capillary tube to a working pressure of 10⁻⁶ Torr. The ions, extracted from the source using purpose-designed ion optics, are guided into the reflectron in order to correct any initial energy dispersion. Electrostatic potentials of +3 kV and +2.5 kV are applied to the sample stage and first ion optic respectively to enable ion extraction. Following a 3 m flight path ions are detected by a multichannel plate detector (Galileo), maintained at a voltage of -2.1 kV, before averaged data is collected over 10 000 sweeps on a digital oscilloscope (LeCroy 9344C). A PC installed with GRAMS/32 software (Galactic) is used for data analysis.

The TOPS femtosecond laser system²⁸ 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 6 mJ** are produced with a duration of 80 fs, a wavelength of 800 nm, and a **repetition rate of 10 Hz**. The 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 Xeⁿ⁺ ionization²⁹ and from calculation using the known pulse parameters and the following equation

$$I = E/\tau \times A$$

where I = intensity (W cm⁻²), E = pulse energy (J) and A = area of focused spot (cm²). A mass spectrum of xenon is presented in Figure 3 as an example of the verification of the calculated intensities. The five observable charged states of this atom correspond to an intensity of 1–2 × 10¹⁵ W cm⁻² which is consistent with the measured value of 1.2 × 10¹⁵ W cm⁻²

Results and Discussion

Mass spectra of relative ion yield versus mass-to-charge ratio were obtained for benzene ($m/z = 78$), toluene ($m/z = 92$), nitrobenzene ($m/z = 123$), and 3-nitrotoluene ($m/z = 137$) over a range of intensities 8.5 × 10¹⁴–1.2 × 10¹⁶ W cm⁻² at $\lambda = 800$ nm. An observable parent ion was detected for each molecule and all spectra contained a degree of molecular fragmentation.

The ionization potentials for the four molecules studied here are, 8.82 eV for toluene, 9.23 eV for benzene, 9.92 eV for nitrobenzene, and 9.43 eV for nitrotoluene. The corresponding values of the adiabaticity parameter ($\gamma \approx 0.25$ for 10¹⁵ W cm⁻²) place each molecule well within the regime for field ionization predicted by both Keldysh⁹ and Ilkov et al.¹⁰

Benzene. Recent work by the Glasgow group^{12,23,24} and others^{15,16,30,31} has provided a valuable insight into the multiple ionization and Coulomb explosion of benzene and other aromatic molecules. Ledingham et al.²³ were the first to report on the double and triple ionization of benzene and the work presented here displays many additional mass spectrometric features.

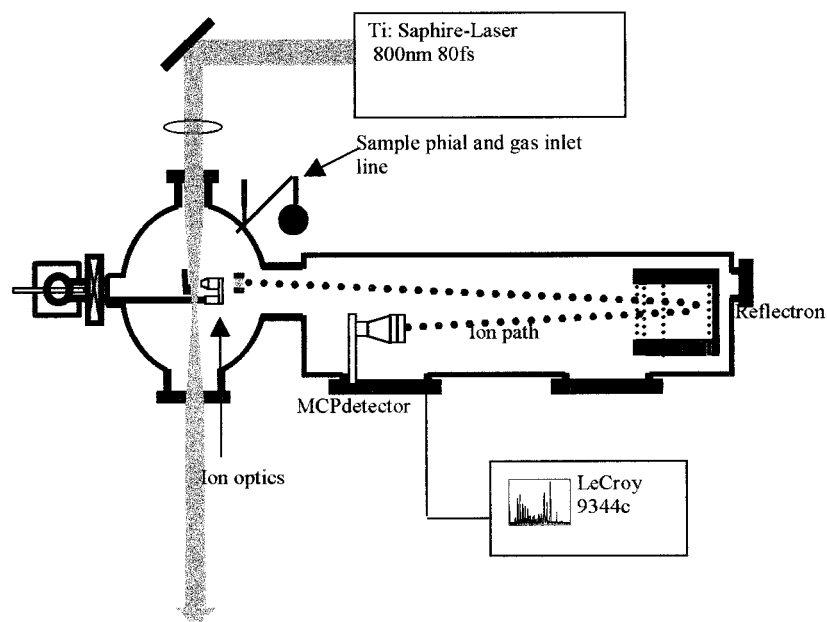


Figure 2. Experimental arrangement.

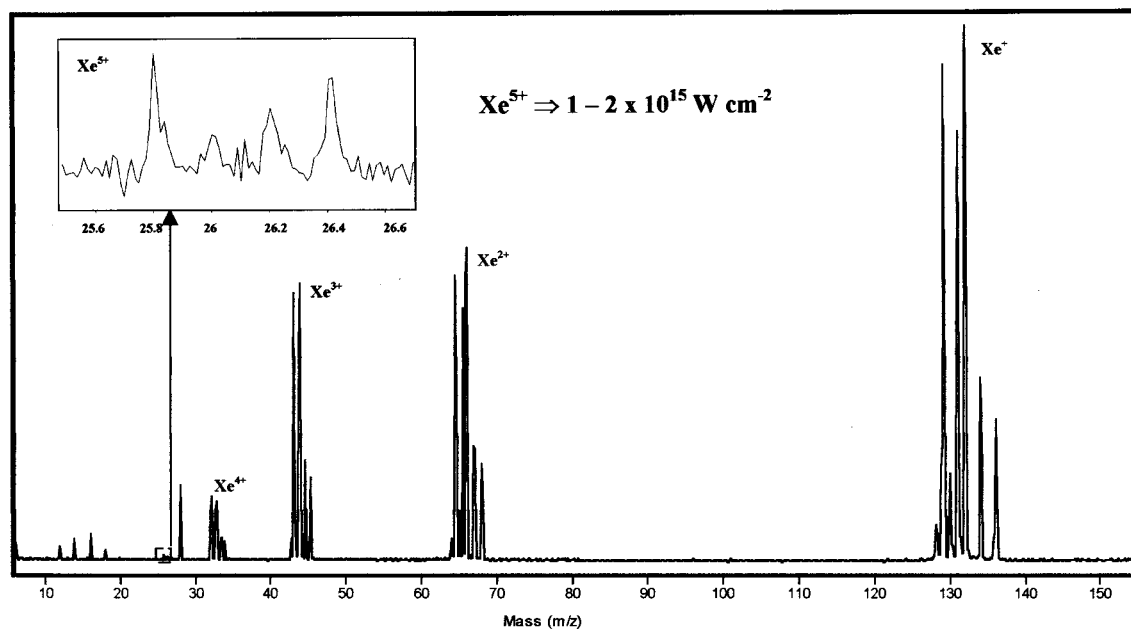


Figure 3. Mass spectrum of xenon taken at a calculated intensity of $1.2 \times 10^{15} \text{ W cm}^{-2}$ (derived using the known pulse parameters). The five observable charged states of this atom correspond to the recorded intensity and therefore provide a verification of this measurement.

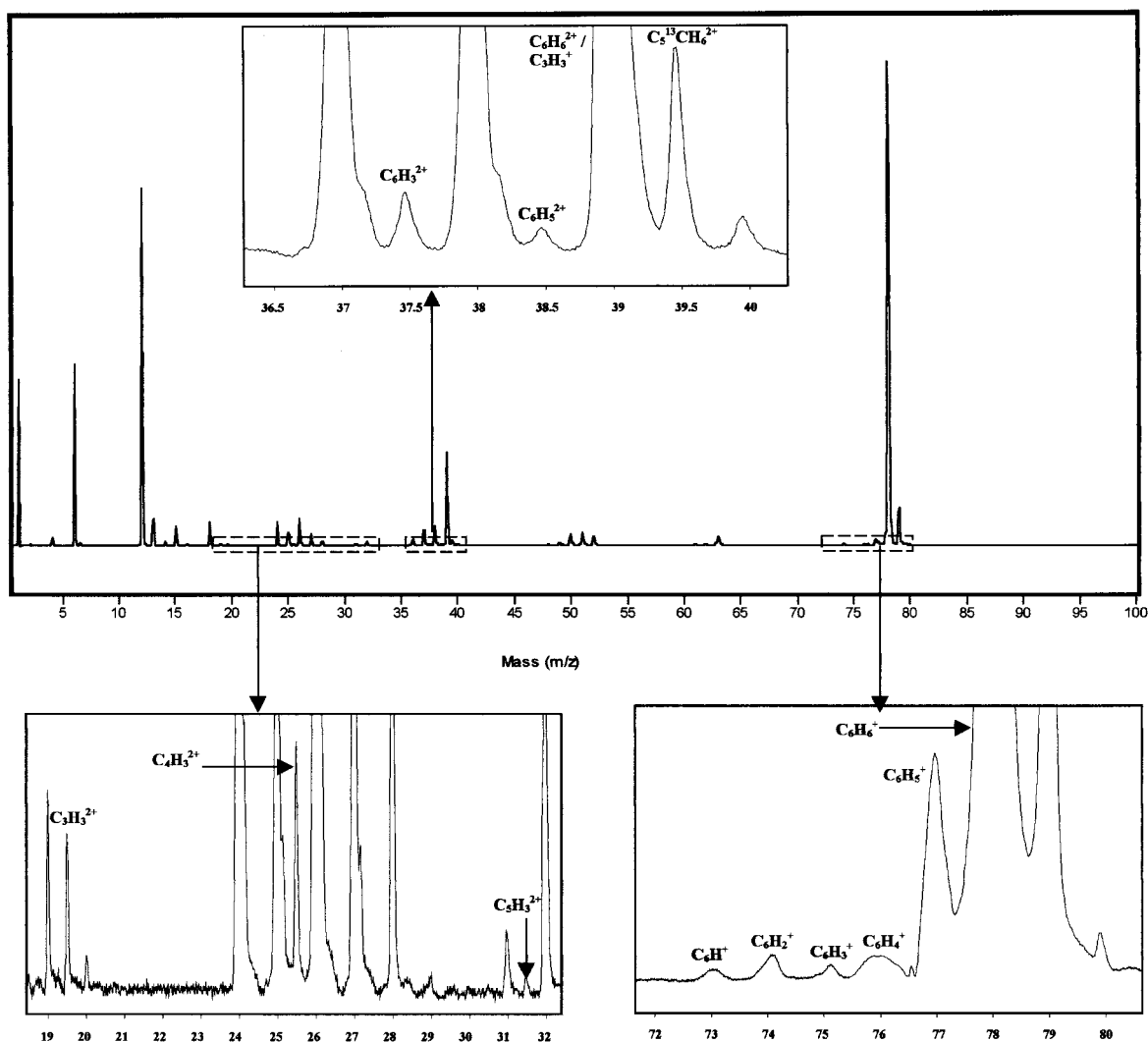


Figure 4. Mass spectrum of benzene recorded at an intensity of $3.5 \times 10^{15} \text{ W cm}^{-2}$.

A strong C_6H_6^+ parent ion is visible in Figure 4 along with a smaller $\text{C}_5^{13}\text{CH}_6^+$ at $m/z = 79$. The lesser of these two peaks

is approximately 7% of the size of the parent ion and the ratio of these isotopes can be used to identify the benzene dication

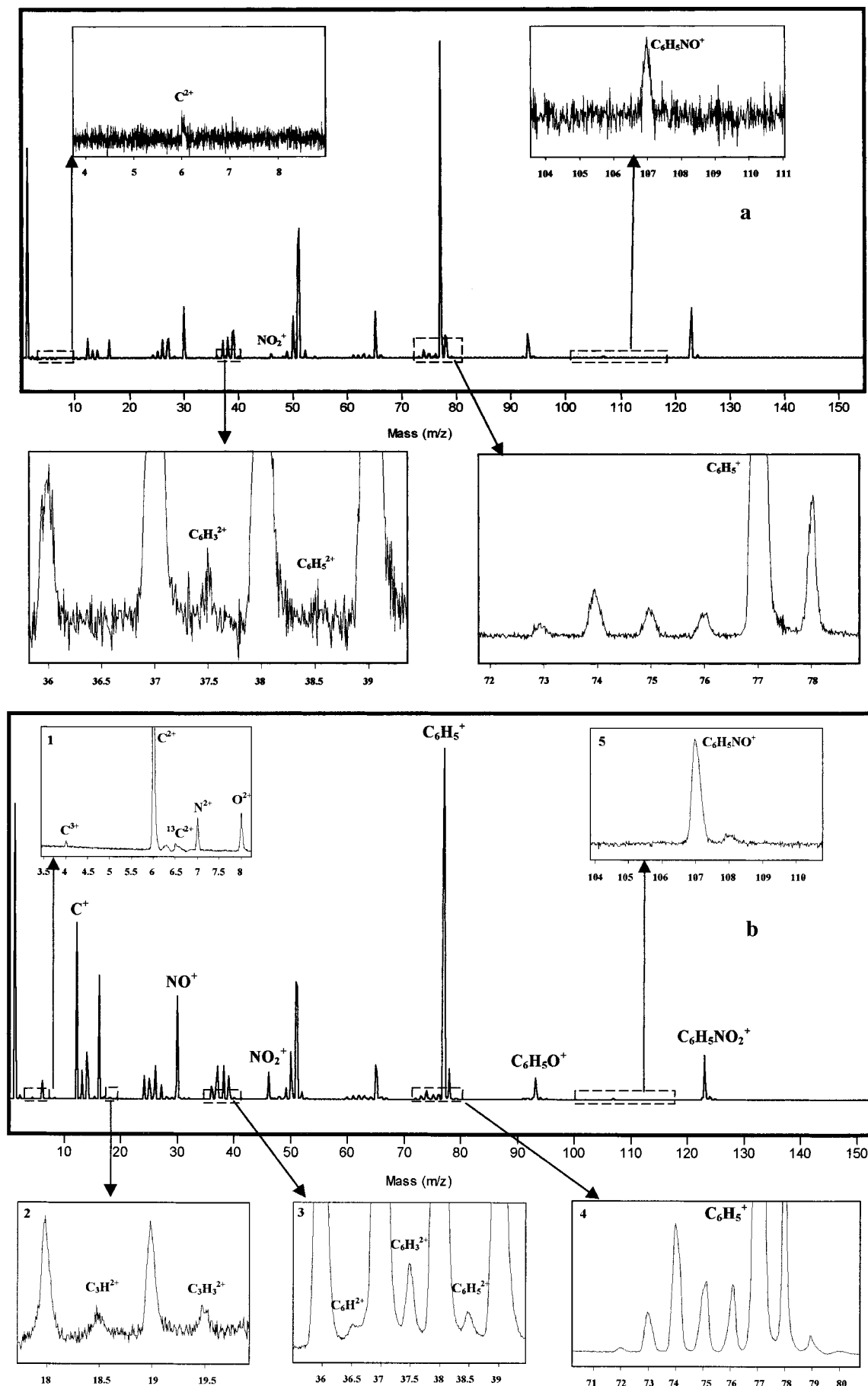


Figure 5. (a) Femtosecond laser mass spectra of nitrobenzene recorded at $1.1 \times 10^{15} \text{ W cm}^{-2}$. (b) Femtosecond laser mass spectra of nitrobenzene recorded at $3.0 \times 10^{15} \text{ W cm}^{-2}$. Insets show enlargements of the following areas: (1) Multiply charged atomic ions; (2, 3) Doubly charged molecular fragments; (4) $[\text{M}-\text{NO}_2]^+$ ion, (5) $[\text{M}-\text{O}]^+$ ion.

TABLE 1: Dissociation Pathways of Nitrobenzene and Their Appearance Potentials

ionic reaction	appearance potential (ev)
$C_6H_5NO_2^+ \rightarrow C_6H_5O^+ + NO$	10.89
$\rightarrow NO^+ + C_6H_5O$	10.89
$\rightarrow C_6H_5^+ + NO_2$	11.08
$\rightarrow C_5H_5^+ + NO + CO$	11.08
$\rightarrow C_3H_3^+ + C_2H_2 + CO + NO$	12.63
$\rightarrow C_4H_3^+ + C_2H_2 + NO$	15.66

at $m/z = 39$. An enlarged inset in the figure displays a peak at $m/z = 39.5$, which can be unambiguously identified as $C_5^{13}CH_6^{2+}$. By taking into consideration the $^{13}C/^{12}C$ ratio for the benzene cation, it is established that the ion peak at $m/z = 39$ corresponds predominantly to the doubly charged parent ion. The dication envelope was also found to contain doubly ionized species attributed to the group of $[M-nH]^{2+}$ ions, with $n = 1-4$.

Other peaks in the mass spectrum corresponding to doubly ionized fragments were observed at $m/z = 19.5$ ($C_3H_3^{2+}$), 25.5 ($C_4H_3^{2+}$), and 31.5 ($C_5H_3^{2+}$). Additional doubly ionized fragments are almost certainly obscured by singly charged ions.

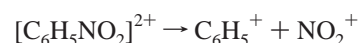
Nitrobenzene. Figure 5(a, b) shows mass spectra for nitrobenzene recorded at intensities of $1.1 \times 10^{15} \text{ W cm}^{-2}$ and $3.0 \times 10^{15} \text{ W cm}^{-2}$ with a pulse duration of 80 fs. Each spectrum displays a prominent molecular ion and the base peak in each case is the $[M-NO_2]^+$ fragment. It is immediately apparent from both the spectra as a whole and from the enlarged local regions that the high resolution throughout enables the unambiguous identification of almost all peaks. In addition, some of these features only become visible after the accumulation of many sweeps (in the present case 10^4).

Although the two spectra display the same structurally characteristic ions, there are notable differences in the low mass fragmentation. The data recorded at $1.1 \times 10^{15} \text{ W cm}^{-2}$ displays relatively few low-mass ions and, with the exception of H^+ and a small C^{2+} peak, no fragments with a mass-to-charge ratio of less than 12. By contrast, the higher intensity spectrum shows a far greater abundance of the CH_n^+ ($n = 1-4$) group as well as the appearance of the C^{3+} ion. The onset of the production of these multiply charged atomic fragments can be attributed to the Coulomb explosion²⁴ of the molecule. At the high intensity used here, the laser electric field is comparable to the internal electrostatic field experienced by the valence electrons. When this is the case, the ejection of these outer electrons produces highly charged transient species which in turn can explode into multiply charged atomic ions.

The dissociation pathways of the nitrobenzene cation are presented in Table 1. Panczel and Baer³² have demonstrated that a cleavage of the C-N bond is responsible for the NO_2 loss from an excited ionic state. Recent work by Kosmidis et al.²² has provided verification of these pathways and the work presented here is in agreement with the previous study. However, one interesting feature observed in the present work, which has not been previously reported, is the double ionization of some high-mass fragments in this molecule. In particular, peaks are clearly visible at $m/z = 38.5$, 37.5, and 36.5 which correspond to the $[M-NO_2]^{2+}$ ($C_6H_5^{2+}$), $[M-NO_2-2H]^{2+}$ ($C_6H_3^{2+}$) and $[M-NO_2-4H]^{2+}$ (C_6H^{2+}) ions. Furthermore, it may be reasonable to expect that the peaks at $m/z = 37$, 38, and 39 also contain a doubly ionized contribution although the integer values of these peaks hinder any direct identification. The peaks at $m/z = 37.5$ and 38.5 are present in the mass spectra taken at both intensities and can be unambiguously identified

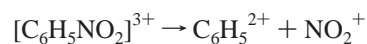
as they fall at half m/z values. Singly charged C_6H_n ($n = 1-5$) fragments have been reported in EI studies of nitrobenzene and they have been recorded in the present experiment too (insert in Figure 5a). It therefore seems reasonable to assume that the doubly charged C_6H_n ions are generated through dissociation channels within the transient doubly charged parent ion and these channels are similar to those observed for the singly charged parent ion (Table 1). This implies, at first glance, that the transient doubly charged nitrobenzene ion preserves the structure of the singly charged parent ion.

Nevertheless, the appearance of the NO_2 ion (Figure 5b) somehow distinguishes the recorded mass spectra of nitrobenzene from those reported previously. To the best of our knowledge, this ion is observed strongly for the first time in mass spectra of nitrobenzene induced by laser beams. Very recently, Cooper et al.³³ have reported the observation of an NO_2 ion in the mass spectra of nitrobenzene induced by synchrotron irradiation. Through this work they found that the appearance energy (AE) for the dissociation channel leading to NO_2 ion production is $26 \pm 1 \text{ eV}$. The IP for the doubly charged nitrobenzene is unknown, but an estimation can be made by using the proposal by Tsai et al.³⁴ that the double ionization potential (IP^{2+}) is 2.8 ± 0.1 times that of single ionization. This therefore implies that the double ionization potential lies within $26.7 \leq IP^{2+} \leq 28.8 \text{ eV}$. In other words, the lower energy limit for the IP^{2+} lies within the experimental error given for the AE of NO_2 ion. Thus, it is reasonable to assume that NO_2 ion production can be attributed to a charged separation process that is taking place within the unstable doubly charged parent ion, i.e.



As discussed above, the onset of doubly charged molecular fragments in the present experiments verifies the double ionization of the parent molecule.

Of course, the onset of C^{3+} ion in the mass spectra of nitrobenzene provides evidence that higher multiply charged (i.e., $q > 2$) species are created in the interaction volume with the laser. Thus, it could be thought that there is a contribution to the NO_2 ion signal from the dissociation of these multiply charged transient molecules through dissociation channels such as



Although these channels cannot be excluded, their contribution is expected to be very small, if any, because the observed relative abundance of NO_2^+ is much higher compared to that of the $C_6H_5^{2+}$ ion.

Small ion peaks were also observed at $m/z = 31.5$ ($C_5H_3^{2+}$), 25.5 ($C_4H_3^{2+}$), 19.5 ($C_3H_3^{2+}$) and 18.5 (C_3H^{2+}). Moreover, it is quite conceivable that additional doubly ionized fragments may be present in the mass spectra but unless they were to fall at half m/z values, it would be difficult to differentiate them from singly charged fragments. It is also worth noting that whereas $[M-NO_2]^+$ was found to be the most abundant of the singly charged ions, the $[M-NO_2]^{2+}$ fragment was not a major component of the doubly charged ion yield.

The comparison of the mass spectra of benzene and nitrobenzene reveals at least two significant differences. The first one concerns the absence of the doubly charged parent ion in the mass spectra of nitrobenzene. As discussed above, there is evidence to suggest that this ion is generated in the interaction volume but is unstable. It is thought that this instability should

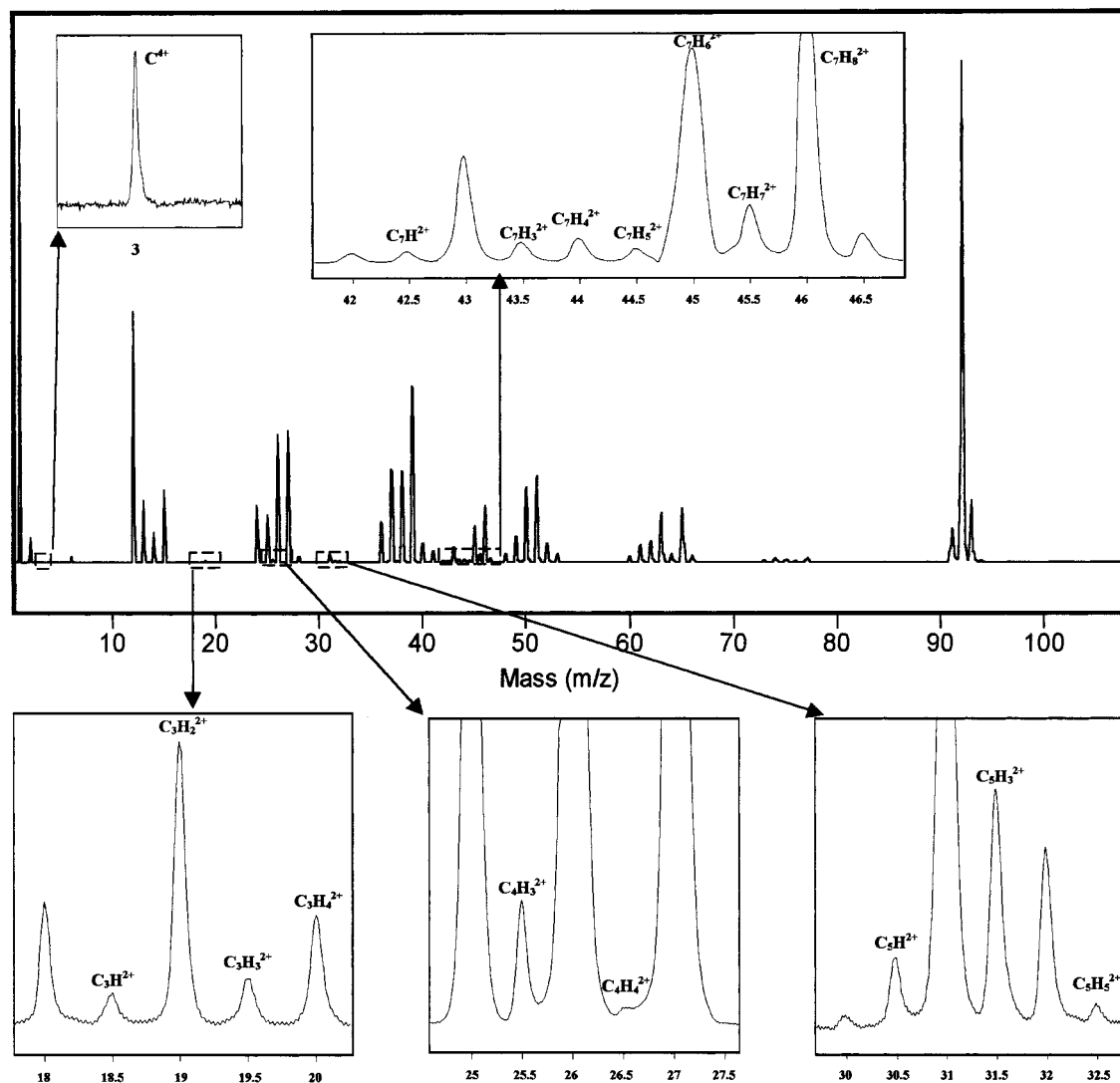


Figure 6. Toluene mass spectrum taken at an intensity of $3.8 \times 10^{15} \text{ W cm}^{-2}$. Singly and doubly charged parent ions are clearly visible.

be attributed to the strong Coulombic repulsion between charges localized in the aromatic and the nitro group.

The second difference is related to the comparatively small abundance of the multiply charged atomic ions in the mass spectra of nitrobenzene. This observation implies that nitrobenzene reaches lower charged states compared to those of benzene. It can therefore be concluded that the molecular coupling with the laser field is more intense in the case of benzene.

Toluene. A mass spectrum of relative ion yield versus mass-to-charge ratio for toluene, taken at an intensity of $3.8 \times 10^{15} \text{ W cm}^{-2}$, is shown in Figure 6. In common with previous studies of toluene carried out by this group,²³ a clear doubly ionized parent ion is evident in the enlarged inset. The identification of this group of peaks is aided by the fact that they fall in an area of the spectrum between the C_3H_n and C_4H_n groups where no singly charged fragments would be expected. Furthermore the use of the isotopic approach used with benzene can be employed to confirm the presence of the $\text{C}_7\text{H}_8^{2+}$ ion. As with the other molecules in this study, several other doubly charged species were observed and are presented in the figure.

One aspect of the ionization of toluene which is easily observable from the mass spectra is the relative abundance of the peaks in the doubly ionized region compared to one another. As expected, doubly charged toluene is the largest peak in this region but as one looks further down the mass spectrum it

appears that the molecule is favoring the double ionization of every second species i.e., $[\text{M}-2\text{H}]^{2+}$ is bigger than $[\text{M}-\text{H}]^{2+}$, $[\text{M}-4\text{H}]^{2+}$ is bigger than $[\text{M}-3\text{H}]^{2+}$, etc. It would seem that the favored dissociation pathway for toluene would involve the removal of two hydrogens simultaneously rather than just a single H atom. This pattern of fragmentation has been observed under laser irradiation for both aromatic^{17,23,35} and nonaromatic^{11;17} molecules, although the effect is more pronounced in the dication envelope for aromatics. In addition to this, it has been reported that the loss of an even number of hydrogen atoms is accompanied by the creation of a double bond in the parent ion.³⁶ If we assume that the present pulse duration makes ladder-switching unlikely, then it seems probable that this favored removal of an even number of H atoms is taking place within the parent. The creation of a double bond in the molecular ion would provide the stability required to enable the observation of these species after travel through the acceleration region. This apparent "odd-even" effect may also be taking place in the photodissociation of benzene. However, as the doubly ionized region of this molecule falls in a part of the spectrum occupied by the C_3H_n group, any observation of this mechanism is rendered impossible.

3-Nitrotoluene. A comparison of the fragmentation of 3-nitrotoluene taken at two different ionizing laser intensities (3.8×10^{15} and $1.2 \times 10^{16} \text{ W cm}^{-2}$) is shown in Figure 7,

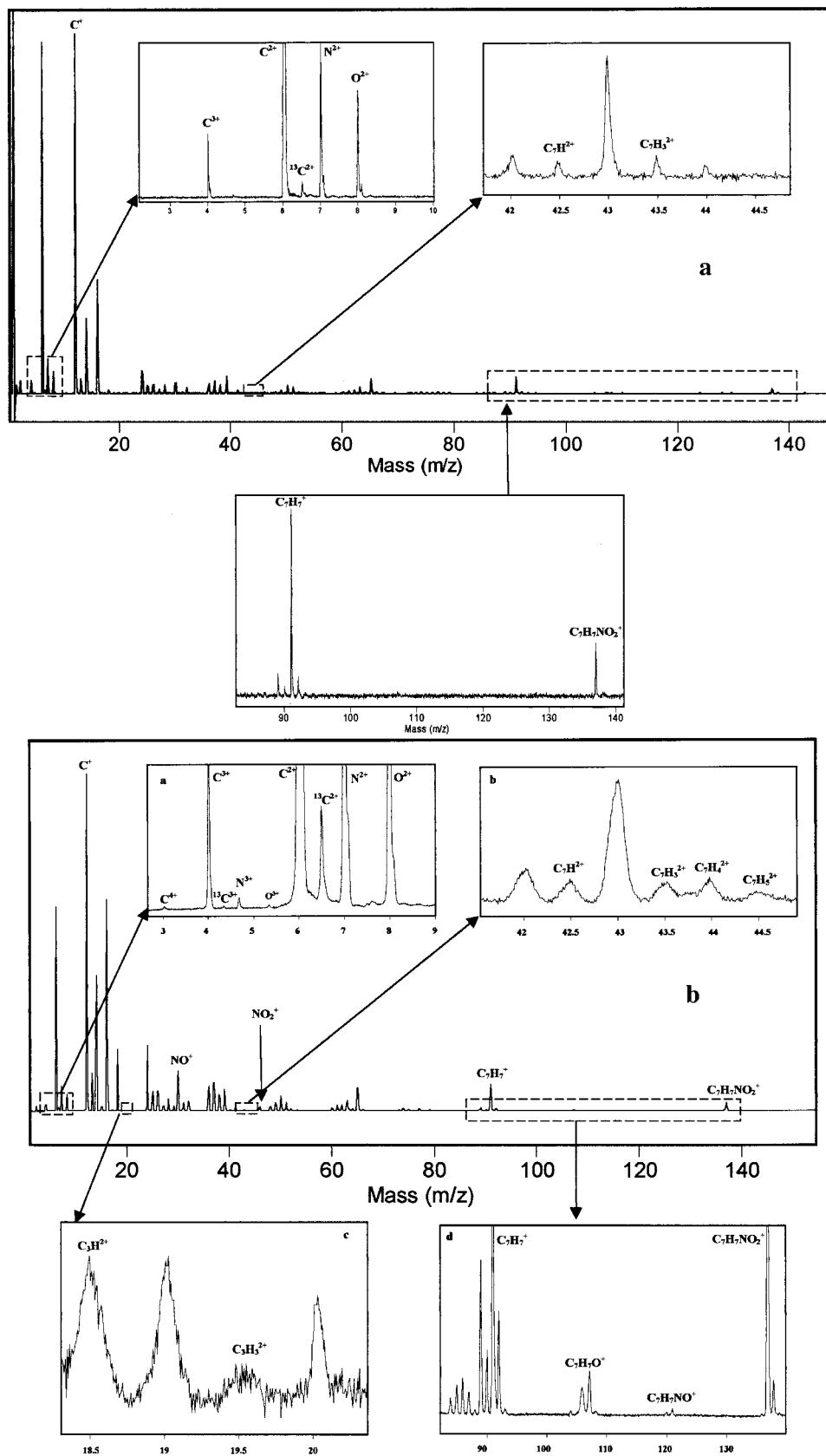


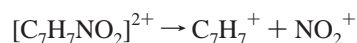
Figure 7. (a) ToF mass spectrum of nitrotoluene recorded at $3.8 \times 10^{15} \text{ W cm}^{-2}$. (b) Femtosecond laser mass spectra of 3-nitrotoluene recorded $1.2 \times 10^{16} \text{ W cm}^{-2}$. Insets are presented for the following regions: (a) Multiply charged atomic fragments; (b, c) Doubly charged molecular fragments; (d) Structurally characteristic ions.

parts a and b. As with nitrobenzene there are obvious and expected similarities between the two spectra: an abundance of low mass fragmentation is present, the $[\text{M}-\text{NO}_2]^+$ ion is the base peak at high mass, and a parent ion peak is observed.

Along with the expected photodissociation products such as $[\text{M}-\text{NO}_2]^+$ and $[\text{M}-\text{NO}]^+$, a doubly ionized molecular region can be seen. As was previously observed for nitrobenzene this region corresponds to the $[\text{M}-\text{NO}_2]^{2+}$ envelope and the doubly

ionized peaks observed here can be unambiguously identified as they fall at half m/z values. It is interesting to note, however, that in the case of nitrotoluene there was no observable double ionization of the principle singly charged high-mass fragment, $[M-NO_2]^+$.

In common with the spectra presented for nitrobenzene, the data shown in Figure 7 allows the observation of the onset of the Coulomb explosion of this molecule. The mass spectrum recorded at an intensity of 1.2×10^{16} W cm⁻² shows an abundance of multiply charged atomic fragments (C^{Z+} , $^{13}C^{Y+}$, N^{Y+} , O^{Y+} , where $Z = 1-3$ and $Y = 1-2$) which are synonymous with the occurrence of a Coulomb explosion^{24;37}. In addition to this, the observation of an NO_2^+ ion at $m/z = 46$ may be indicative of a charge separation process involving a doubly charged transient species. This could occur in the following way



Because any charge separation process is expected to be taking place within a doubly charged parent it is probable that the two ejected electrons were localized in one C-C bond resulting in ring opening. Therefore, as far as the structure of the transient doubly charged parent is concerned, it is believed that an acyclic (linear) formation cannot be excluded. It is noteworthy that ring opening processes induced by strong laser irradiation have been reported recently.³⁷

The observation in the mass spectra (Figure 7b) of C^{3+} and C^{4+} raises the possibility that NO_2 formation may be the byproduct of a Coulomb explosion involving a much higher multiply charged species ($q > 2$). Such a process could occur in the following way



However, in common with nitrobenzene it is thought that this is not the most common dissociation channel because NO_2^+ was found to be far more abundant than the $[M-NO_2]^{2+}$ envelope.

A comparison of the mass spectra for toluene and nitrotoluene reveals similar differences to those found for benzene and nitrobenzene. First, it was found that, whereas a prominent dication was observed for toluene, no doubly charged parent ion was recorded in the mass spectra of nitrotoluene. This is thought to be due to the instability caused by Coulomb repulsion. An even more striking observation is related to the fact that, for the case of nitrotoluene, no pathway was observed for the double ionization of the principle high-mass fragment. Finally, it appears that the laser-molecule coupling is more efficient for toluene. This was apparent from the observation that the onset of C^{4+} production was found to occur at almost an order of magnitude less in the case of the nonnitro molecule. This therefore implies that nitrotoluene reaches lower charged states than toluene for the same intensity.

Conclusions

Femtosecond laser mass spectra have been recorded for the molecules benzene, nitrobenzene, toluene, and nitrotoluene using pulses of 80 fs duration and $\lambda = 800$ nm. An observable parent ion was detected in each case along with other structurally specific high-mass fragment ions. In addition to this, all molecules displayed numerous doubly ionized species in the mass spectra. In the case of the aromatics, these corresponded to a doubly charged parent ion with an additional doubly ionized

contribution coming from certain lower mass fragments. Furthermore, in the envelope of doubly charged toluene ions it was observed that the molecule seemed to favor the double ionization of every second species, leading to an apparent "odd-even" effect in the mass spectra. Various doubly ionized species were also observed for the nitroaromatics although no doubly charged parent was produced for either nitrobenzene or nitrotoluene, possibly due to the rapid dissociation involving the labile NO_2 group. However, the observation of a singly ionized parent for these nitro-molecules along with multiply charged atomic states and, most notably, the group of $[M-NO_2-nH]^{2+}$ ions is indicative of the fact that nanosecond dissociation pathways have been largely defeated by the use of intense femtosecond radiation. A singly ionized NO_2 fragment was also observed for both nitro molecules, and this was thought to suggest a charge separation process involving a transient doubly charged parent ion.

This work highlights the effect that the addition of the substituent NO_2 group has on the ionization and fragmentation of aromatic molecules. The destabilizing effect of this group is particularly prominent in the multiple ionization of the nitroaromatic molecules studied. No doubly charged parent was observed for these molecules and in both cases the most prominent singly ionized fragment was found not to be a major contributor to the doubly ionized yield. Moreover, it was found that the addition of the NO_2 group weakened the laser-molecule coupling.

Acknowledgment. A.D.T. and L.R. would like to acknowledge EPSRC for postgraduate studentships. S.M.H. acknowledges the receipt of a NERC postdoctoral fellowship.

References and Notes

- (1) Ledingham, K. W. D.; Singhal, R. P. *Int. J. Mass Spectrom. Ion Proc.* **1997**, *163*, 149.
- (2) DeWitt, M. J.; Levis, R. J. *J. Chem. Phys.* **1999**, *110*, 11 368.
- (3) Lubman, D. D.; Naaman, R.; Zare, R. N. *J. Chem. Phys.* **1980**, *72*, 3034.
- (4) Boesl, U.; Neusser, H. J.; Schlag, E. W. *Chem. Phys. Lett.* **1982**, *87*, 1.
- (5) Gedanken, A.; Robin, M. B.; Kueblar, N. A. *J. Phys. Chem. A* **1982**, *86*, 4096.
- (6) Yang, J. J.; Gobeli, D. A.; El-Sayed, M. A. *J. Phys. Chem. A* **1985**, *89*, 3426.
- (7) Zandee, L.; Bernstein, R. B. *J. Chem. Phys.* **1979**, *71*, 1359.
- (8) Protopapas, M.; Keitel, C. H.; Knight, P. L. *Rep. Prog. Phys.* **1997**, *60*, 389.
- (9) Keldysh, L. V. *Sov. Phys. JETP* **1960**, *20*, 1307.
- (10) Ilkov, F. A.; Decker, J. E.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1992**, *25*, 4005.
- (11) Prall, B. S.; DeWitt, M. J.; Levis, R. J. *J. Chem. Phys.* **1999**, *111*, 2865.
- (12) Kosmidis, C.; Tzallas, P.; Ledingham, K. W. D.; McCanny, T.; Singhal, R. P.; Taday, P. F.; Langley, A. J. *J. Phys. Chem. A* **1999**, *103*, 6950.
- (13) Muller, A. M.; Uiterwaal, C. L. G. L.; Witzel, B.; Wanner, B.; Kompa, K.-L. *J. Chem. Phys.* **2000**, *112*, 9289.
- (14) Talebpour, A.; Larochelle, S.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, 2769.
- (15) Shimizu, S.; Kou, J.; Kawato, S.; Shimizu, K.; Sakabe, S.; Nakashima, N. *Chem. Phys. Lett.* **2000**, *317*, 609.
- (16) Nakashima, N.; Shimizu, S.; Yatsuhashi, T.; Sakabe, S.; Izawa, T. *J. Photochem. Photobiol. C: Photochem. Rev.* **2000**, *1*, 131.
- (17) Cornaggia, C. *Phys. Rev. A* **1995**, *52*, 4328.
- (18) Castillejo, M.; Couris, S.; Koudoumas, E.; Martin, M. *Chem. Phys. Lett.* **1999**, *308*, 373.
- (19) Kosmidis, C.; Ledingham, K. W. D.; Clark, A.; Marshall, A.; Jennings, R.; Sander, J.; Singhal, R. P. *Int. J. Mass Spectrom. Ion Proc.* **1994**, *135*, 229.
- (20) Ledingham, K. W. D.; Kilic, H. S.; Kosmidis, C.; Deas, R. M.; Marshall, A.; McCanny, T.; Singhal, R. P.; Langley, A. J.; Shaikh, W. *Rap. Comm. Mass Spectrom.* **1995**, *9*, 1522.

- (21) Tonnies, K.; Schmid, R. P.; Weickhardt, C.; Reif, J.; Grottemeyer, J. *Int. J. Mass Spectrom.* **2001**, *206*, 245.
- (22) Kosmidis, C.; Ledingham, K. W. D.; Kilic, H. S.; McCanny, T.; Singhal, R. P.; Langley, A. J.; Shaikh, W. *J. Phys. Chem. A* **1997**, *101*, 2264.
- (23) Ledingham, K. W. D.; Smith, D. J.; Singhal, R. P.; McCanny, T.; Graham, P.; Kilic, H. S.; Peng, W. X.; Langley, A. J.; Taday, P. F.; Kosmidis, C. *J. Phys. Chem. A* **1999**, *103*, 2952.
- (24) Smith, D. J.; Ledingham, K. W. D.; Singhal, R. P.; McCanny, T.; Graham, P.; Kilic, H. S.; Tzallas, P.; Langley, A. J.; Taday, P. F. *Rap. Comm. Mass Spectrom.* **1999**, *13*, 1366.
- (25) Marshall, A.; Clark, A.; Jennings, R.; Ledingham, K. W. D.; Singhal, R. P. *Int. J. Mass Spectrom. Ion Proc.* **1992**, *112*, 273.
- (26) Tasker, A. D.; Robson, L.; Hankin, S. M.; Ledingham, K. W. D.; Singhal, R. P.; Fang, X.; McCanny, T.; Kosmidis, C.; Tzallas, P.; Langley, A. J.; Taday, P. F.; Divall, E. J. *Las. Part. Beams* **2001**, *19*, 205.
- (27) Borthwick, I. S. *Ph.D. Thesis, University of Glasgow*, 1993.
- (28) Jaroszynski, D. A.; Ersfeld, B.; Giraud, G.; Jamison, S.; Jones, D. R.; Issac, R. C.; McNeil, B. M. W.; Phelps, A. D. R.; Robb, G. R. M.; Sandison, H.; Vieux, G.; Wiggins, S. M.; Wynne, K. *Nucl. Instrum. Methods Phys. Res. A* **2000**, *445*, 317.
- (29) Larochele, S.; Talebpour, A.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, 1201.
- (30) Talebpour, A.; Bandrauk, A. D.; Chin, S. L. *Laser Physics* **2000**, *10*, 210.
- (31) Itakura, R.; Watanabe, J.; Hishikawa, A.; Yamanouchi, K. *J. Chem. Phys.* **2001**, *114*, 5598.
- (32) Panczel, M.; Baer, T. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *58*, 43.
- (33) Cooper, L.; Shpinkova, L. G.; Rennie, E. E.; Holland, D. M. P.; Shaw, D. A. *Int. J. Mass Spectrom.* **2001**, *207*, 223.
- (34) Tsai, B. P.; Eland, J. H. D. *Int. J. Mass Spectrom. Ion Proc.* **1980**, *36*, 143.
- (35) Tzallas, P.; Kosmidis, C.; Philis, J. G.; Ledingham, K. W. D.; McCanny, T.; Singhal, R. P.; Hankin, S. M.; Taday, P. F.; Langley, A. J. *Chem. Phys. Lett.* **2001**, *343*, 91.
- (36) Porter, Q. N.; Baldas, J. *Mass Spectrometry of Heterocyclic Compounds*; Wiley: New York, 1971.
- (37) Tzallas, P.; Kosmidis, C.; Ledingham, K. W. D.; Singhal, R. P.; McCanny, T.; Graham, P.; Hankin, S. M.; Taday, P. F.; Langley, A. J. *J. Phys. Chem. A* **2001**, *105*, 529.
- (38) Nishimura, T.; Das, P. R.; Meisels, G. G. *J. Chem. Phys.* **1986**, *84*, 6190.