On the Fragmentation of Nitrobenzene and Nitrotoluenes Induced by a Femtosecond Laser at 375 nm

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The photodissociation of nitrobenzene and the nitrotoluene isomers at 375 nm, induced by a 90 femtosecond laser, is analyzed and compared with the fragmentation by a 10 nanosecond laser at the same wavelength. The molecular ionization is attributed to a nonresonant multiphoton process, and the observed fragmentation can be explained predominantly by an above ionization mechanism (ladder climbing). The mass spectra of the three nitrotoluene isomers show differences which can be used for analytical purposes. The molecular rearrangement taking place prior to the dissociation is also discussed. For nitrobenzene, it is suggested that most of the dissociation occurs from the nitrobenzene structure rather than that of phenyl nitrite. In the case of *o*-nitrotoluene, it seems that the hydrogen transfer from the $-CH_3$ to the NO_2 group (ortho effect) is favored in ionic states, while the rearrangement to a nitrite structure is possible in the excited electronic states.

Introduction

The photodissociation of nitrobenzene and the nitrotoluene isomers has been extensively studied using different techniques.[1−13] The fragmentation pathways of these molecules have recently been identified by nanosecond UV laser studies.[14−16] Dissociation occurs through multiphoton processes and has been interpreted by two main fragmentation mechanisms.[15,16] In the first mechanism, fragmentation of the neutral molecule is followed by ionization (DI mechanism[17]), while in the second ionization is followed by dissociation (ID mechanism).

Despite the extensive studies, the fragmentation pathways of these molecules are not well understood. Complications arise from the fact that some of the recorded fragments can be attributed to a molecular isomerization (rearrangement). Thus, the −NO loss dissociation channel in nitrobenzene and in some nitrotoluenes can be more easily explained if a molecular rearrangement takes place prior to fragmentation. A change of the nitrobenzene to phenyl nitrite structure, i.e. a change of $C-NO_2$ to a $C-ONO$ bond, could be such a rearrangment.

In a recent work by Clenewinkel-Meyer and Crim,[18] a theoretical treatment of the nitrobenzene isomerization has been presented. They concluded that phenyl nitrite is stable with respect to dissociation into phenoxy (C_6H_5O) and nitric (NO) radicals, and the estimated barrier between the two isomers (nitrobenzene−phenyl nitrite) is about 1.13 eV. In this model, after internal conversion of the energy, the excited nitrobenzene molecule undergoes a rearrangement into vibrationally excited phenyl nitrite which subsequently dissociates. To the best of our knowledge, there are no similar calculations for the case of the nitrotoluenes, although the −NO loss channel has also been observed for these molecules.[16]

Moreover, an additional dissociation channel, related to the −OH loss, has been recorded for *o*-nitrotoluene. This channel can proceed only after a molecular rearrangement and has been studied extensively,[6,19−21] but until now the structure of the intermediate species remains unclear.

In the present work, the fragmentation of nitrobenzene and the three nitrotoluene isomers has been studied at 375 nm using 90 femtosecond laser pulses. The potential of the femtosecond mass spectrometry for analytical purposes has been demonstrated recently.[22] It was shown that the molecular ion can be reached with high efficiency bypassing dissociative molecular excited states and that ladder-switching processes from both neutral and ionic states are suppressed. In the present work the ability of a femtosecond laser-based system for elucidating fragmentation dynamics and the identification of the three nitrotoluene isomers is discussed.

Experimental Section

The experimental setup has been described in detail elsewhere.[15,22] Briefly, pulses of 45 femtosecond duration are produced from a mode-locked titanium sapphire oscillator pumped by an argon ion laser (both Spectra Physics). A simple stretcher was used to chirp the pulses to about 700 femtosecond prior to amplification in a three-stage dye laser (LDS 751). The pulses were recompressed to 90 femtosecond by a 4 cm block of SF10 glass. The pulses at $\lambda = 375$ nm were produced by focusing the output of the laser into a 200 μm thick type 1 BBO crystal. Before entering the time-of-flight (TOF) chamber, the pulse energy was typically 10 μJ before being focused with a 30 cm fused silica lens to provide estimated intensities of about 10^{13} W cm^{-2}.

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TABLE 1: Dissociation Reactions of Nitrobenzene and Their Appearance Potentials

neutral reaction	appearance[a] potential (eV)	ionic reaction	appearance[b] potential (eV)
$C_6H_5NO_2 \rightarrow C_6H_5 + NO_2$	3.05 (1)	$C_6H_5NO_2^+ \rightarrow C_6H_5O^+ + NO$	10.89 (4)
$\rightarrow C_6H_5O + NO$	0.74 (2)	$\rightarrow NO^+ + C_6H_5O$	10.89 (5)
$\rightarrow C_6H_5NO + O$	3.96 (3)	$\rightarrow C_6H_5^+ + NO_2$	11.08 (6)
		$\rightarrow C_5H_5^+ + NO + CO$	11.08 (7)
		$\rightarrow C_3H_3^+ + C_2H_2 + CO + NO$	12.63 (8)
		$\rightarrow C_4H_3^+ + C_2H_2 + NO$	15.66 (9)

[a] Reference 14. [b] Reference 33.

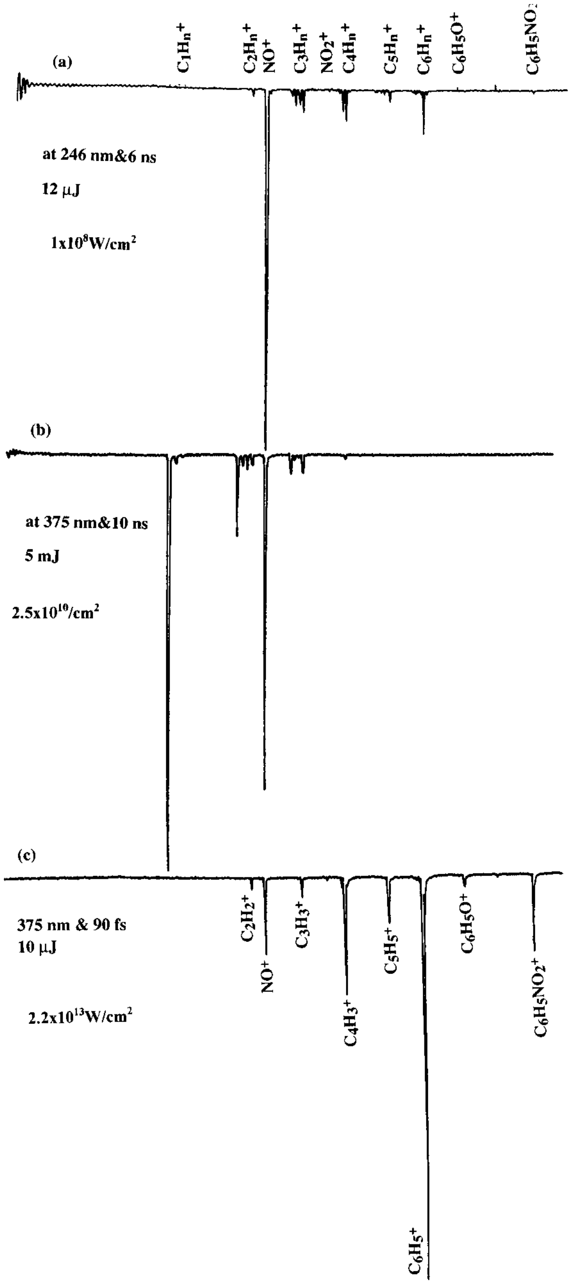

Figure 1. Mass spectra of nitrobenzene (NB) induced by (a) 6 ns laser pulses at $\lambda = 246$ nm (pulse energy = 12 μJ), (b) 10 ns laser pulses at 375 nm (5mJ), and (c) 90 femtosecond laser pulses at 375 nm and 10 μJ. All the spectra were recorded using the same TOF and signal-processing system. The corresponding laser intensities are shown.

The nanosecond laser system consists of a XeCl excimer pumped dye laser (Lumonics TEM860-M and EPD330) with pulse width of about 10 ns. For 375 nm, TMI dye was used, while the laser beam at 246 nm was generated by frequency doubling the coumarin 47 dye output with a BBO crystal. The mass spectra were recorded with a linear TOF spectrometer of length 1.2 m, based on a Wiley-McLaren design with a typical mass resolution of 200 at 100 Da. The samples were introduced effusively from the inlet system to the vacuum chamber through a needle valve. The ions were detected by a Thorn EMI electron multiplier connected with a LeCroy 9304 digital oscilloscope.

The same mass spectrometer and signal-processing system were used in the experiments with both the femtosecond and nanosecond lasers. The samples were obtained from the Aldrich Chemical Co and were used as supplied by the manufacturers.

Results and Discussion

The electric field from a focused femtosecond laser is very intense and nearly matches or even surpasses the molecular Coulombic field felt by the valence electrons. Under such conditions the ionization of the molecules can take place through a field ionization (tunneling ionization) mechanism or through multiphoton absorption−ionization processes. It should be pointed out that for high laser intensities, saturation of the ionization processes takes place before tunneling takes place. A qualitative criterion for the kind of mechanism involved in the ionization is the adiabatic parameter γ, defined by Keldysh[23]

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

where E_i is the zero-field ionization potential expressed in eV, I is the laser intensity in W/cm^2, and λ is the laser wavelength in μm. When $\gamma \ll 1$ field ionization prevails, while for $\gamma \gg 1$ multiphoton processes are the main mechanism. Recently this criterion has been reconsidered, and a more pragmatic definition of tunneling ionization is $\gamma < 0.5$.[24] DeWitt and Levis[25] attributed the photoionization time-of-flight mass spectra of some polyatomic molecules to a field ionization mechanism, although for some of the studied molecules the Keldysh parameter was greater than unity ($\gamma = 4.5$) at the lower laser power densities used. Alternatively Chun He and Becker[26] in a very recent paper dealing with photoionization of both sputtered and gaseous samples have claimed that for laser intensities $<7 \times 10^{13}$ W/cm^2 at 532 nm, multiphoton ionization is the dominating process. In the present work, the calculated values for the Keldysh parameter are between 3.5 and 11 for the range of the laser power densities applied. These values are in the intermediate regime, and, at least for the higher laser intensities and at the wavelength used, field ionization may become an important mechanism.

The ionization potential (IP) for the four molecules studied in this work has been reported to be 9.86 eV for nitrobenzene[27] and 9.42, 9.45, and 9.46 eV for *o*-, *m*-, and *p*-nitrotoluene, respectively.[9,21,27] Therefore, multiphoton ionization at 375 nm requires at least the absorption of three photons. The absorption of the first photon is not a resonant step, while the second photon brings the molecules to an excited electronic state (6.6 eV), whose broad one-photon absorption spectrum implies short lifetimes and thus the existence of very fast nonradiative processes.[28] For ionization to take place, these nonradiative processes must be “defeated” and it is believed that this can be achieved by using ultrashort laser pulses. In the case of some small molecules, fragmentation prior to the ionization even with ultra short laser pulses; i.e. a DI mechanism,[29] has been observed. However, for polyatomic molecules the dominant mechanism seems to be the ID route when short pulses are used and the fragment ions are generated through a ladder-climbing mechanism.[30,31] The latter means that for extremely short laser pulse widths the photon absorption occurs only in the parent molecular ion from which all smaller fragments originate either directly or indirectly.

Nitrobenzene. Figure 1 shows the laser-induced mass spectra of nitrobenzene with (a) $\lambda = 246$ nm and 6 nanosecond pulse duration, (b) $\lambda = 375$ nm and 10 nanosecond pulse duration, and (c) $\lambda = 375$ nm and 90 femtosecond pulse duration. All spectra have been recorded using the same experimental setup. A comparison of the mass spectra of some other nitro-aromatics using nanosecond and femtosecond laser pulses has been presented elsewhere.[22]

As far as the different dissociation pathways are concerned, it is obvious that their identification is almost impossible from the mass spectrum produced with a nanosecond laser at 375 nm, because this is dominated by the small mass ion peaks. These peaks are generated from the sequential dissociation of the daughter fragments (ladder-switching mechanism). This is due to the long laser pulse duration and the relatively high pulse energies needed for the three-photon ionization process. In the nanosecond excitation regime at shorter wavelengths, much lower laser intensities are sufficient for the molecular ionization (Figure 1a). Even at 246 nm, when molecular ionization can be achieved via a $(1 + 1)$ excitation process, the heavier mass ion peaks are extremely weak.[16] Using a 90 femtosecond pulsed laser at 375 nm, the heavy mass ion peaks become prominent (Figure 1c), and the mass spectrum represents more precisely the primary fragmentation pattern of the parent molecule.

In Table 1 the known dissociation channels of nitrobenzene and its molecular ion are presented. It is worth noting that no nitrosobenzene (C_6H_5NO) ions ($m/e = 107$) were detected in the photodissociation studies of the nitrobenzene ion.[32,33] Therefore the presence of the $m/e = 107$ peak in the mass spectra of nitrobenzene could be evidence of a DI route.[15] The thermochemical threshold for the -O loss channel (reaction 3) is 3.96 eV, and the absorption of two photons ($\lambda = 375$ nm) is required for the observation of this channel. This two-photon absorption corresponds to the $W_s \leftarrow W_0$ excitation (the notation of Nagakura et al.[28] is followed) which is equivalent to the $\pi\pi^*$ $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene. In the mass spectra induced by the femtosecond laser (Figure 1c), the nitrosobenzene ion is almost absent. The extremely weak appearance of the $m/e = 107$ peak could be explained by the assumption that the dissociation processes are much slower than the time duration of the laser pulse.

The power dependence (Figure 2 a,b) of the parent molecular ion production was found to be about $n = 2.2$, which supports a three-photon absorption process. It can also be seen that in Figure 2b the gradients of the principal fragments are similar to that of the parent. The near absence of the nitrosobenzene ion peak and the power dependences support the hypothesis that after the absorption of three photons to produce the molecular ion, dissociation takes place.

The dissociation pathways presented in Table 1 are verified by the ion peaks which appear in the femtosecond mass spectra (Figure 1c). It can be seen that the ions produced in reactions 4−9 are the ones which are generated first in the femtosecond spectra at the lowest laser intensities. As the intensity increases, other peaks become visible, almost certainly produced by ladder switching from the ion state. In addition, peaks with $m/e = 27$ and $m/e = 17$ (at the highest laser intensities) have been observed. The latter is attributed to OH^+, and an explanation for its presence has been given recently,[22] while the $m/e = 27$ peak could be assigned to HCN^+ or to $C_2H_3^+$.

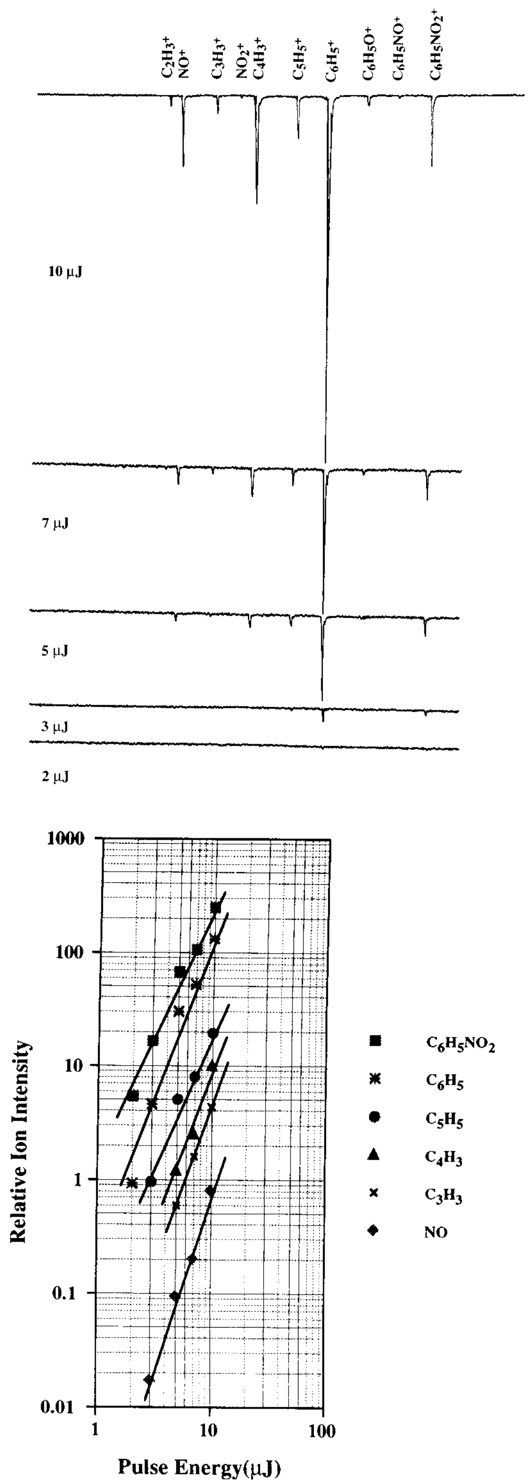

Figure 2. (a) Mass spectra of NB induced by 90 femtosecond laser pulses at 375 nm and several different pulse energies. (b) Intensities of the different ion peaks as a function of laser pulse energy. The gradient of the parent ion peak is about 2.2, and the other fragment gradients are similar.

Because of the low molecular symmetry (C_{2v}) of $C_6H_5NO_2$, the matrix elements for electric dipole multiphoton transitions are nonzero for all initial and final states regardless of their symmetry. Thus, all ionic states appearing in the (single-photon) photoelectron spectra[34] can be reached in the present experiment without selection rules restrictions.

Panczel and Baer[35] concluded that the $-NO_2$ loss occurs from an excited electronic state of the ion by a simple C−N bond cleavage. This implies the preservation of the nitrobenzene structure at least for this reaction, and it was the first time that the direct dissociation from an excited state was reported for such a large ion as nitrobenzene. The transition to the excited electronic states of the parent ion is interesting because it is related with the proposed generation of $C_6H_5^+$ and $C_5H_5^+$ ions by their direct dissociation.[32] It should be noted that the $-NO_2$ loss channel and all the other reactions of Table 1 are also compatible with the isomerization to the phenyl nitrite structure by breaking the C_6H_5-ONO bond or the C_6H_5O-NO bond and so on. The −NO loss channel is favored in a phenyl nitrite structure and can be formed through the vibronic relaxation of electronic excited states of the nitrobenzene ion. This is consistent with the relatively low appearance potential (AP) of the −NO loss channel. The internal conversion of the electronic excitation energy of the ion requires the absence of strongly repulsive excited states, which would cause fast decomposition before much of the electronic energy is degraded. This condition could be satisfied for excitations from molecular orbitals (MOs) which are not localized in one particular bond. Such are the π-MOs of the aromatic ring, which are spread all over the ring, and therefore their excitation causes a small weakening of all bonds. On the other hand, excitation from a MO localized on one bond results in a drastic weakening of this particular bond, causing the resulting electronic state to be strongly repulsive. It has been proposed for nitrobenzene that the first two IPs correspond to excitations from a ring π-type MO.[34] Thus, the excitation to these ionic states is likely to be followed by electronic to vibronic energy redistribution, and the resulting molecular rearrangement could provide the reasons for the observation of $C_6H_5O^+$ and NO^+ ions.

To the best of our knowledge there is no assignment for the bands appearing in the photoelectron spectra produced by the absorption of four and five photons with $\lambda = 375$ nm. In any case the $-NO_2$ loss channel which has been shown to take place from an excited state,[35] is expected to be generated by an excitation from a localized MO, presumably from an n-type MO. Furthermore, since the efficiency of the ion detector used is essentially the same for all the ion masses recorded in this experiment and photodissociation of the daughter fragments is expected to be limited on the femtosecond time scale, the relative intensities of the peaks in the mass spectra can be regarded as indicative of the branching ratios between different pathways (Table 1). Since $C_6H_5^+$ is the base peak in the spectrum, it may be concluded that the majority of the molecules fragment from the nitrobenzene structure. This is in agreement with the results of collision-induced-dissociation (CID) experiments conducted by Cassady et al.[36]

Nitrotoluene Isomers. A comparison of the fragmentation of *m*-NT at 375 nm for both femtosecond and nanosecond pulses is shown in Figure 3. This shows that the ionization efficiency for the same pulse energy is much greater for femtosecond fragmentation than for nanosecond pulses, a conclusion which has also been reached by Aicher et al.[37] In addition, the femtosecond fragmentation produces a lot more heavy mass fragments including a strong parent mass. It is clear that the femtosecond spectrum has a much greater potential for analytical and structural interpretation than the nanosecond spectrum. The femtosecond mass spectra at similar pulse energies for the three nitrotoluene isomers are presented in Figure 4. The parent ion peak and a number of heavier mass peaks are clearly recorded for all isomers, while these were missing when nanosecond pulses of the same wavelength were used.

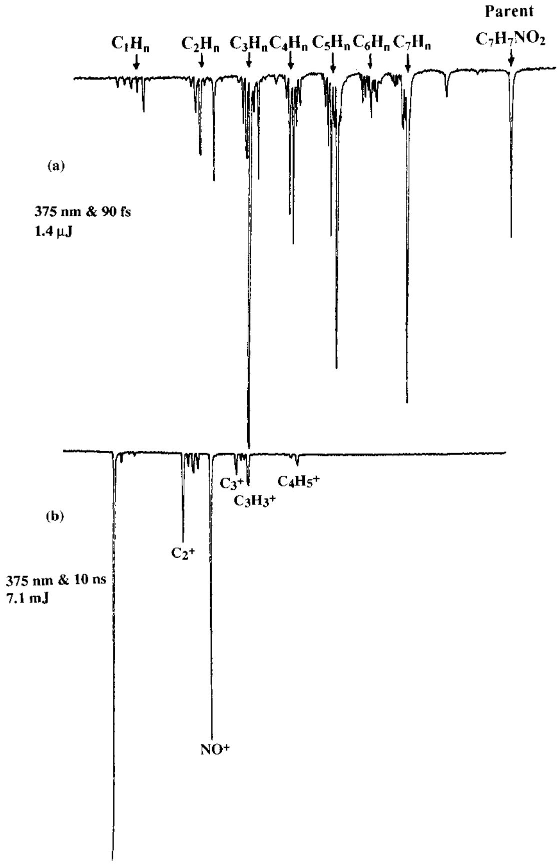

Figure 3. Comparison of femtosecond and nanosecond fragmentation spectra from *m*-NT at 375 nm. Only the femtosecond spectrum shows the parent and heavy mass peaks.

Figure 5 shows the power dependence for the parent peak and the most prominent peaks for *m*-NT. The power dependence in this case is only between 1 and 1.5 for the parent and the fragments, and since it requires three photons to ionize the isomers, two of the steps must be close to saturation at these laser intensities. The power dependence of a two-or three-photon absorption process in molecules is often dependent only on the first step since subsequent steps are generally saturated.[38] The power dependence of the parent ion production using nanosecond pulses[16] was also about 1 whereas that of the NO ion was about 3, indicating that both DI and ID channels were operating in the nanosecond regime. In the present experiment however, using femtosecond pulses, the gradients for all the fragment power dependences are very similar, suggesting that ID is likely to be the principal dissociation mechanism. The power dependences of the other isomers were similar.

The differences in the femtosecond laser-induced mass spectra of the nitrotoluene isomers facilitate the identification of the three isomers. For their identification many techniques have been used, including liquid and gas chromatography, ion mobility spectrometry,[39] cyclotron resonance mass spectrometery,[40,36] and laser mass spectrometry.[16] The increased activity for their detection is clearly related to the strategic importance of these molecules.[41] Using 90 femtosecond laser pulses at 375 nm, the mass spectra of nitrotoluenes offer some unique "fingerprints" (Figure 6), which allow their easy distinction taking into account only the four heavier mass ion peaks (m/e = 92, 120, 121, 107). Thus, apart from the relatively intense parent ion peak in the mass spectra of the isomers, which is very important for analytical purposes, the peak at m/e = 120

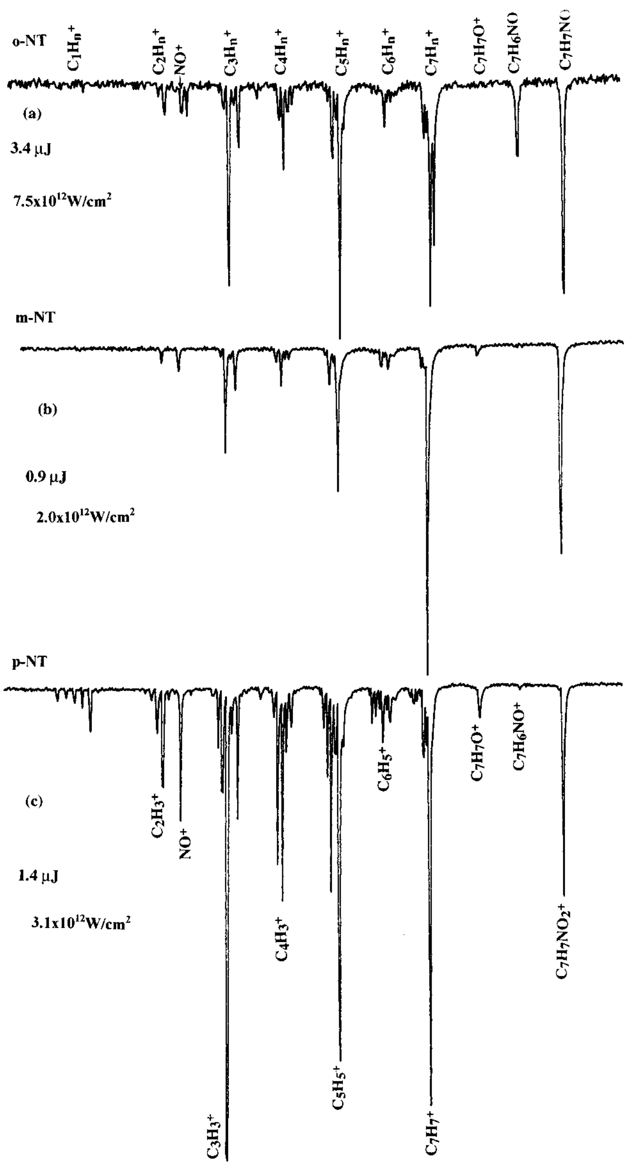

Figure 4. Mass spectra for the three isomers of nitrotoluene at similar pulse energies recorded using 90 femtosecond pulses at 375 nm.

is apparent (with no peak at *m*/*e* = 107) only in the mass spectra of *o*-nitrotoluene, the peak at *m*/*e* = 121 (accompanied by a peak at *m*/*e* = 107) has been recorded only in *p*-nitrotoluene, and while in the mass spectra of *m*-nitrotoluene none of the peaks at *m*/*e* = 121, 120 have been detected and the parent ion peak is accompanied only by the *m*/*e* = 107 peak. The peak at *m*/*e* = 92 [C_6H_6N] is a prominent feature only in the *o*-NT spectrum and has been seen in nanosecond fragmentation of both the parent molecule and ion studies.[16,18,40]

When the laser wavelength was changed to 750 nm and the intensity increased to about 10^{14} W cm^{-2}, the fragmentation pattern of the *o*-NT relative to that taken at 375 nm changed. Figure 7 shows the two spectra taken at approximately the same pulse energy. It can be seen that for the longer wavelength the intensities of the heavier fragments is reduced. The heavier part of the mass spectra for the *o*-and *m*-isomers is shown in Figure 8 indicating that for the *o*-NT the parent ion peak has almost disappeared and the −OH loss peak has grown substantially while the *m*-isomer retains its parent mass peak.

The irradiation of *o*-nitrotoluene with nanosecond laser pulses in the 210−270 nm wavelength region[16] has shown the existence of some other reactions like the −NO loss, the −O loss, and −OH loss channels. Using nanosecond laser pulses, the first two channels were detected also for the other two isomers. It is interesting to note that the −NO loss reaction has not been observed in the electron impact spectra of *o*-nitrotoluene, and its appearance in the nanosecond laser-induced spectra has been attributed to a DI route after a rearrangement of the C−NO_2 bond to a C−ONO structure.[16]

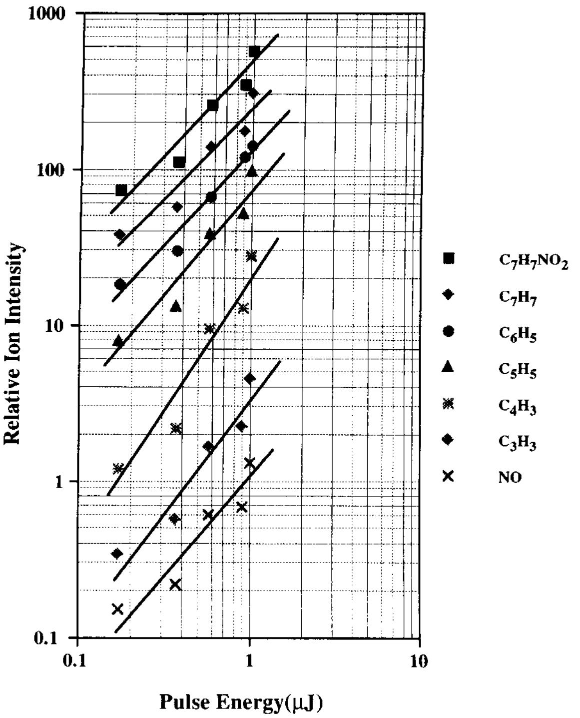

Figure 5. Intensities of the different fragment ion peaks from *m*-NT using 90 femtosecond pulses at 375 nm as a function of pulse energy. 1 μJ pulse energy corresponds to a laser intensity of about 1.2 × 10^{11} W/cm^2. All the gradients are similar between 1 and 1.5.

In the present work, no peak has been recorded in the mass spectra of *o*-nitrotoluene with *m*/*e* = 121 (−O loss) while an extremely weak peak at *m*/*e* = 107 (−NO loss) has been observed. Thus, the near absence of the *m*/*e* = 107 is again consistent with the conclusion that the fragmentation in this experiment is mainly an above ionization dissociation, precluding the dissociation from a molecular excited electronic state. A possible problem with this interpretation would appear to be the recorded ion peak at *m*/*e* = 30 (NO^+). There are, however, a number of other dissociation channels which yield NO ions and neutrals.[36] In addition, the generation of the NO^+ ions could be attributed to the fragmentation of NO_2 produced by the −NO_2 loss channel. A very small NO_2^+ ion peak has been observed in the mass spectrum of *o*-nitrotoluene, and its size relative to the NO^+ ion peak is not inconsistent with the recent measurement of photodissociation of NO_2 gas by 90 femtosecond laser pulses at 375 nm.[42] As far as the −OH loss channel in *o*-nitrotoluene is concerned, it is found that the OH group is generated by a −H transfer from the −CH_3 to the −NO_2 group (the ortho effect). In a femtosecond pump−probe experiment, Herek et al.[43] have determined that the time needed for hydrogen atom intramolecular transfer in methyl salicylate is shorter than 60 femtosecond. For this particular molecule, Nagaoka et al.[44,45] concluded that the intramolecular proton transfer occurs only in some of the excited electronic states owing to the character of the wave function. Unfortunately, for the case of *o*-nitrotoluene there are no similar calculations, and the mechanism for the formation of the intermediate species for this dissociation reaction is still unknown. Nevertheless, the observation in the present experiment of the −OH loss reaction (peak at *m*/*e* = 120) in conjunction with the results of the study where

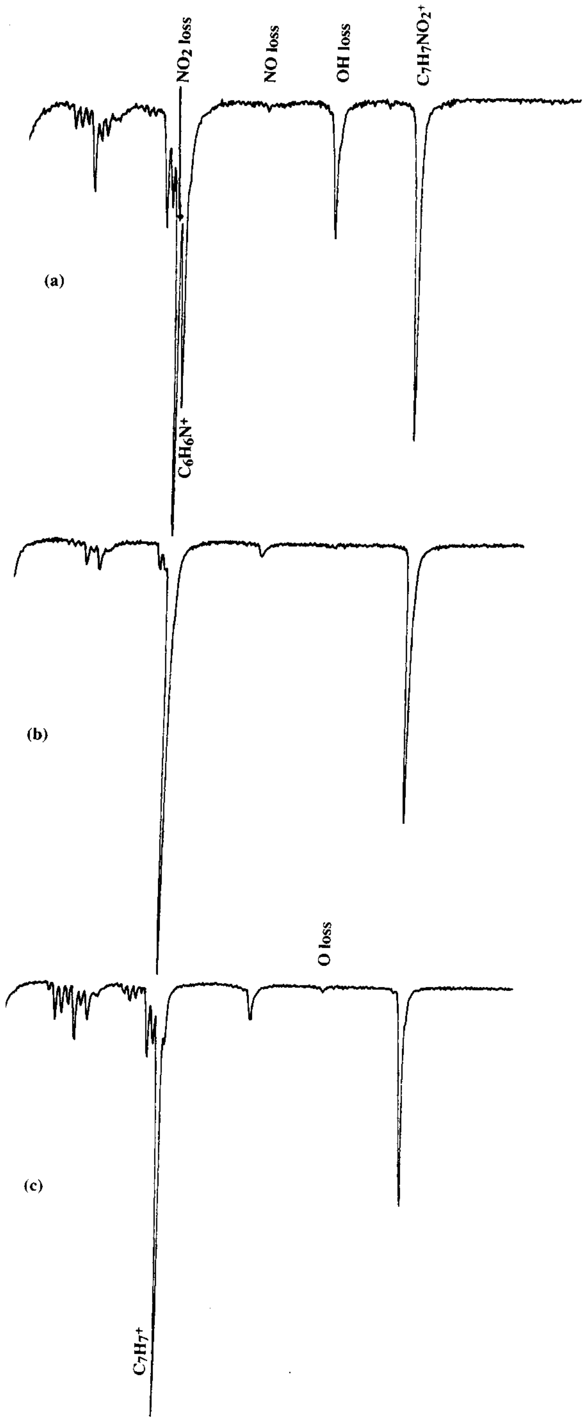

Figure 6. Mass spectra of *o*-, *m*-, and *p*-NT isomers recorded using 90 femtosecond laser pulses at 375 nm. The spectral range of the heavier masses is shown, and as can be seen there are differences which can be exploited for analytical purposes. The detailed differences are described in the text.

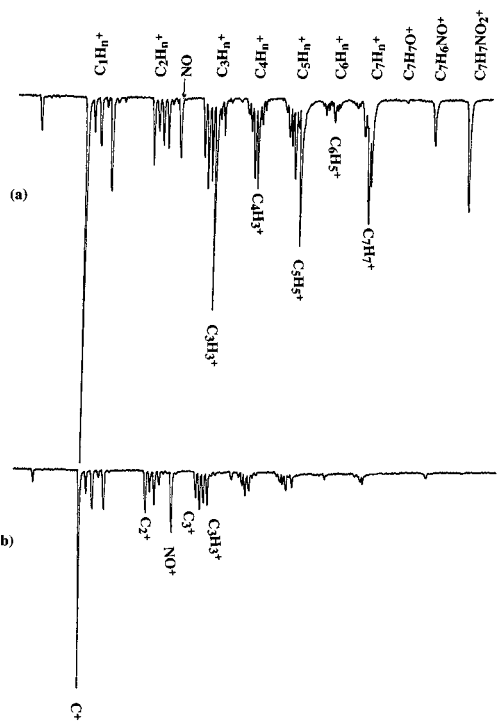

Figure 7. Comparison of the fragmentation patterns for *o*-nitrotoluene at (a) 375 nm, 90 femtosecond and (b) 750 nm, 90 femtosecond with similar pulse energies. For the longer wavelength the intensities of the heavier masses are reduced with a concomitant growth of the lighter mass fragments.

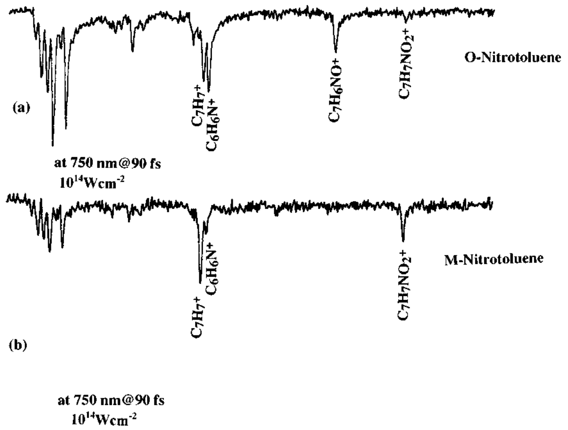

Figure 8. Mass spectra of *o*- and *m*-NT isomers recorded at 750 nm and 90 femtosecond and at an intensity of 10^{14} W/cm^2. Although the parent ion is reasonably strong in the *m*-NT spectrum, it is almost invisible in the *o*-NT spectrum, which however shows a very strong $-$OH loss peak (C_7H_7NO). The parent peak in the *o*-NT spectrum completely disappears at lower laser intensities.

nanosecond laser pulses were used[16] shows that the $-$OH channel proceeds after the molecular ionization.

The spectra of *m*- and *p*-nitrotoluene with respect to the different dissociation pathways are very close to those observed previously using nanosecond laser pulses, except that the $-$O loss channel is absent for *m*-nitrotoluene. It should be noted that differences in the photofragmentation process of *p*-and *m*-nitrotoluene have also been observed by CID studies.[36] These have been attributed to the nitro-to-nitrite rearrangement of the para-substituted molecular ion. The mechanism of this process is unknown but could be due to the relative position of the CH_3 group in the aromatic ring causing different electronic structures for the two isomers. It is known that in the case of methylpyridines the higher occupied MO is not the same for the three isomers.[46] It has been demonstrated that for the *o*- and *m*-methylpyridine (α, β picolines) the higher occupied MO is a π-type, while for the *p*-methylpyridine it is an n-type MO. As mentioned above, there exists a close relation between the type of the MO and the molecular dissociation, but for the nitrotoluenes there is no such information in the literature about the nature of the molecular orbits.

Conclusions

In this work the photodissociation of nitrobenzene and the nitrotoluene isomers has been studied using 90 femtosecond laser pulses at $\lambda = 375$ nm. The mass spectra are compared with those observed with a 10 nanosecond dye laser at the same wavelength using the same experimental setup. The recorded mass spectra are different, as expected. The parent ion and the heavier fragment peaks have been clearly observed only in the spectra with femtosecond laser pulses. The present work has shown that analytically multiphoton ionization in the nanosecond regime has severe limitations especially where there are fast dissociative states in the neutral excited state manifold. Mass spectra for these molecules are of little use for analytical purposes since neither parent nor structural information is available. Alternatively, by applying very short pulses, it has been shown that for these nitro-compounds, the dissociative states can largely be bypassed and produce fragments whose mass spectra are again characteristic of the compound under investigation. Thus ultrafast laser mass spectroscopy does extend the multiphoton analytical techniques for these difficult molecules. In a recent exciting paper,[47] Grotemeyer's group has shown similarly that femtosecond laser activation defeats the fast dissociative states in metal organic compounds to produce very useful mass spectra.

The analysis of the mass spectra shows that the ionization of these molecules takes place under a multiphoton ionization process, while the Keldysh parameter has values in the range $3.5 < \gamma < 11$. The absence in the femtosecond mass spectra of some dissociation pathways observed previously under nanosecond laser irradiation and the power dependence of the ion peaks suggest that the molecular fragmentation for all molecules studied follows the ladder-climbing mechanism. The analysis also leads to the conclusion that most of the dissociation reactions take place directly from excited ionic states.

On the other hand, some fragmentation pathways follow from a molecular rearrangement. For nitrobenzene, the present experiment shows that most of the observed fragmentation takes place from the nitrobenzene structure rather than phenyl nitrite. In the case of *o*-nitrotoluene, it is proposed that the molecular rearrangement depends on the kind of molecular excitation involved. For ionic states it is found that the hydrogen transfer from the methyl to the nitro group dominates, while when the molecule is excited to neutral molecular electronic states, it seems that the nitrite structure is preferred.

The mass spectra of the three isomers show significant differences, which could be exploited also for analytical purposes. The differences may be due to the influence of the $-CH_3$ group on the highest occupied MO. Unfortunately, for the nitrotoluene isomers the available theoretical calculations are very limited. To the authors knowledge there are no predictions about the type of higher occupied MOs as well as about various possible molecular rearrangements. Obviously, such calculations would contribute to a better understanding of the photodissociation processes in these molecules.

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