Multiphoton Ionization and Dissociation of Nitromethane Using Femtosecond Laser Pulses at 375 and 750 nm

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The photochemistry of nitromethane has been studied extensively for many years. Although it is generally agreed that the principal photodissociative process is cleavage of the C−N bond to yield the methyl radical and nitrogen dioxide, there is some evidence of minor competing dissociation channels. A number of different groups have used lasers of different wavelengths, but the results of these studies vary considerably and no clear picture of the minor dissociative channels has yet emerged. The use of femtosecond (fs) duration laser pulses for photoionization of molecules is currently an area of considerable interest, since the process can lead to the efficient production of intact molecular ions. It was felt that femtosecond laser mass spectrometry (FLMS) could provide added information on the dissociation pathways of nitromethane. Laser pulses of 90 fs time duration at wavelengths of 375 and 750 nm, coupled to a time-of-flight mass spectrometer, have been used in this study, and contrary to photoexcitation using nanosecond (ns) pulses, a large parent ion, 61 ($CH_3NO_2^+$), is detected together with strong peaks at $m/e = 15$ (CH_3^+), 30 (NO^+), 46 (NO_2^+) as well as a number of other minor peaks. This fragmentation pattern can be explained by a predominantly ID (ionization followed by dissociation) route.

Introduction

The photochemistry of nitromethane (CH_3NO_2) has been extensively studied for many years[1−25] principally because the molecule is an important prototypical energetic material. Its ultraviolet absorption spectrum consists of two bands: a weak band around 270 nm with very little absorption strength at wavelengths longer than 350 nm and a very much stronger band at about 198 nm.[26] There have been a number of photodissociative studies using pulsed lasers around both these absorptive wavelengths in an attempt to determine the primary photodissociation fragments. The experimental results vary widely in their findings, and as yet no clear picture of the dissociation pathways has emerged.

The primary photodissociation process at either of these absorption maxima is cleavage of the C−N bond to yield a methyl radical and nitrogen dioxide.

$$CH_3NO_2 + h\nu \rightarrow CH_3 + NO_2 \qquad (1)$$

The C−N dissociation cross section has been determined by Blais[13] to be $1.7 \times 10^{-17} cm^2$ at 193 nm with near unity quantum yield. The experimental work of Butler et al.,[12] Moss et al.,[20] and Lao et al.,[22] all at 193 nm, support eq 1 as the primary dissociative pathway and proposes two pathways by which CH_3 and NO_2 radicals are produced. The major channel leaves the NO_2 radical in the 1^2B_2 excited state, which is known to rapidly dissociate to NO + O [27] with a decay rate of about 8.5×10^9 s^{-1}.[28] The corresponding CH_3 radical is produced with little internal energy. The minor channel is produced in the 2^2B_2 excited state of NO_2, which absorbs a second 193 nm photon to dissociate to NO + O.

There is conflicting evidence of relatively minor competing dissociation channels for nitromethane using a Kr flash photolysis lamp[1] and a mercury arc lamp at 313 nm.[7]

$$CH_3NO_2 + h\nu \rightarrow CH_2O\ (m/e = 30) + HNO\ (m/e = 31)$$

$$CH_3NO_2 + h\nu \rightarrow CH_3NO\ (m/e = 45) + O$$

Kwok et al.[9] detected no dissociation products following the collision-free excitation of nitromethane at 266 nm, whereas at the same wavelength under similar collisional conditions, Zabarnick et al.[16] produced ground-state OH via the reaction

$$CH_3NO_2 + h\nu \rightarrow CH_2NO\ (m/e = 44) + OH$$

CH_3O [$m/e = 31$] was observed by Wodtke et al.[17] following infrared multiphoton dissociation of nitromethane using a CO_2 laser and is postulated to be formed via methyl nitrite in the following way:

$$CH_3NO_2 + nh\nu \rightarrow (CH_3ONO)^* \rightarrow CH_3O\ (m/e = 31) + NO$$

In a number of these photodissociative studies, measurable ion signals in the mass spectrometers were detected at $m/e = 46$ (0.2), 30 (2.8), 16 (0.9), 15 (0.4), 14, 13 corresponding to the ions of NO_2, NO, O, CH_3, CH_2 or N, and CH with the typical relative intensities in parentheses. No significant signals were observed at $m/e = 61$ (CH_3NO_2), 47 (HONO), 45 (CH_3NO), 44 (CH_2NO), 32 (O_2), 31 (CH_3O,HNO), or 29 (CH_3N,CHO).[12,13] The presence of the CH and CH_2 fragments observed by 193 nm induced decomposition of nitromethane is postulated to result from sequential photofragmentation of the primary CH_3 fragment.[15,19,23,24] Table 1 shows all the primary photodisso-

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TABLE 1

dissociation channel	method of detection	dissociation wavelength (nm)	ref
$CH_2O + HNO$	photolysis	200−300	3
	photolysis	240−360	5
$CH_3O + NO$	multiphoton processes	266	9
	flash photolysis	199.9−206.4	4
$CH_3 + NO_2$	photolysis	313	7
	flash photolysis	193	12
	photolysis	253.7, 313	2
$CH_2NO + OH$	pump−probe	266	16
$CH_2 + HONO$	emission spectrosc	193	12
$CH_2NO_2 + H$	photolysis	253.7, 313	2
$CH_3NO + O$	photolysis	253.7, 313	2
$CH_3 + NO + O$	multiphoton processes	193	20

ciative pathways that have been identified for nitromethane with the corresponding fragmentation wavelength.

The reason for the lack of a strong parent mass ion is that nitro compounds have fast dissociative states, and specifically for nitromethane, Schoen et al.[10] have shown that the dissociation time of the principal channel is less than 5 ps, in agreement with the work of Mialocq and Stephenson.[25]

Multipohoton absorption by molecules can lead to fragmentation by two distinct mechanisms.[29,30] First, the molecule can absorb a number of photons to reach a dissociative state below the ionization level. If the laser pulse length is longer than the lifetime of the state, then the molecule fragments form neutral moieties. Depending on the laser intensity, these fragments may absorb additional photons within the initial laser pulse to ionize or further fragment. This process is dissociation followed by ionization (DI) or ladder switching. On the other hand, if the pulse is very much shorter than the lifetime of the dissociative state, then the up pumping rate may be so high that the ionization level is reached. The manifold of ion states can absorb additional photons and fragment. This process is ionization followed by dissociation (ID) or ladder climbing. Many molecules fragment by ID alone, e.g., the aromatics, while others, e.g., the thermally labile molecules, fragment principally by the DI route. Often the two mechanisms compete, with ladder climbing becoming more dominant as the pulse width decreases. For analytical purposes, DI fragmentation is often of little use, since neither the parent nor structurally discriminating ions are formed.

Thus, femtosecond laser mass spectrometry can often "defeat" these dissociative states by fast up pumping to the parent ion states, resulting in a large parent ion peak or at least many more high-mass ion fragments, which makes the interpretation of the mass spectra much less ambiguous. Furthermore, if neutral fragments are generated, these may be ionized with high efficiency, since very high fluxes are used in femtosecond laser mass spectroscopy (FLMS). A number of recent publications have demonstrated very elegantly the enormous potential for femtosecond laser mass spectrometry.[27,28,30−38]

It was decided to carry out an excitation and dissociation/ionization study of nitromethane at 90 fs and to compare this with the dissociation in the nanosecond regime. As part of this study, it was felt that a simultaneous study of the femtosecond dissociation/ionization of NO_2 gas might be helpful to explain the dissociation of nitromethane, since one of the principal dissociative fragments is likely to be the NO_2 neutral radical.

Experimental Section

Femtosecond Laser System. The femtosecond laser system coupled to the linear time-of-flight mass spectrometer is shown in Figure 1. The laser is described in greater detail elsewhere,[39] but essentially, pulses of 50 fs duration are derived from a mode-locked titanium sapphire oscillator pumped with about 7 W from an all-lines "Beamlok" argon ion laser (both Spectra Physics). A simple stretcher, comprising two pairs of BK7 prisms in a double-pass arrangement, was used to negatively chirp the pulses to about 700 fs prior to amplification in a three-stage dye laser. The dye LDS 751 was used in preference to the higher gain rhodamine 700 normally used at this wavelength because only the former dye was found to have sufficient gain bandwidth to support 50 fs pulses. A 4 cm block of SF10 glass served to recompress the pulses down to 50 fs after the amplifier.

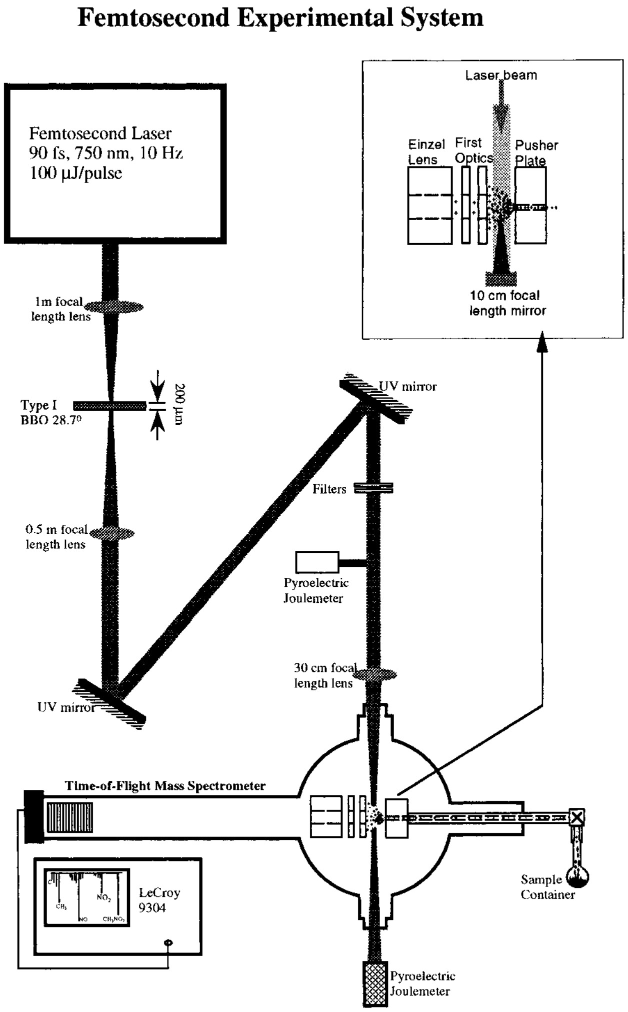

Figure 1. Femtosesond laser system coupled to the linear time-of-flight mass spectrometer. The inset shows the mirror arrangement to enable laser intensities up to 10^{14} W cm^{-2} to be attained.

Pulses at 375 nm were generated by focusing the output of the laser with a 1 m lens (*f*/50) into a 200 μm thick, type I BBO crystal cut at 28.7°. The 375 nm light was recollimated with a 0.5 m fused silica lens to give a beam diameter of 1 cm. The 375 nm pulses were directed toward the mass spectrometer with broad band UV mirrors. It was not possible to obtain directly the duration of the 375 nm pulses, but autocorrelation measurements of the 750 nm beam showed that the pulses have been lengthened from 50 fs to a pulse width entering the TOF of 90 fs. At the entrance of the TOF chamber, the 375 nm pulse energy was typically 10 μJ before being focused with a 30 cm fused silica lens. Estimated intensities as high as 1×10^{13} W cm^{-2} could thus be generated, although smaller pulse intensities were also used. A modification to the system was fitted to permit laser intensities as high as 10^{14} W cm^{-2} to be generated, and this is shown in the inset of Figure 1. A mirror of 10 cm focal length was inserted behind the ion extraction region. The laser beam entered the TOF with a diameter of about 1 cm, and this was focused to a spot size of about 10 μm diameter between the pusher and first extract electrode.

Nanosecond Laser System. This has been described in detail in a number of previous publications[40,41] and in their cited references. It consists of a Lumonics excimer-pumped dye laser system (Models TEM 860-M and EPD 330) with pulse and line widths being nominally 10 ns and 0.01 nm and operated at 10 Hz. The laser dye used in the experiment was stilbene BBQ (382 nm) and TMI (375 nm). The laser pulse energies in the 375−380 nm region were typically a few millijoules, and the beam was focused using a 30 cm lens to give fluxes of 10^8−10^9 W cm^{-2}.

Time-of-Flight Mass Spectrometer (TOF). The TOF is a conventional linear system of 1.2 m length pumped by a turbo pump to a base pressure of 10^{-8} Torr. The operational parameters of the extract optics are based on a Wiley−McLaren design, and the ions were detected by a Thorn EMI electron multiplier. An einzel lens placed immediately after the extract optics increased the ion transmission through the system. The mass resolution was typically 200 at 100 D.

The CH_3NO_2 sample was admitted effusively from the inlet system to the high-vacuum system through a needle valve. The gas was admitted through a tiny hole in the pusher electrode of the TOF, and the positioning of the ionizing laser beam with respect to this hole was rather critical. The sample inlet system could be heated and pumped by a roughing pump to a pressure of 10^{-3} Torr. The inlet line to the high-vacuum chamber could be heated independently as well as the entire TOF system. Normally, the inlet line operated at about 120 °C to prevent the samples from sticking to the walls. Sample pressures during data collection were typically 10^{-5}−10^{-6} Torr.

The time-of-flight mass spectra were recorded by taking the electron multiplier output directly into a LeCroy 9304 digital oscilloscope and averaging over hundreds or thousands of shots.

Results and Discussion

Nitrogen Dioxide (NO_2). The multiphoton absorption of NO_2 gas, the competition between direct photoionization (NO_2^+) and dissociation to NO, and subsequent multiphoton absorption and ionization to NO^+ have been the subject of two recent papers[27,42] for a number of different laser pulse widths from nanoseconds to femtoseconds and at different wavelengths 248, 496, and 375 nm. It was shown for 248 nm that the NO_2/NO ion ratio increased as the laser pulse width decreased. By use of nanosecond pulses, the ratio was typically 1% or less and increased to about 60% for 300 fs at 248 nm. Depending on whether the laser pulse widths are nanoseconds or femtoseconds, the $NO_2 \rightarrow NO + O$ dissociative lifetimes vary from about 40 ps to less than 1 ps.[29] In contrast, at 496 nm the NO_2/NO ion ratio remained small even for excitation with short laser pulses. At 375 nm and 90 fs the NO_2/NO ion ratio was typically about 6−10%. All these results can be adequately explained using a rate equation model[43] with the appropriate one- and two-photon excitation and ionization cross sections. Thus, the ratio is a function of pulse width, photon energy, and wavelength.

In Figure 2 the mass spectra of NO_2 at 375 nm, 90 fs, and typically 10 μJ pulse power are shown with a NO_2/NO ion ratio of about 6% compared to that at 375 nm and 10 ns pulse width where the NO_2 peak cannot be seen. In addition, the femtosecond spectrum of NO_2 at higher fluxes shows O and N ion peaks directly from NO_2 or from the subsequent fragmentation of NO. The results for NO_2, which are presented here, are similar to those that were obtained by Ravindra Kumar et al.[34] using laser fields between 10^{13}−10^{14} W cm^{-2} and 35 ps pulses at 532 nm.

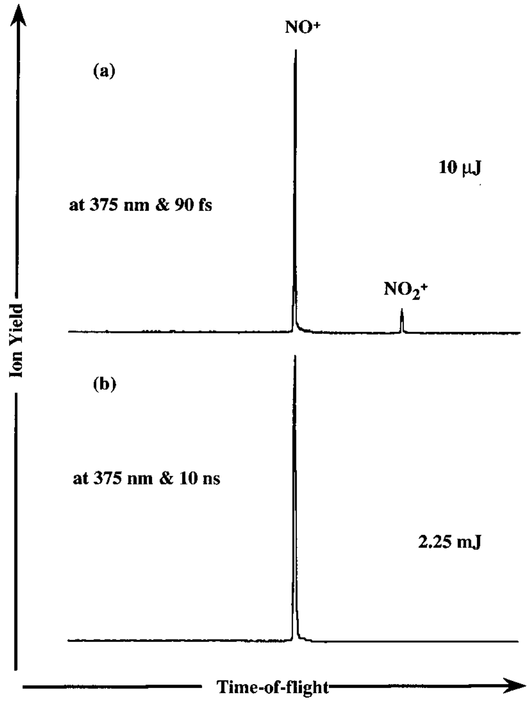

Figure 2. Comparison of the femtosecond and nanosecond excitation and ionization of NO_2 gas at 375 nm. Further details of the femtosecond photodissociation of NO_2 are given in ref 42.

Figure 3 shows the wavelength-dependent spectrum of the NO fragment from NO, NO_2, and CH_3NO_2 for wavelengths between 372 and 384 nm showing the $(2 + 1)[D^2\Sigma(\nu = 0) \leftarrow X^2\Pi(\nu = 0)]$ NO transition at 375 nm and the $(2 + 1)[C^2\Pi(\nu = 0) \leftarrow X^2\Pi(\nu = 0)]$ NO transition around 382 nm using 10 ns pulses from a dye laser. It takes three photons with a wavelength of 375 nm to ionize either the ground-state NO_2 or NO molecules. This spectrum is included to show the fragmentation of ground-state NO_2 and NO molecules, which can then be compared with the dissociation of nitromethane, which produces NO and NO_2 neutral radicals. It can be seen that the rotational activity of the NO ion from NO_2 is much more intense than that of the NO from CH_3NO_2. This suggests that in the 375 nm nanosecond regime, the dissociative pathway of $CH_3NO_2 \rightarrow NO$ is more intense than the pathway to NO_2 and subsequently to NO, indicative of an isomerization process to CH_3ONO before fragmentation.

Nitromethane (CH_3NO_2). The ionization potential of nitromethane is 11.28 eV,[44] and thus, it takes four photons of 375 nm to ionize this molecule. Figure 4 shows some of the energetically allowed dissociation channels[12,45] for both neutral and ion fragmentation, and it is clear that a number of dissociation pathways are opened after the absorption of one or two photons at 375 nm. The ultraviolet absorption spectrum of nitromethane[26] shows that the probability of absorption at 375 nm is, however, very small, and thus, the absorption of two photons is necessary to permit most of these pathways to be opened with a high probability.

The position of the focal point of the laser beam with respect to the inlet hole of the gaseous sample is very important, and it critically affects the relative sizes of the parent and fragment ion peaks. Figure 5 shows how the fragmentation patterns from the irradiated nitromethane sample change considerably as the vertical height of the laser beam is raised by a few millimeters. Before any data are taken, the position of maximum ion intensity was always carefully determined. The spectra in Figure 5 can be understood when one considers that for a given laser position in the TOF, only nitromethane molecules with transverse

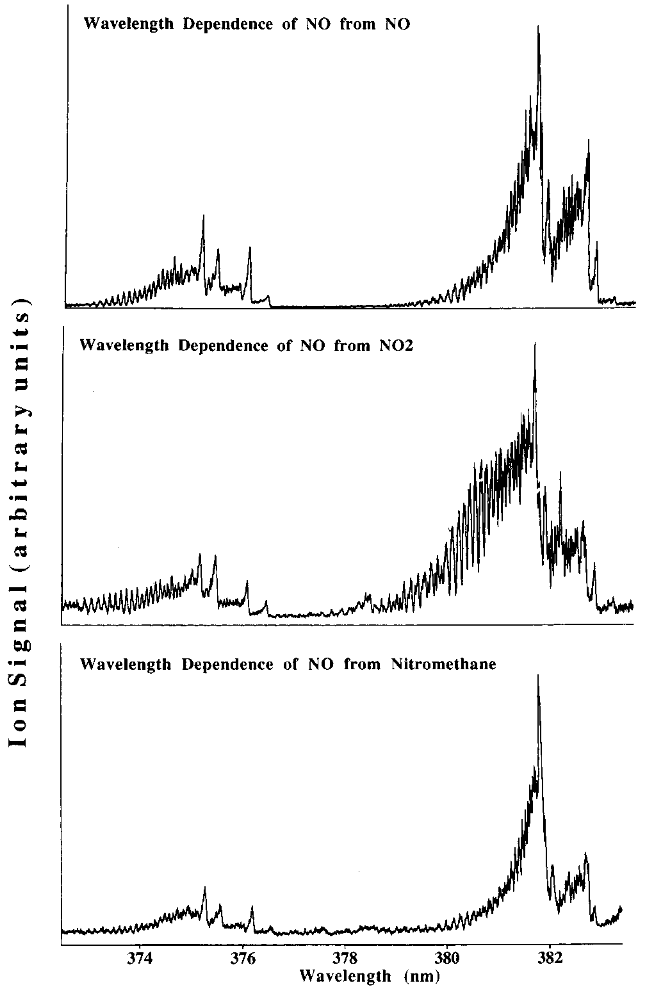

Figure 3. Wavelength dependence of the NO radical from NO, NO_2, and CH_3NO_2 between 372 and 384 nm. 375 nm is clearly in a resonant region. The wavelength dependence of NO from CH_3NO_2 is more similar to that from NO than from NO_2.

velocities ($v_\perp$) in a well-defined range may reach the interaction volume. The photofragments also move with this value of $v_\perp$. Since along the TOF axis the heavier fragments move more slowly, spending more time traversing the drift space, they are more likely to have trajectories that miss the detector.

Figure 6 are bar diagrams showing the fragmentation intensity data taken by Butler et al.[12] at 193 nm and nanosecond pulses (thin bars) and results taken at 248 nm and 7 ps (thick bars). It can be seen that even at 7 ps, there is still no parent peak visible, consistent with a dissociative lifetime considerably less than 7 ps and in agreement with the measurement of Schoen et al.[10] and Mialocq and Stephensen[25] that the lifetime of the principal fragmentation channel is less than 5 ps. The very large peak at *m*/*e* = 18 in the 248 nm, 7 ps spectrum is present because of the strong pumping of the two-photon resonant transition at 80 625 cm^{-1} in H_2O. This has been seen in other experimental data at 248 nm.[27]

The NO_2^+/NO^+ ratio from nitromethane in the 5 ps regime at 248 nm is similar to the ion ratio from ground-state NO_2 gas. This fact together with the lack of the parent ion suggests a DI route in this regime with the principal neutral fragmentation pathway being $CH_3 + NO_2$. On the other hand, the wavelength dependence of the NO fragments in Figure 3 is more suggestive of a strong NO neutral pathway ($CH_3O + NO$).

A comparison of the femtosecond and nanosecond multiphoton ionization and dissociation for nitromethane at 375 nm is shown in Figure 7. It should be emphasized that the intensities and bandwidth of the two lasers are, however, completely different with the irradiation conditions for the femtosecond and the nanosecond being 1.8×10^{13} W cm^{-2}/5 nm and 6×10^{10} W cm^{-2}/0.01 nm, respectively. Since the focusing conditions for the two laser beams were very similar, the laser fluxes are proportional to the measured pulse energies. The nanosecond spectrum shows only one peak at *m*/*e* = 30 (NO) with no parent peak. This indicates that with nanosecond pulses, apart from the NO ion, neutral fragments are created (DI) that cannot be subsequently ionized with the laser fluxes available. Alternatively, the femtosecond spectrum shows a large number of peaks with the principal peaks being *m*/*e* = 61 (CH_3NO_2), 46 (NO_2), 30 (NO), and 15 (CH_3). Many other fragment peaks were also visible.

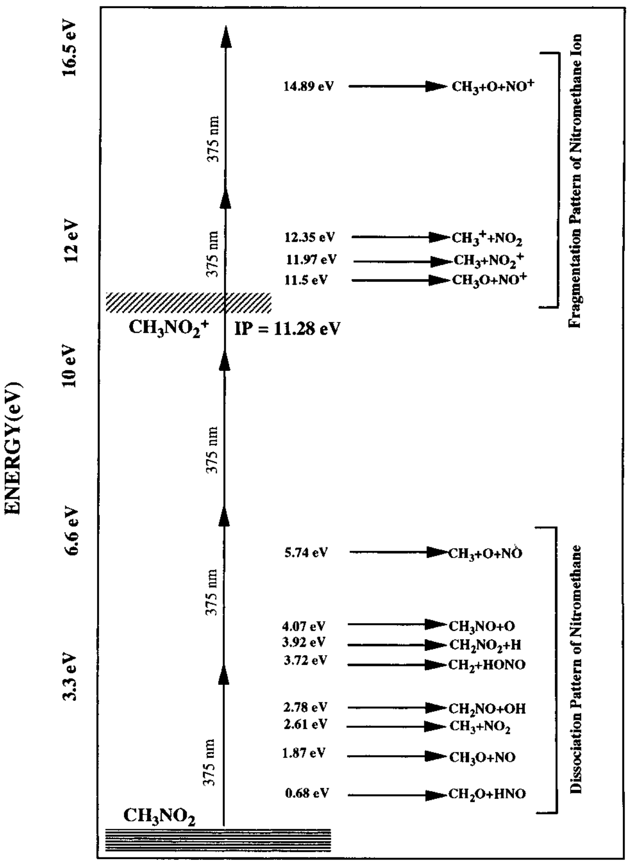

Figure 4. Energetically allowed fragmentation pathways in the neutral and ionic manifold of states. The absorption of four photons will permit access to the parent ion and the most important ionic dissociative pathways.

The laser pulse energy dependences of the principal ion peaks at 375 nm is shown in Figure 8a. The fact that the CH_3NO_2 ion peak is visible at all indicates that the molecule absorbs at least four photons at 375 nm. The power dependence of the parent ion peak for a number of different spectra was between 2 and 3, in agreement with a four-photon absorption process assuming that one or two of the transitions are saturated. It can be seen that the smaller mass fragments have also similar gradients, which suggests that the parent ion is likely to be the precursor. Furthermore, it can be seen from Figure 4 that after the neutral parent molecule has absorbed four photons at 375 nm, the parent ion has sufficient energy to dissociate directly to produce the four principal ions, parent, CH_3, NO_2, and NO, without the absorption of further photons. Ogden et al.[45] have shown that the principal dissociation channels of the nitromethane ion are indeed CH_3^+, NO_2^+, and NO^+, in agreement with the present work. In addition, of the other ion peaks, it is

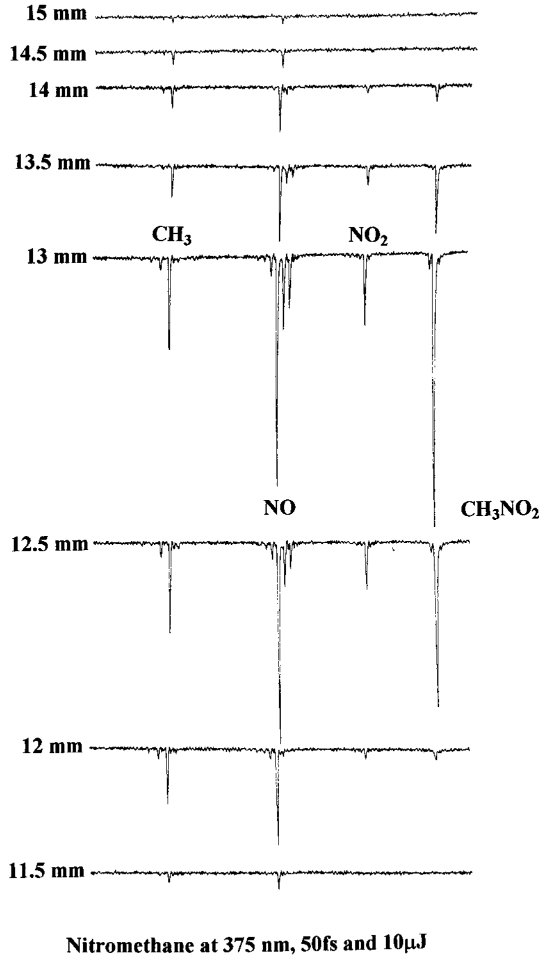

Figure 5. Fragmentation patterns from the excited nitromethane sample as a function of the vertical height of the laser beam. Before any data were taken, the position of the maximum ion intensity was always carefully determined.

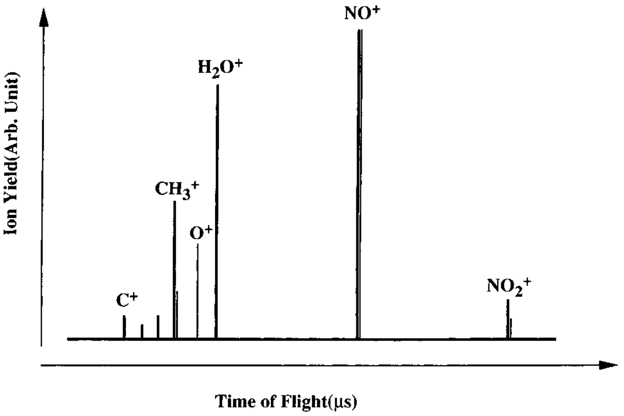

Figure 6. Comparison of the fragmentation patterns of nitromethane at 193 nm in the nanosecond regime (thick bars[12]) and 248 nm at 7 ps (thin bars). No parent ion is visible in either spectrum, and also the NO_2/NO ion ratio is very similar to that from NO_2 gas.

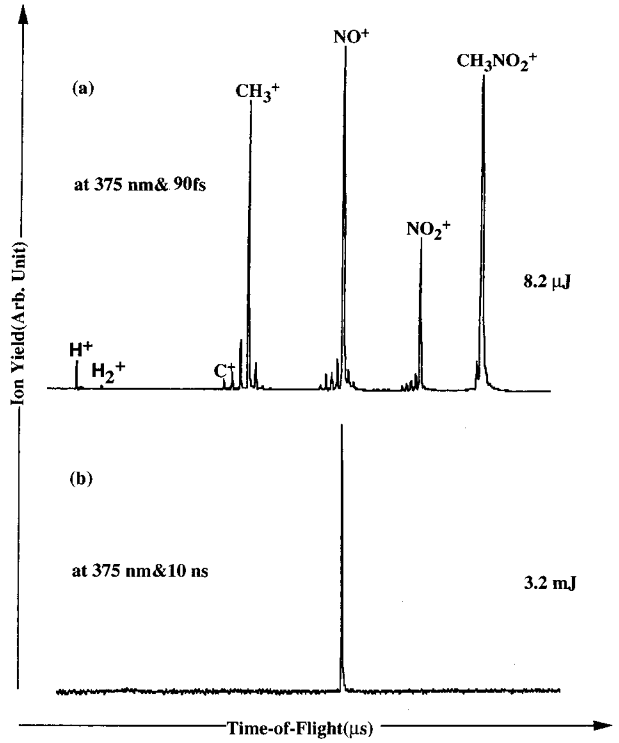

Figure 7. Comparison of 90 fs (1.8×10^{13} W cm^{-2}) and 10 ns (6×10^{10} W cm^{-2}) from nitromethane at 375 nm. The nanosecond excitation only shows the single NO peak, while femtosecond excitation produces the parent and many other fragment ions.

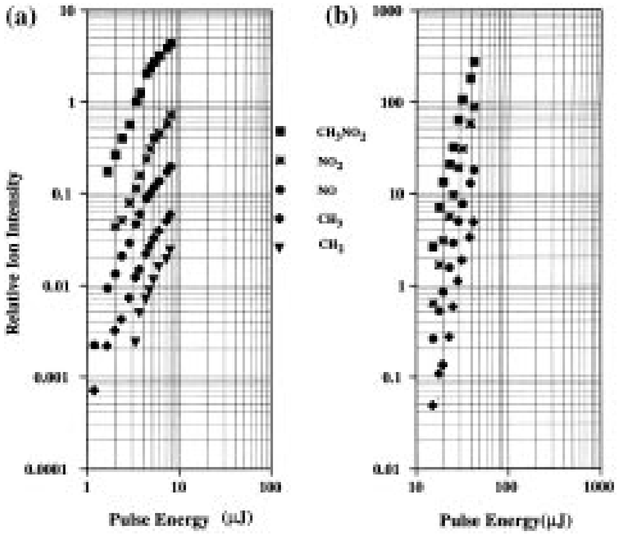

Figure 8. (a) Dependence of ion intensity as a function of laser pulse energy at 375 nm. These curves are relative and do not indicate the absolute intensities. All the gradients are similar and are about 2. For lower laser intensities other sets of curves have gradients of up to 3. (b) Energy dependences of the fragments at 750 nm with gradients between 4 and 5.

likely that the ion peaks, C, CH, and CH_2, come directly from the CH_3 ion, since it has been shown that the power dependences are all similar. On the other hand, the gradient of the peak at mass 16 (O^+) is considerably greater than the lower-mass peaks, and hence, the most likely dissociation route is from the NO_2 ion after the additional absorption of one or two photons.

A similar graph for the energy dependences of the principal peaks at 750 nm is shown in Figure 8b. The gradients of the graphs have increased to between 4 and 5, supporting the view that the ionization process is predominantly a multiphoton process at these laser intensities.

It is postulated that the dominant fragmentation mechanism in the femtosecond regime follows an ID route. The reasons for this interpretation are (a) there is a large parent ion peak, (b) the pulse energy dependences of the principal fragments are very similar, suggesting a common parent precursor, and (c) the NO_2/NO ion ratio (Figure 7) from nitromethane is very much larger (45%) than the same ratio from ground-state NO_2 (6−10%) at 375 nm and 90 fs, which follows a DI route.[42] However, the fragmentation pattern for nitromethane using

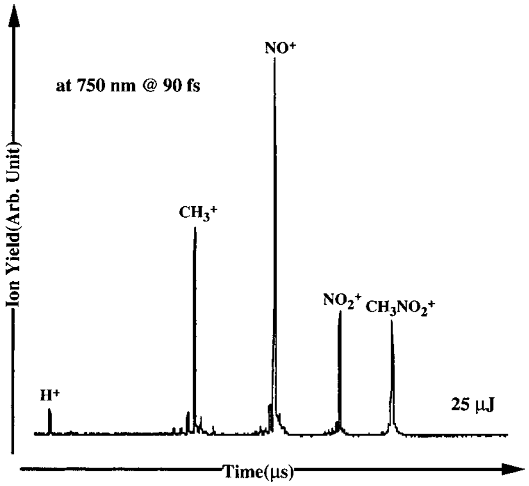

Figure 9. Fragmentation spectrum taken at 750 nm and 90 fs (1 × 10^{14} W cm^{-2}). The ratios of the principal peaks are different from the spectrum at 375 nm, especially the intensity of the parent peak, which has been reduced considerably.

picosecond pulses shows strong NO_2, NO, CH_3, CH_2/N, CH, and C ion peaks (although in very different ratios to the femtosecond spectrum), and hence, the DI route for femtosecond excitation cannot be ruled out entirely.

Figure 9 shows the dissociation/ionization mass spectrum of nitromethane at 750 nm and 90 fs at an intensity of about 10^{14} W cm^{-2}. The spectrum is similar to that taken at 375 nm, but the parent peak intensity is considerably reduced. A similar effect has been recently seen with *o*-nitrotoluene.[46] The corresponding pulse energy dependences for the principal fragments at 750 nm are shown in Figure 8b.

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 field ionization is provided by the adiabatic parameter γ defined by Keldysh:[47]

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

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 thought to be $\gamma < 0.5$.[48] DeWitt and Levis[35] 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, He and Becker[49] 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 value for the Keldysh parameter is >1 for the range of the laser intensities applied. These values are in the intermediate regime, and although it is felt that in the present work multiphoton ionization is the dominant mechanism, at least for the higher laser intensities used, the field ionization mechanism cannot a priori be excluded.

Conclusions

The femtosecond and nanosecond fragmentation and ionization of nitromethane at 375 nm have been carried out using a time-of-flight mass spectrometer. In the nanosecond regime there is only one strong peak at mass $m/e = 30$ (DI). When 90 fs laser pulses are used, a large number of strong peaks are observed with the principal peaks being $m/e = 61$ (CH_3NO_2), 46 (NO_2), 30 (NO), and 15 (CH_3). The parent mass ion peak shows a power dependence between 2 and 3 at laser intensities of $10^{12}-10^{14}$ W cm^{-2}. This can be explained by a four-photon absorption process from the ground state if one or two of the steps are saturated. In addition, the three other principal peaks 46 (NO_2), 30 (NO), and 15 (CH_3) have similar power dependences, indicating that ionization followed by dissociation (ladder climbing) is the most likely mechanism.

The present work has shown that, analytically, multiphoton ionization in the nanosecond regime has severe limitations for nitromethane because of fast dissociative states in the neutral excited-state manifold. It would have been very instructive if it could have been ascertained whether the nitromethane molecule reached a dissociative state after the absorption of one or two photons at 375 nm, but to the authors' knowledge, no details of the dissociative molecular states in nitromethane have been identified. Nanosecond mass spectra for this molecule is of little use for analytical purposes, since neither parent nor structural information is available. Alternatively, by application of very short pulses, it has been shown in the present work that the dissociative states can largely be bypassed and can 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,[50] 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.

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