

Angular distributions of fragment ions arising from tetrahedral CH₃I and isomer identification using intense laser fields

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Abstract

Utilizing an ultraintense (10^{16} W cm⁻²) fs laser, the laser/matter interaction of the tetrahedral CH₃I molecule is investigated. A mass spectrum and the angular distributions of fragment ions arising from Coulomb explosion of molecular ions, obtained with linearly polarized light, are presented. The distributions for Iⁿ⁺ ($n \leq 7$), CH_m⁺ ($m \leq 3$), C^{p+} ($p \leq 4$) and H⁺ ions are all anisotropic and maximal when the polarization lies along the spectrometer axis. The molecule hence seems to behave as a diatomic, with the fragment ions being ejected along the field direction. Also presented are mass spectra of the isomers 1- and 2-nitropropane, which are explosive species, taken for horizontal and vertical polarizations at both 375 and 750 nm. It is shown that femtosecond laser mass spectrometry (FLMS) can be used to distinguish between these two isomers through their differing dissociation patterns. Isomer identification is important for many different applications and FLMS may provide a means of achieving this for a wide range of molecules.

1. INTRODUCTION

Over the last decade, with the rapid progress in ultrashort (femtosecond, 10^{-15} s) pulse generation (Backus *et al.*, 1998), allowing laser intensities greater than 10^{15} W cm⁻², experimentalists have been able to probe the boundaries in the field of “femtoscience.” Such work has included the investigation of atoms and molecules in such intense fields (Normand *et al.*, 1996; Sheehy *et al.*, 1996; Corkum *et al.*, 1997, and refs. therein; Levis & DeWitt, 1999; DeWitt *et al.*, 1998, 2000), where the electric field strength of the laser is comparable to those that electrons experience in molecules. Molecular ions may experience large induced polarizabilities and Stark shifts, since the electron charge density shifts with the laser electric field. The resulting induced electric dipole moment may couple with the linearly polarized electric field of the intense laser pulse and tend to align along the field direction.

In the photodissociation of the parent ions, the resulting fragment ion yield can be measured as a function of polarization angle to determine the preferred direction of ejection

with respect to the laser field. The resulting distribution may be due to molecular alignment, in some cases. However, observed anisotropies in the distributions may alternatively be interpreted as an ionization rate dependent upon the angle made with the laser field (Ellert & Corkum, 1999). Since rotational periods for CH₃I ions are of the order of picoseconds, alignment within a 50-fs pulse is not thought likely, even in the intense laser fields used here. This could be more clearly determined from a series of angular dependence studies taken at different femtosecond laser intensities or pulse durations. However, time restrictions on the laser did not permit this to be carried out. Thus, the anisotropies observed here are interpreted as arising from an angle-dependent ionization rate.

The angular distributions of fragment ions from several small molecules have previously been studied in both the picosecond and femtosecond regime. The alignment of CS₂ is suggested by Couris *et al.* (1999) for pulse duration of several hundred femtoseconds in diffuse conditions. They also find that alignment is more pronounced for shorter wavelengths. The molecular sample is a diffuse molecular beam in the experiments described here and alignment of CS₂ could not be verified in experiments with CS₂ by expanding the femtosecond pulse out to picosecond durations

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(Graham *et al.*, 1999). Laser-induced alignment of several diatomic molecules such as H₂, N₂, and I₂ has been studied using pump-probe techniques by Posthumus *et al.* (1998, 1999a, 1999b), where it was shown that the lighter H₂ and N₂ molecules are dynamically aligned but I₂ is not, even at intensities greater than 10¹⁵ W cm⁻².

It is possible with time-of-flight (TOF) mass spectrometry to determine both the fragment ion direction (via angular distributions) and kinetic energies, if split fragment ion mass peaks exist in the mass spectra to determine bond angles and lengths (Graham *et al.*, 1999, 2000b).

To the authors' knowledge, this is the first time that angular distributions of fragment ions from a tetrahedral molecule have been presented using only femtosecond laser pulses and for fragments other than singly charged methyl and iodine ions from the CH₃I molecule. These experimental results extend previous work done (Graham *et al.*, 1999, 2000a, 2000b) for triatomic molecules to more exotic molecular structures.

Recent experiments (Marshall *et al.*, 1994; Ledingham *et al.*, 1999; Fang *et al.*, 1999) on analytical trace chemical analysis have demonstrated the power of femtosecond laser mass spectrometry (FLMS), which not only gives information on molecular structure, but also *which* species are present. Furthermore, the technique is nonselective, sensitive, and efficient with 100% ionization of the species within the interaction volume (Fang *et al.*, 1999).

The ionization/dissociation mechanism can be studied by observing the fragmentation patterns in the mass spectra obtained. This fragmentation pattern is generally species-dependent, hence providing a "fingerprint" to the molecule under investigation. For example, a study of various dangerous explosives has been previously reported by this group (Marshall *et al.*, 1994). These include: nitro-benzene; 2-nitrotoluene; 2,4-dinitrotoluene; 2,4,6-trinitrotoluene; ethyleneglycol dinitrate (EGDN); pentaerythritol tetranitrate (PETN); 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), and SEMTEX. The results showed that FLMS techniques could distinguish these different explosives and detect them with great sensitivity. Similar results were obtained for small molecules (Fang *et al.*, 1999). Therefore, it is possible that this technique could be utilized to differentiate isomers by observing the differences in fragmentation patterns in mass spectra obtained from a TOF system. Other techniques exist to distinguish isomers. The isomers of OC-IH (McIntosh *et al.*, 1999) were identified by examining their bending and stretching modes to identify the isomeric structure. It is hoped that the results presented herein show the FLMS technique to be just as powerful.

2. EXPERIMENTAL

The experimental apparatus has been described elsewhere (Ledingham *et al.*, 1999). Briefly, a species was admitted effusively into a chamber pumped to a base pressure of 10⁻⁸ Torr by a turbomolecular pump. The sample pressure

was 10⁻⁶ Torr. The TOF spectrometer is a conventional linear system, the field-free length being 1.2 m. Ion optics are of Wiley-McLaren design. Extraction fields of ~500 V/cm were used and the mass resolution was 200 at 100 Da. Ions were detected with a Thorn-EMI electron multiplier. Mass spectra were obtained and stored using a LeCroy 9344C 500 MHz digital oscilloscope.

The laser system used to obtain the angular distributions is based on the chirped pulse amplification technique (Strickland & Mourou, 1985) and produces pulses of about 7 mJ of 790 nm at 10 Hz. The laser pulse entered the TOF perpendicular to the effusive molecular beam and was focused using an *f*/10 spherical mirror mounted inside the chamber to give intensities of about 10¹⁶ W cm⁻². The polarization of the laser was rotated by placing a $\lambda/2$ wave plate in the beam, located in front of the quartz window of the TOF vacuum chamber.

The laser used in the isomer experiments is an Ar-ion pumped femtosecond oscillator, whose pulses are amplified in a laser-dye-filled cell. This produces 100- μ J pulses at 750 nm and 50 fs duration. A nonlinear crystal (BBO) frequency doubles to 375 nm and 90 fs duration. A $\lambda/2$ wave plate is used to change from horizontal to vertical polarization with respect to the TOF axis.

3. RESULTS

3.1. Experiments with methyl iodide

Results from the study of the tetrahedral CH₃I molecule are presented for a laser intensity of about 10¹⁶ W cm⁻² and 50-fs pulse duration. A mass spectrum for horizontal polarization is shown in Figure 1. The parent ion is clearly visible, but sizeable fragment ion peaks are also present. Peaks for I ions up to I⁶⁺ and I⁷⁺ are observed, along with CH_{*m*}⁺ (*m* ≤ 3), H⁺, and C^{*p*+} (*p* ≤ 4) peaks. There is a small peak at about *m/z* = 18 and it is thought that this has a contribution from an I⁷⁺ ion and a H₂O impurity.

A peak corresponding to the CH₂²⁺ fragment ion is also present in the CH₃ group in the mass spectra and appears to be the only multiply charged fragment observed in the CH₃ group, for reasons that are not well understood. Since the pulse duration is only 50 fs, it is unlikely that significant postdissociative ionization occurs. Hence, the parent molecule is highly ionized and Coulomb explodes to produce these multiply charged fragment ions. Although multiply charged parent ions are not directly observed, their role in the production of I^{*n*+} (*n* ≤ 7) and C^{*p*+} (*p* ≤ 4) is inferred.

The I^{*n*+} mass peaks narrow with increasing charge. This may be due to production of higher charged ions in a physically smaller more intense portion of the beam and a narrowing of the acceptance volume of the TOF for highly charged ions imparted with large velocity. The main dissociation mechanism is bond breaking of the C-I bond, giving

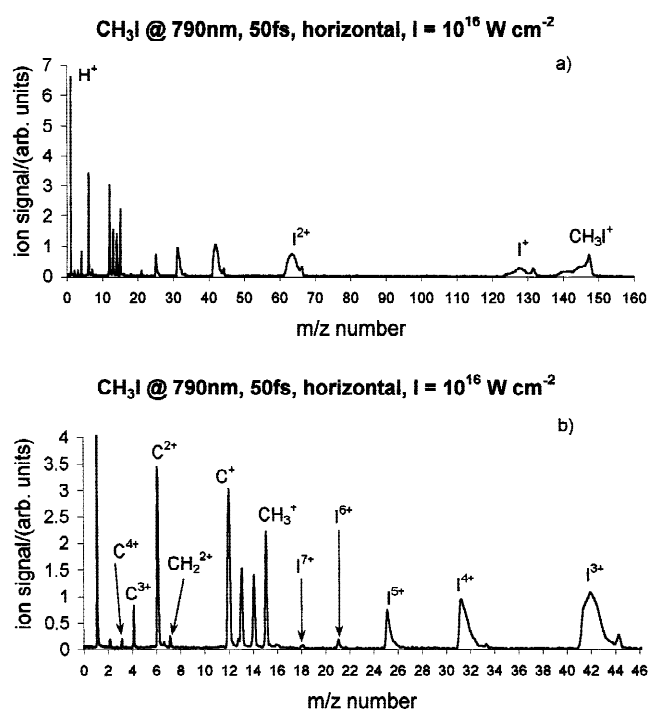


Fig. 1. Mass spectrum of CH_3I for horizontal polarization at a laser intensity of $10^{16} \text{ W cm}^{-2}$ and 50 fs, (a) main spectra and (b) expansion of lower-mass region.

rise to I ions and CH_m ($m \leq 3$) or C and H ions. This may be concluded from the absence of CI^+ ions.

The angular distributions of several fragment ions from CH_3I are shown in Figure 2. As in the case for the peripheral ions from CS_2 , CO_2 , and N_2O (Graham *et al.*, 1999, 2000b), the I ion distributions show maximum ion intensity in the direction of collinearity between the polarization and TOF axis (0° and 180°). All the fragment ion distributions from CH_3I are similar in appearance, with the minimum ion intensity occurring at $\pm 90^\circ$. The ionization and dissociation process is enhanced when the molecular axis is oriented along the laser polarization direction. This is similar to the CS_2 molecule (Graham *et al.*, 1999). When the C-I bond orientation is along the TOF axis, the ions resulting from Coulomb explosion are efficiently detected resulting in the maximum of the ion-angle distribution.

A further feature of the I ion distributions to note is an isotropic component that decreases as the charge state increases. Isotropy suggests a “soft” fragmentation of parent precursors giving rise to low kinetic energy fragments. The higher-charged fragments originate from highly charged unstable transient states of the parent molecule, which results in higher kinetic energies. This decreases the probability of detecting them when the molecule is orthogonally orientated to the TOF axis, reducing the isotropy of the distribution. Also, the distribution of the CH_2^{2+} ion is more anisotropic than for CH_2^+ , as can be seen in Figure 2, as expected for multiply charged ions.

Distributions of CH_m^+ ($m \leq 3$), CH_2^{2+} , H^+ , and C^{p+} ($p \leq 4$) ions were also measured. Since these are similar to those for the I fragments, the molecule hence behaves as a diatomic in a laser field, with the I atom at one end.

3.2. Isomeric distinguishability of 1- and 2-nitropropane

Mass spectra of 1- and 2-nitropropane (1- and 2-NP), $\text{C}_3\text{H}_7\text{NO}_2$ at $m/z = 89$, are shown in Figures 3–6. These show the similarities and differences of the dissociation patterns between the isomers for horizontal and vertical polarization at both 750 nm and 375 nm.

As can clearly be seen, the mass spectra show that the fragmentation patterns between the isomers are different for both wavelengths and polarizations. Importantly, it is observed that in none of the mass spectra shown is the parent molecular ion ($m/z = 89$) present. Indeed, no peak above m/z of 58 is detected in any of the spectra, showing that the time for efficient dissociation of the parent is rapid. This is important for analytical studies, as one of the drawbacks of ns-REMPI that was overcome by use of FLMS was the efficacy of the parent ion to dissociate, by rapid up-pumping through predissociative states. The peaks at $m/z = 57$ and 58 are $\text{C}_3\text{H}_7\text{N}$, that is, the parent ion minus the two O atoms and CNO_2 , which forms from breaking of the C-C bond in both isomers, respectively. Both these ions are absent at 375 nm, but clearly visible at 750 nm. Another peak observed in all spectra is that for $m/z = 43$, that is, C_3H_7 from the cleavage of the C-N bond. The NO_2 ion peak is quite small, as was also observed for other nitro-compounds (Marshall *et al.*, 1994), where the NO_2 tended to dissociate into NO. However, the NO peak is itself a fairly small ion peak in the spectra. Furthermore, there is a sizeable O_2 peak in the spectra for 1-NP that is not as prominent in the 2-NP spectra. It is unlikely this originates from an air leak, however, as it is a bigger peak than the $m/z = 28$ peak, which would be N_2 .

At both wavelengths, the relative ion yields in the C and C_3 groups are fairly similar for the two isomers. The C group exhibits CH_n ($n \leq 3$) peaks, but roughly half the size in the 2-NP spectra. The C_3 group exhibits C_3H_p ($p \leq 7$) peaks for the two isomers at both wavelengths. However, the main peaks in this group are C_3H_7 , C_3H_5 , and C_3H_3 . The C_3H_7 is formed by the dissociation of the C-N bond, leaving the C_3H_7 and NO_2 ion. The former then mainly loses two and four H atoms to form the other two big peaks in the group. There is thus a prominent odd–even effect in this group, with the odd ion masses larger than their even counterparts. The ionic yields are approximately equal for the two isomers.

Other mass peaks observed for both isomers include $m/z = 30$, 46, 57, 58 and possibly a very small peak at 73. These correspond to NO, NO_2 , $\text{C}_3\text{H}_7\text{N}$, CNO_2 , and $\text{C}_3\text{H}_7\text{NO}$, respectively. This last peak occurs from the loss of a single O atom from the parent.

What gives the two isomers a fingerprint of identification however, is the C_2 group, which is very different in the

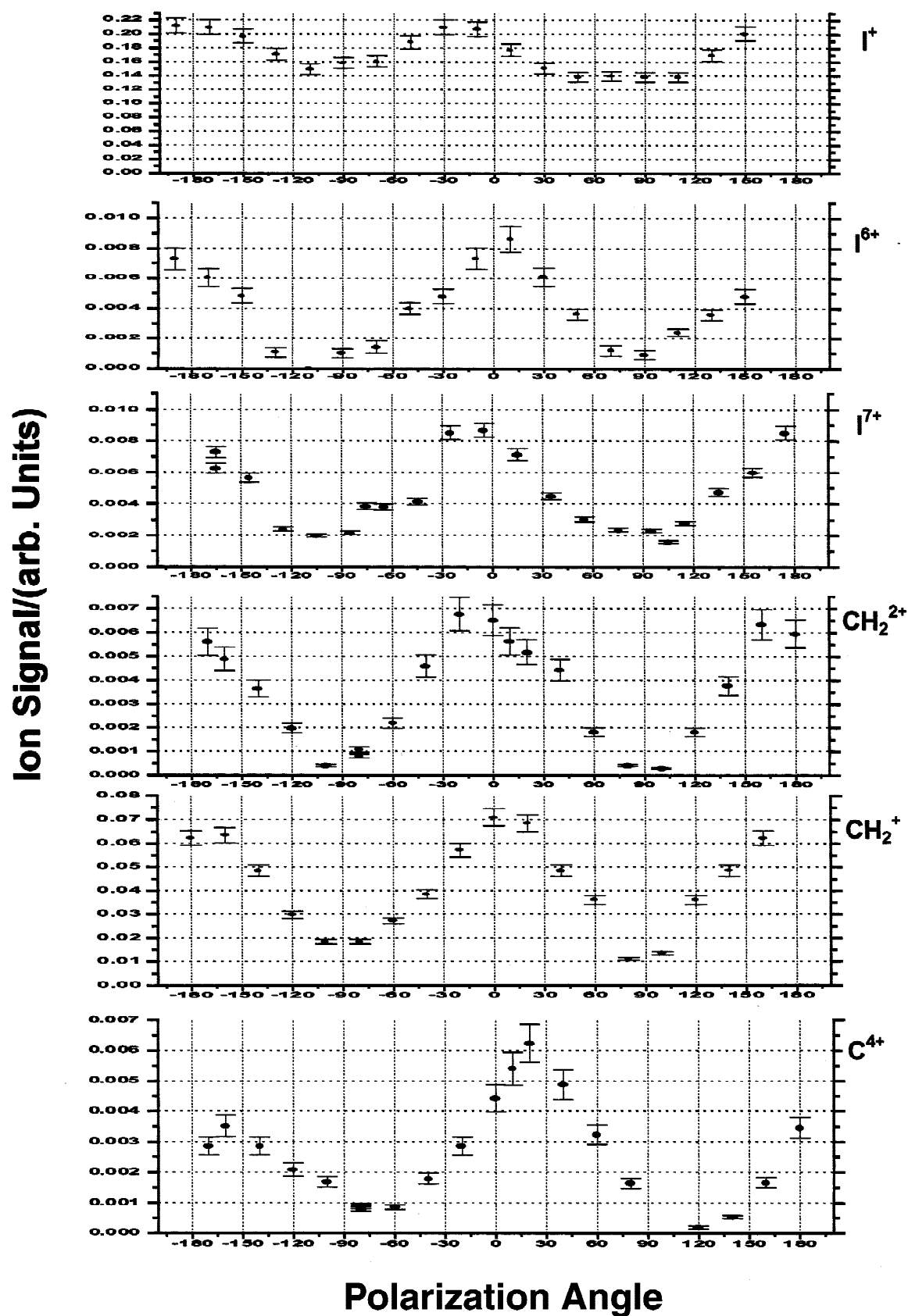


Fig. 2. Angular distributions of fragment ions of I^+ , I^{6+} , I^{7+} , CH_2^{2+} , CH_2^+ , and C^{4+} showing that they are peaked for when the laser polarization vector and TOF axis are collinear. The distribution widths are similar and the anisotropy increases with charge state. This result is similar to that for a diatomic molecular ion.

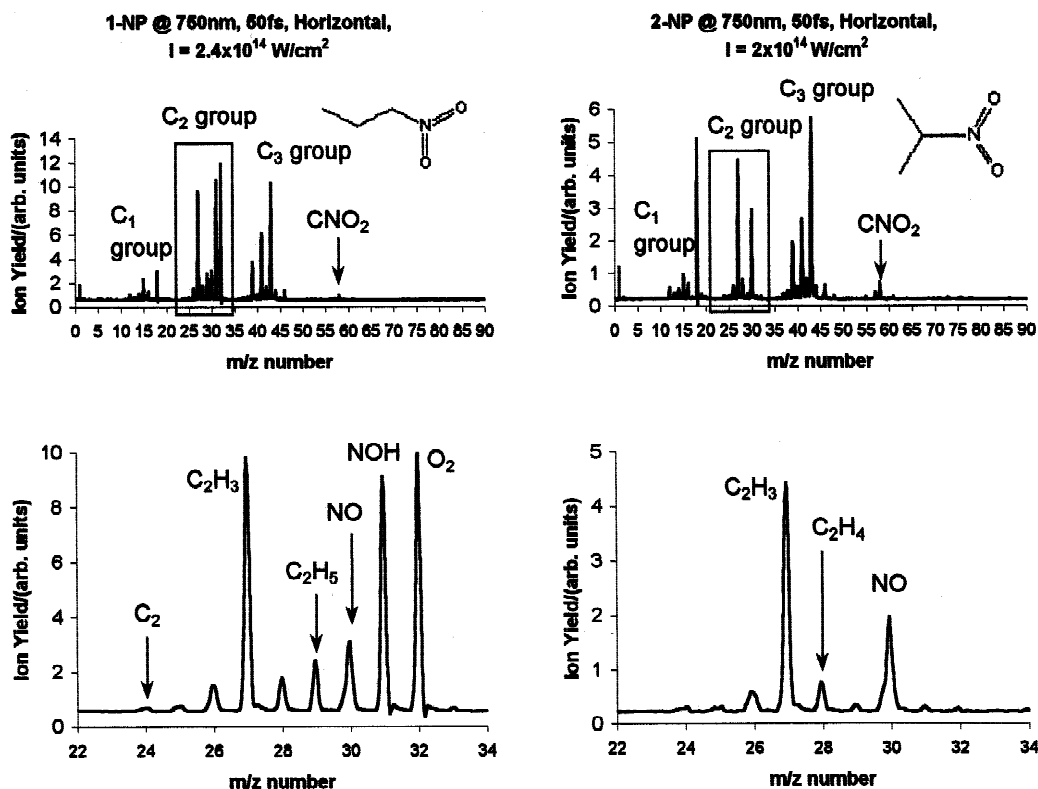


Fig. 3. Mass spectra of 1- and 2-nitropropane taken for the conditions of 790 nm, 50 fs, and intensity of about 2×10^{14} W cm⁻² at horizontal polarization. An expanded view of the C₂ group is shown to highlight the differences observed between the two isomers. The molecular structures are shown as an inset in the full spectrum.

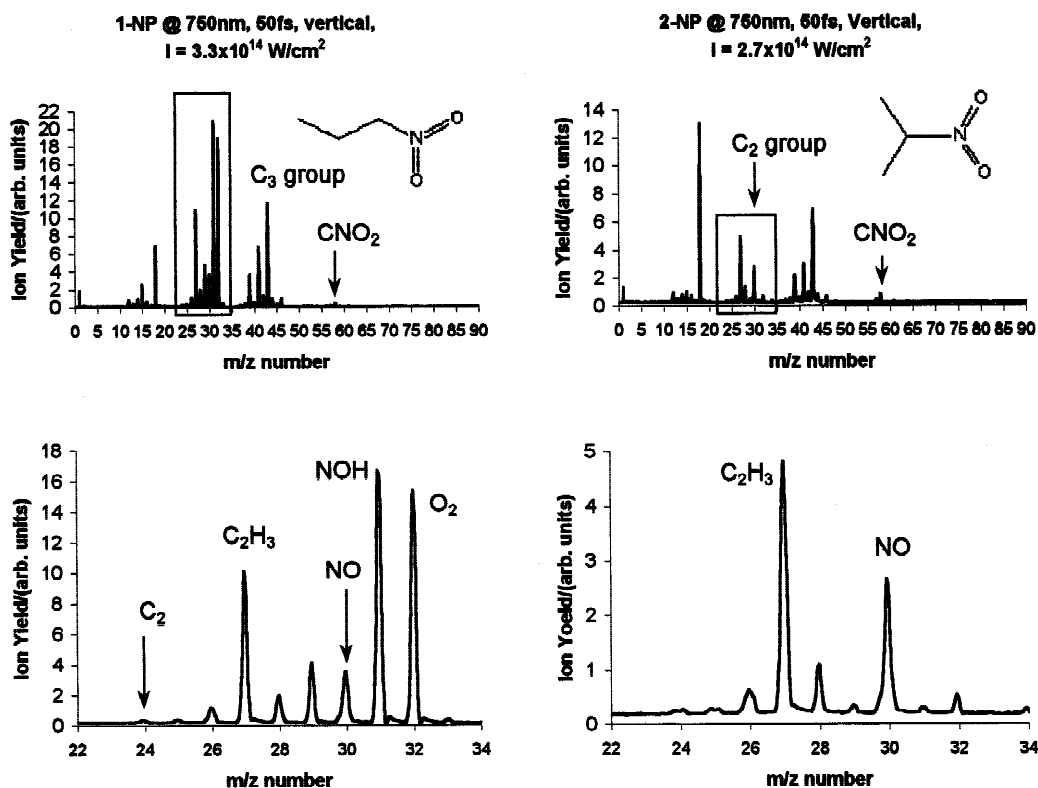


Fig. 4. As for Figure 3, but at vertical polarization.

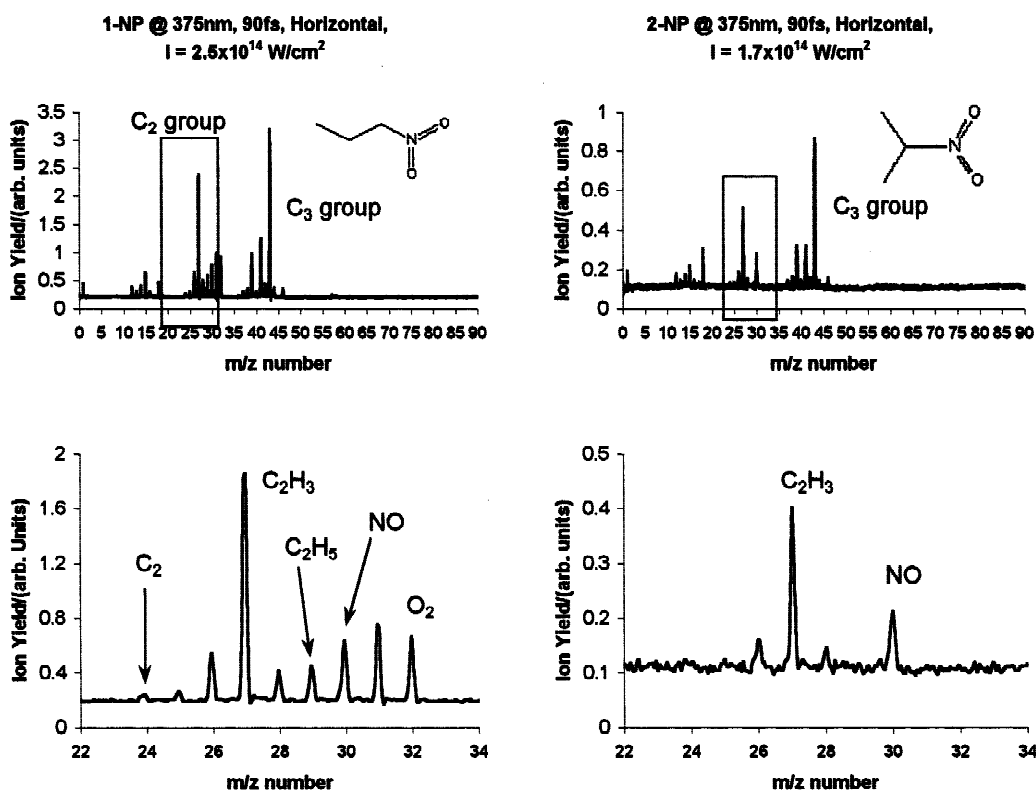


Fig. 5. Mass spectra of 1- and 2-nitropropane taken for the conditions of 375 nm, 90 fs, and intensity of about $2 \times 10^{14} \text{ W cm}^{-2}$ at horizontal polarization. An expanded view of the C₂ group is shown to highlight the differences observed between the two isomers. The molecular structures are shown as an inset in the full spectrum.

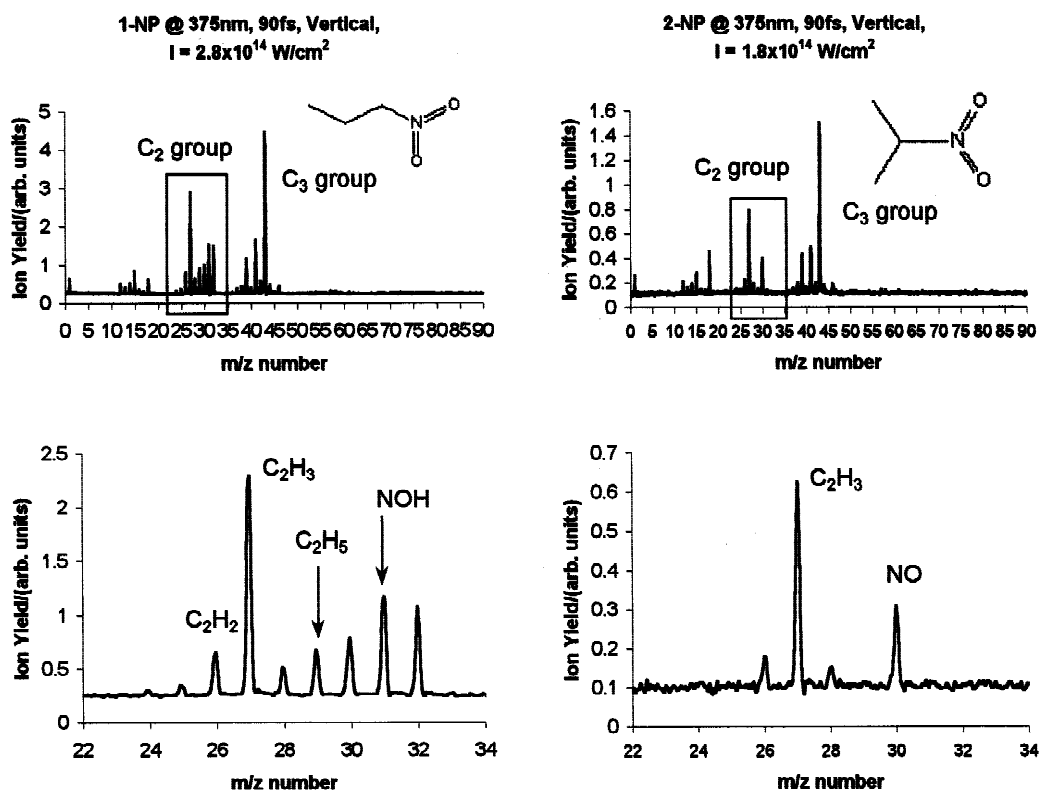


Fig. 6. As for Figure 5, but at vertical polarization.

spectra for both isomers. For both wavelengths, the 1-NP spectra exhibits peaks at $m/z = 24\text{--}32$, which is C_2H_n ($n \leq 5$), NO, NOH, and O_2 . For 2-NP, only two peaks are dominant in this portion of the spectra at both wavelengths and polarization orientations, that is, C_2H_3 and NO. Ion peaks of C_2H_n ($n \leq 4$) are clearly visible, but only a very small C_2H_5 is present and only for 750 nm. Peaks at $m/z = 31$ and 32, which may be NOH and O_2 are also missing in 2-NP spectra at 375 nm and very small at 750 nm. The dominant peaks in the C_2 grouping in 1-NP spectra are C_2H_3 , NOH, and O_2 , with the other peaks decreasing monotonically with mass at both polarizations and wavelengths.

The conclusion from these results is that the FLMS technique provides a way to identify isomers of a molecule via a fingerprint, that is, the difference in the fragmentation pattern. This pattern is independent of intensity, so lower intensities may be used to achieve a soft ionization process so to obtain the sought-after fingerprint *and* the parent ion needed for positive identification.

4. CONCLUSIONS

Mass spectra and angular distributions of fragment ions arising from the tetrahedral CH_3I molecules were studied at laser intensities of about $10^{16} \text{ W cm}^{-2}$, in the femtosecond-regime (50 fs). The ionization of the parent precedes the fragmentation and the fragment ions arise either from soft dissociation or Coulomb explosion of the methyl iodide precursor. The lack of multiply charged parent ions shows that the parent ion is unstable for multiply charged states. For molecules such as CH_3I , the observed anisotropies of the fragment ion distributions most likely arise from an enhanced ionization and dissociation when the molecular axis is parallel to the laser field. The I ion peaks up to I^{7+} are observed for the first time and show a marked anisotropy. Peaks for C ions up to C^{4+} are also observed. Angular distributions of C and CH_n ions are anisotropic and maximum when the laser field is orientated along the TOF axis. This suggests that the fragment ions are ejected in opposite directions and the molecule behaves as a diatomic in the intense laser field.

The experiments performed based on the FLMS give good initial indications for the possibility of isomer differentiation and identification using conventional time-of-flight mass spectrometry apparatus. The fragmentation patterns observed in mass spectra were slightly different between both isomers due to the different molecular geometry and this can be used as a fingerprint to identify which isomer is being observed. Therefore, this technique may also be useful to chemists who wish to study the geometry of the molecular structure. This may well be a general effect, which has far-reaching implications, especially in medical applications.

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