Multiphoton ionization of nitrotoluenes by means of ultrashort laser pulses

K. Tönnies[a], R.P. Schmid[a], C. Weickhardt[a], J. Reif[b], J. Grotemeyer[c],*

[a]*Lehrstuhl Physikalische Chemie und Analytik, Brandenburgische Technische Universität Cottbus, Erich-Weinert-Strasse 1, 03044 Cottbus, Germany*
[b]*Lehrstuhl Experimentalphysik II, Brandenburgische Technische Universität Cottbus, Erich-Weinert-Strasse 1, 03044 Cottbus, Germany*
[c]*Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Ludwig-Meyn-Strasse 8, 24098 Kiel, Germany*

Abstract

The potential of ultrashort laser pulses in the laser mass spectrometry of photounstable molecules is demonstrated for the case of nitrotoluenes. Nitro compounds tend to quickly dissociate after photoexcitation producing only unspecific fragments under conventional nanosecond multiphoton ionization conditions. The mass spectra of two isomers of mononitrotoluene, two isomers of dinitrotoluene and trinitrotoluene were recorded following multiphoton ionization with 170 fs laser pulses either with a wavelength of 412 or 206 nm. Although even these laser mass spectra are characterized by intense fragmentation they exhibit a clear molecular ion or OH loss signals depending on the substitution positions. Although the two mononitrotoluenes can be distinguished by their mass spectra at both wavelengths the two isomers of dinitrotoluene investigated show characteristic features which allow their clear differentiation only at 412 nm. (Int J Mass Spectrom 206 (2001) 245–250) © 2001 Elsevier Science B.V.

Keywords: Multiphoton ionization; Mass spectrometry; Ultra short laser pulses; Nitrotoluenes; Explosives

1. Introduction

Explosives, e.g. nitrotoluenes, form a group of chemicals of considerable interest for environmental and analytical chemistry [1]. Their analysis in soil and water samples is a standard problem in connection with the characterization and remediation of military residual waste sites or training areas. Further, the detection of explosives is of importance in (preventive) forensic chemistry. Usually, large numbers of samples have to be investigated for a single site and the routine techniques are time and cost intensive. Thus, methods would be desirable which allow the rapid screening of many samples without the need of complicated preparation techniques.

During the last decade laser mass spectrometry has shown to be a versatile technique in several very different areas of analytical chemistry [2–8]. The technique further gains popularity as the rapid developments in the field of laser technology make available more powerful, reliable and user-friendly systems. Laser mass spectrometry combines multiphoton ionization [9–11] (MPI) with time-of-flight mass spectrometry [12,13] resulting in a two-dimensional analytical method which in many cases allows the

---

* Corresponding author. E-mail: grote@phc.uni-kiel.de

selective ionization of certain substances in even complex mixtures and their fast mass selective detection with high sensitivity. Because of these advantageous features the list of analytically significant substances which were studied by multiphoton ionization spectroscopy and laser mass spectrometry is growing continuously. Unfortunately, it turns out that a large portion of these compounds are subject to fast relaxation processes after the excitation into excited states [14]. Such intramolecular energy redistribution may either be due to internal conversion, intersystem crossing or fast dissociation processes. In any case this greatly reduces the probability for the absorption of the additional photons necessary for ionization. In addition, the resulting mass spectra are often characterized by small, unspecific fragments which do not allow the unambiguous identification of a certain compound.

Meanwhile it has been demonstrated that the use of ultrashort laser pulses in the sub-picosecond range can solve this problem. In this case the interaction time, and hence the multiphoton ionization process is finished before the intermediate level can be significantly depleted. A recent review on the work of the many groups who contributed in this field can be found in [15].

From the chemical behavior of explosives it becomes immediately obvious that they belong to the group of molecules which are problematic for conventional nanosecond laser mass spectrometry because they undergo very fast dissociation. Thus, in addition to the use of nanosecond lasers the multiphoton ionization of nitrotoluenes was rather early studied by ultrashort laser pulses [16]. Nevertheless, strong fragmentation was observed and the mass spectra obtained are not sufficiently characteristic for a clear substance identification. A possible reason might be that for the wavelength used in [16] the absorption of four photons and, therefore very high laser intensity was necessary for ionization, thus opening a variety of possible decay channels.

In this work we studied the femtosecond laser mass spectra of several nitrotoluenes using two photon ionization at 206 nm and compared them to spectra obtained at 412 nm by four photon MPI. It was the goal of this work to investigate whether by the use of wavelengths short enough for a low order multiphoton ionization process nitrotoluenes can be photoionized in such a way that they yield compound specific and well identifiable mass spectra. Absorption of one photon at 206 nm leads to the excitation of higher singlet states in all nitrotoluenes. Because of the high density of electronic states at this internal energy and their lifetime broadening no narrow discrete spectral features can be expected and thus, the possibilities to influence the selectivity of the ionization are very limited. This drawback can not be overcome by cooling of molecular rotations and vibrations in a supersonic gas beam [17,18]. On the other hand, the reduced laser intensity should result in mass spectra with a moderate degree of fragmentation, reducing the problem of mass spectrometric interferences. For the individual analytical problem it has to be checked, whether or not cross sensitivities influence the measurement at the laser wavelength employed.

2. Experimental Setup

The reflectron time-of-flight mass spectrometer [19] used in these experiments is a home-built gridless instrument with a total length of the drift region of 1.5 m. It is equipped with a Wiley-McLaren type ion source [20] and a microsphere plate detector [21] from which the signal is directly transferred to a digital oscilloscope, connected to a PC for further data processing. The samples were purchased in technical quality and introduced into the mass spectrometer in a Knudsen cell like oven placed under the first acceleration region of the ion source. For nitrotoluene and the dinitrotoluenes the oven was kept at room temperature. For TNT it was resistively heated to a temperature of about 100 °C. This is well below the temperature for thermal dissociation of the compound.

Multiphoton ionization was achieved using either the second or the fourth harmonic of the output of an amplified Ti:sapphire femtosecond laser system. This laser system delivered Gaussian pulses with a duration of 120 fs at a repetition rate of 1 kHz with pulse

energies of 370 μJ at 824 nm, 40 μJ after frequency doubling to 412 nm in a LBO crystal with a thickness of 1 mm, and 4 μJ after frequency quadrupling to 206 nm in a 1 mm BBO crystal. The pulselength of the fundamental beam was measured by autocorrelation and is bandwidth limited. At a wavelength of 412 nm the pulses are stretched to a duration of 170 nm. Their duration at 206 nm could not be measured.

The use of longer wavelengths would be of interest in order to produce molecular ions with lower excess energy. Unfortunately, they could not be produced with this laser system. The laser beam was focussed into the center of the first acceleration region of the ion source by means of a quartz lens with a focal length of 200 mm.

3. Results and discussion

In the following, we will discuss the time-of-flight spectra of 1-methyl-4-nitrobenzene (4-MNT), 1-methyl-2,4-dinitrobenzene (2,4-DNT), 1-methyl-2,6-dinitrobenzene (2,6-DNT), and 1-methyl-2,4,6-trinitrobenzene (2,4,6-TNT), obtained by multiphoton ionization with ultrashort laser pulses at the wavelengths 206 and 412 nm. All of these compounds require the absorption of two photons at 206 nm or four photons at 412 nm, which corresponds to an energy of 2×6.0 eV $= 4 \times 3.0$ eV $= 12.0$ eV.

Fig. 1 compares the mass spectra of 2-MNT [Fig. 1(a)] and 4-MNT [Fig. 1(b)] ionized at a laser wavelength of 206 nm. In both cases the sample was kept at room temperature at which they exhibit a similar vapor pressure of 0.16 and 0.13 hPa, respectively. The spectra are characterized by intense molecular ion signals and have the fragments and $C_7H_7^+$, and $C_5H_5^+$ in common which are typical for toluene derivatives. The fragment $C_7H_6NO^+$ (resulting from the molecule's OH loss) is characteristic for the 2-MNT isomer while $C_7H_7O^+$ (emerging from the molecule's NO loss) is only observed for 4-MNT. This is due to a well known ortho effect in the fragmentation of these compounds giving rise to their mass spectrometric differentiation.
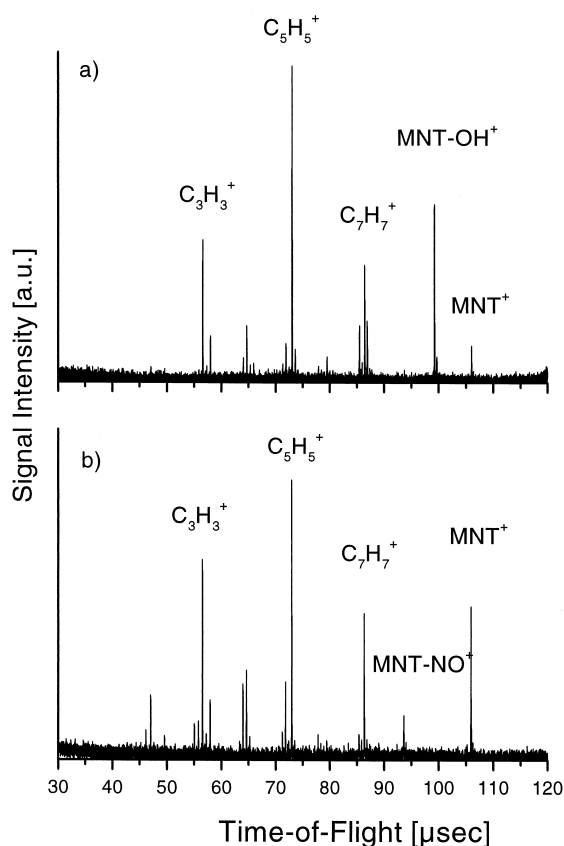
The UV laser mass spectra of two isomers of

Fig. 1. Time-of-flight mass spectra of 1-methyl-2-nitrobenzene (a) and 1-methyl-4-nitrobenzene (b) ionized by sub-picosecond laser pulses at the wavelength 206 nm.

dinitrotoluene are compared in Fig. 2. The molecular ion is observed as a weak signal in the case of 2,4-DNT [Fig. 2(a)] it is completely missing for 2,6-DNT [Fig. 2(b)]. In both spectra the molecule's OH loss signal is the base peak. Besides this, the mass spectrum of 2,4-DNT shows a higher degree of fragmentation than that of 2,6-DNT but no significant features can be found which allow a clear differentiation of the two. The relative signal intensity of the two spectra [Fig. 2(a) and (b)] is about 1 to 2.5 and corresponds to the different vapor pressures of the two isomers at room temperature (1.3 hPa for 2,4-DNT and 3.1 hPa for 2,6-DNT).

The situation changes slightly when the ionization laser wavelength is tuned to 412 nm. Besides a general increase in the degree of fragmentation, which
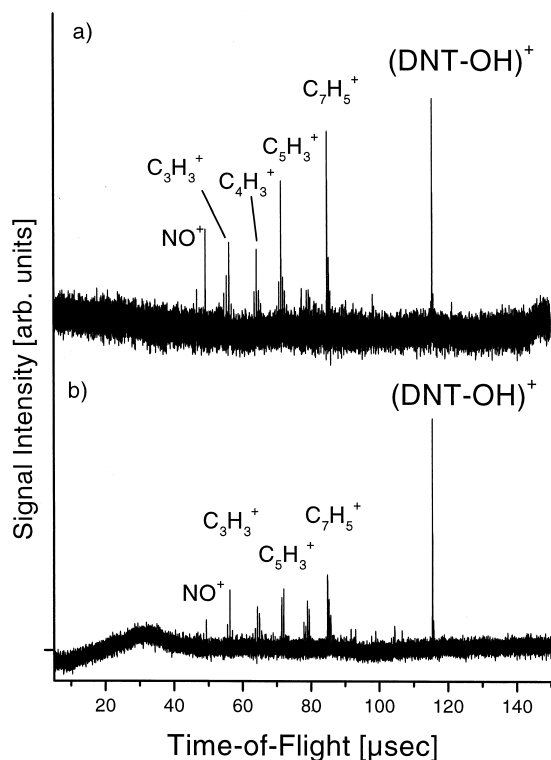
Fig. 2. Time-of-flight mass spectra of 1-methyl-2,4-dinitrobenzene (a) 1-methyl-2,6-dinitrobenzene (b) ionized by sub-picosecond laser pulses at the wavelength 206 nm.
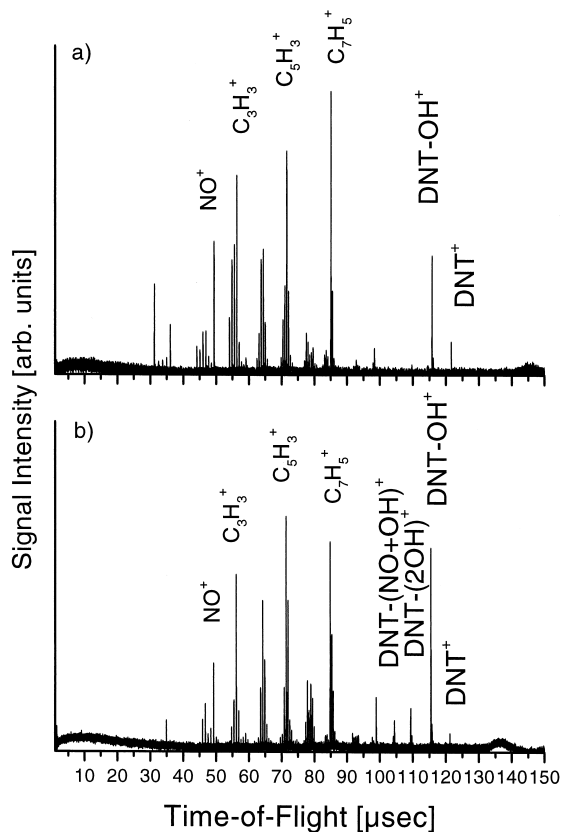

Fig. 3. Time-of-flight mass spectra of 1-methyl-2,4-dinitrobenzene (a) 1-methyl-2,6-dinitrobenzene (b) ionized by sub-picosecond laser pulses at the wavelength 412 nm.

is due to the higher laser intensity necessary for ionization at these lower photon energies, additional signals related to the loss of $(OH)_2$ and $(OH + NO)$, respectively, appear in the mass spectrum of 2,6-DNT [Fig. 3(b)]. Corresponding signals are missing for 2,4-DNT [Fig. 3(a)]. By increasing the laser intensity the degree of fragmentation can be increased until hydrogen and carbon are the base peaks in the spectra. However, no new features appear and thus we assume the fragmentation to be the result of a ladder climbing process [22,23]. An exception is the NO^+ ion whose relative signal intensity depends much weaker on the applied laser intensity. Thus, we assume that NO^+ is formed by the postionization of neutral NO formed very rapidly after the absorption of one 206 nm photon or two photons at 412 nm.

As can be expected from the mass spectra of 2,6-DNT the molecular ion signal is also missing in

the spectrum of 2,4,6-TNT at a laser wavelength of 206 nm [Fig. 4(a)] and is only weak at 412 nm [Fig. 4(b)]. Its OH loss is clearly observed in both spectra whereas the signals resulting from the loss of $(OH)_2$ and $(OH + NO)$ can only be found at the longer wavelength. Also in this case four photon MPI results in a higher degree of fragmentation to small fragment ions. An intense NO^+ signal can be found in these spectra indicating that this decomposition channel of TNT is fast enough for the NO fragments to be post ionized by a laser pulse with a duration as short as 170 fs.

For four photon ionization our results are significantly different from those obtained by Ledingham and co-workers [16] at 375 nm. The degree of fragmentation is significantly higher in their experi-
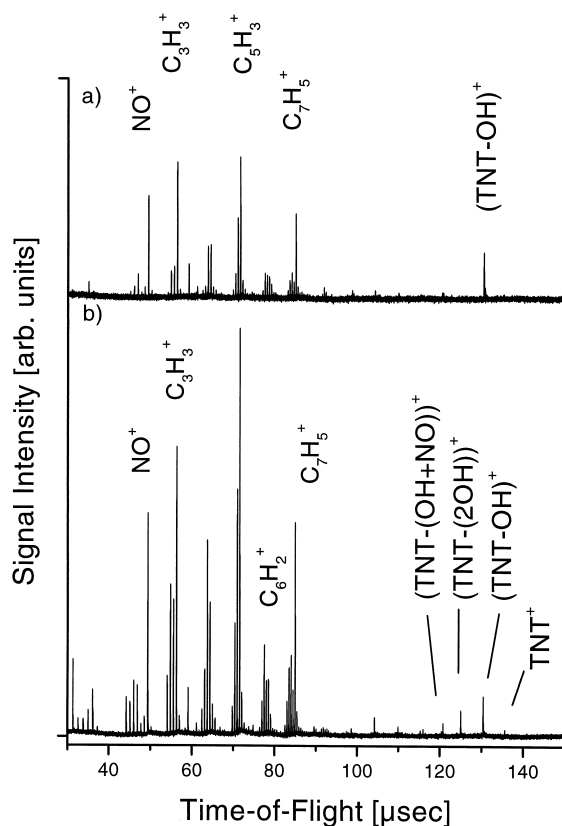
Fig. 4. Time-of-flight mass spectra of 1-methyl-2,4,6-trinitroben-zene ionized by sub-picosecond laser pulses at the wavelength 206 nm (a) and 412 nm (b).

ments and the NO^+ signal shows a much higher intensity. No molecular ion and only a very weak OH loss signal were observed for DNT and TNT. There are several possible reasons for these differences. The shorter wavelength of 375 nm leads to an excess energy after ionization which is about 0.9 eV higher than at 412 nm. This can result in stronger dissociation. In addition the laser intensity in their experiment is higher by about an order of magnitude and the pulse duration is only 50 fs. The strong NO^+ signal can be explained by the fact that at 375 nm NO can be efficiently ionized by a $(2 + 1)$-MPI process via the transition $D^2\Sigma(v = 0) \leftarrow X^2\Pi(v = 0)$. Finally, we cannot estimate the influence of sample vaporization parameters on the results.

4. Summary

In this work the mass spectra of several nitrotoluenes obtained by multiphoton ionization with sub-picosecond laser pulses with the wavelengths 206 and 412 nm are presented. Compared to laser mass spectra obtained by nanosecond multiphoton ionization and even to such from shortpulse resonantly enhanced MPI published so far the spectra show a considerable improvement concerning their quality and the degree of fragmentation. The intensity of the molecular ion signal decreases with increasing degree of substitution, particularly when the nitro groups are in meta position in respect to the methyl group. For dinitrotoluene and trinitrotoluene the OH loss fragment becomes the dominant peak in the higher mass range. At the laser intensities applied in this work the mass spectra obtained at 412 nm show a higher degree of fragmentation than those at 206 nm, but also reveal characteristic features in the higher mass range not observed in the UV-MPI spectra.

Despite the high dissociation rate constants of nitrotoluenes after photo excitation all mass spectra obtained by ultrashort pulse MPI are characteristic and allow the identification of the compound as a nitrotoluene with a certain degree of substitution. Although the two MNT isomers can be easily distinguished by their mass spectra at both laser wavelengths significant differences in the mass spectra of the two dinitrotoluenes were only observed at an ionization wavelength of 412 nm. Further investigations will be carried out in order to check if and at which laser wavelengths the other nitrotoluenes can be distinguished by their individual mass spectra and if their specific features are clear enough in order to allow their identification even in complex mixtures. At the present status we are not able to estimate the sensitivity nor the detection limit of our technique.

Acknowledgement

References

[1] J. Yinon, S. Zitrin, Modern Methods and Applications in Analysis of Explosives, Wiley, New York, 1996.

[2] R. Tembreull, C.H. Sin, P. Li, H.M. Pang, D.M. Lubman, Anal. Chem. 57 (1995) 1186.

[3] M.J. Dale, A.C. Jones, S.J.T. Pollard, P.R.R. Langridge-Smith, Environ. Sci. Technol. 27 (1993) 1693.

[4] C. Weickhardt, U. Boesl, E.W. Schlag, Anal. Chem. 66 (1994) 1062.

[5] J.M. Orea, B. Bescós, C. Montero, A. Gonzales Ureña, Anal. Chem. 70 (1998) 491.

[6] R. Thanner, H. Oser, H.-H. Grotheer, Eur. Mass Spectrom. 4 (1998) 215.

[7] H.J. Heger, R. Zimmermann, R. Dorfner, M. Beckmann, H. Griebel, A. Kettrup, U. Boesl, Anal. Chem. 71 (1999) 46.

[8] S. Schmidt, M.F. Appel, R.M. Garnica, R.N. Schindler, Th. Benter, Anal. Chem. 71 (1999) 3721.

[9] V.S. Letokhov, Laser Photoionization Spectroscopy, IOP, Bristol, 1986.

[10] D.M. Lubman, Ed. Lasers and Mass Spectrometry, Oxford University Press, New York, 1990.

[11] C. Weickhardt, F. Moritz, J. Grotemeyer, Eur. Mass Spectrom. 2 (1996) 151.

[12] Time-of-Flight Mass Spectrometry, in R.J. Cotter (Ed.), American Chemical Society, Washington, DC, 1994.

[13] C. Weickhardt, F. Moritz, J. Grotemeyer, Mass Spectrom. Rev. 15 (1996) 139.

[14] C. Grun, R. Heinicke, C. Weickhardt, J. Grotemeyer, Int. J. Mass Spectrom. 185/186/187 (1999) 307.

[15] For a recent review see: K.W.D. Ledingham, R.P. Singhal, Int. J. Mass Spectrom. Ion Processes 163 (1997) 149.

[16] K.W.D. Ledingham, H.S. Kilic, C. Kosmidis, R.M. Deas, A. Marshall, T. McCanny, R.P. Singhal, A.J. Langley, W. Shaikh, Rapid Commun. Mass Spectrom. 9 (1995) 1522.

[17] R.E. Smalley, L. Wharton, D.H. Levy, Acc. Chem. Res. 10 (1977) 139.

[18] D.H. Levy, Science 214 (1981) 263.

[19] B.A. Mamyrin, D.V. Karataev, D.V. Shmikk, V.A. Zagulin, Sov. Phys. JETP 37 (1973) 45.

[20] W.C. Wiley, I.H. McLaren, Rev. Sci. Instrum. 26 (1955) 1150.

[21] A.S. Tremsin, J.F. Pearson, J.E. Lees, G.W. Fraser, Nucl. Instrum. Methods, Phys. Res. A 368 (1996) 719.

[22] F. Rebentrost, A. Ben-Schaul, Chem. Phys. Lett. 74 (1981) 3255.

[23] J.J. Yang, D.A. Gobeli, M.A. El-Sayed, J. Phys. Chem. 89 (1985) 3426.