

Detection of explosives using a vacuum ultraviolet ionization time-of-flight mass spectrometry (VUV-TOFMS)

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Abstract

In recent years, real-time monitoring devices for explosives are highly needed to safeguard against terrorism. The vacuum ultra-violet single photon ionization time-of-flight mass spectrometry (VUV-SPI-TOFMS) is expected as one of the attractive options for rapid and sensitive detection of explosives. Especially for 2,3-dimethyl-2,3-dinitrobutane (DMNB) which is explosive taggant species, it is very important to know its mass spectrum pattern for the practical applications. To evaluate the possibility of explosives detection using the VUV-SPI-TOFMS at 10.5 eV, ionization energies of typical explosives and explosives-related compounds (ERCs) were estimated by density functional theory (DFT) calculations. From the calculation results, it is suggest that most of explosives and ERCs can be ionized with a 10.5 eV photon energy. Though calculated ionization energy of DMNB is 9.38 eV according to a DFT calculation, a clear parent peak is not observed in the mass spectrum of DMNB measured by the VUV-SPI-TOFMS at 10.5 eV. Instead, many peaks which include the thermal decomposition products are observed in the mass spectrum of DMNB. From the DFT calculations, it is shown that a peak at $m/z=84$ cation which is caused by the elimination of two NO_2 groups can be produced by the ionization at 10.5 eV.

Keywords : VUV-SPI-TOFMS, Detection of explosives, DMNB, DFT calculations

1. Introduction

Recently, the threat of terrorism has dramatically increased and it is imperative that effective systems be developed to counter terrorists. To forestall terrorism, the detection of explosives especially at airports and stations is very important. For successful detection of explosives, it is necessary to develop a sensitive, real-time monitoring device.

As a rapid and selective device to detect the explosives, a laser based ionization techniques combined with mass spectrometry has attracted attention. Some of research groups reported that resonance enhanced multiphoton ionization (REMPI) or single photon ionization (SPI) cou-

pled with time-of-flight mass spectrometry (TOFMS)¹⁾²⁾³⁾⁴⁾ should be an effective and rapid technique for explosives detection. Single photon ionization (SPI) using a vacuum ultraviolet (VUV) photon is expected especially for the selective detection without false detections because VUV photons with a wavelength of 118 nm (a photon energy of 10.5 eV), which can be easily generated by frequency tripling the third harmonic output (355 nm) of a Nd:YAG laser in xenon, can ionize most of organic compounds efficiently with little fragmentation of parent ion.

We focused on the VUV-SPI-TOFMS for the real-time monitoring method of explosives. For the application, it is necessary to accumulate the mass spectral pattern

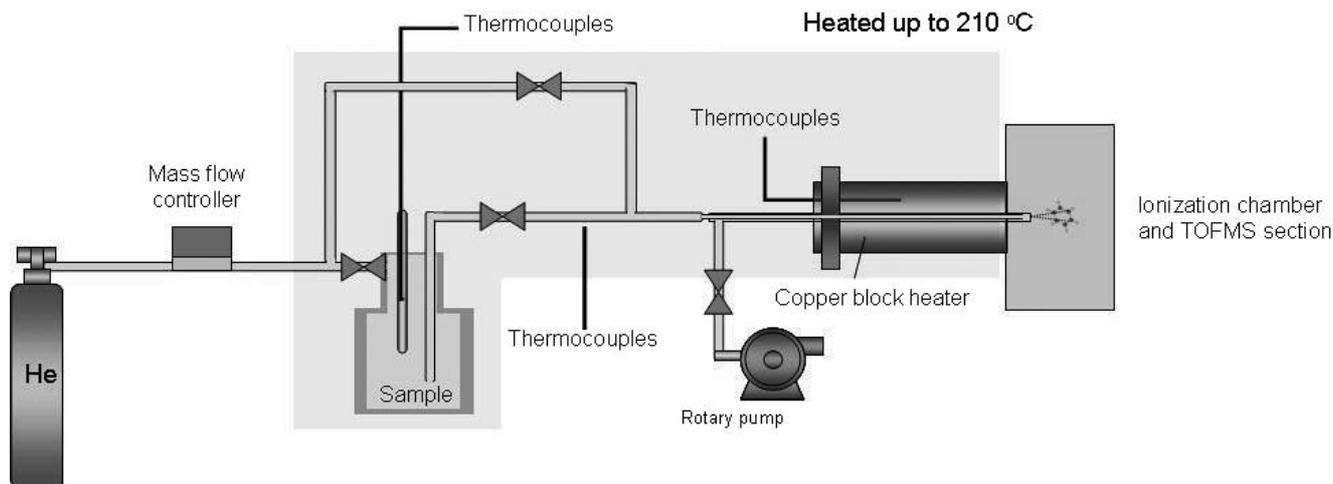


Fig. 1 Sampling section details of experimental setup.

data of explosives, explosives related compounds (ERCs), and other compounds which exist frequently in the environments. Especially for 2,3-dinitro-2,3-dimethyl butane (DMNB), it is important to know its fragment pattern to identify the explosives because DMNB is one of most popular detection taggant species for explosives which is added to most of practical explosives.

Our objectives in this study were evaluations of the VUV-SPI-TOFMS technique for the explosives detection. First, ionization energies of typical explosives and ERCs were estimated by the density functional theory (DFT) calculations to investigate the possibility of ionization with the 10.5 eV photon energy. Second, the mass spectra of DMNB were measured using the VUV-SPI-TOFMS, and the mechanism of ionization of DMNB with 10.5 eV photon was discussed on the basis of the DFT calculations.

2. Experiments

2.1 Experimental apparatus

Detailed descriptions of a VUV-SPI-TOFMS equipment used in this study were described elsewhere⁵⁾. The differences from previous setup and improvements especially in the sampling system are described briefly. The experimental setup of the sampling system is shown in Fig. 1.

Since DMNB is solid and has relatively low vapor pressure at the room temperature (0.27 Pa at 25 °C⁶⁾), a sample holder and sample lines were heated up to 210 °C at maximum. All the lines including nozzle to supply the vapors into the ionization chamber were made of glasses to prevent the catalytic decomposition on the metal wall. Apiezon H grease (M&I Materials Ltd.) was used for glass cocks. For heating the glass lines, ribbon heaters were used and temperature was measured by thermocouples at several points.

DMNB sample was into the glass sample holder and separated from the system by closing the glass cocks, and the carrier gas (helium) was delivered into the chamber by another bypass line. All lines except the sample holder were heated up to a certain temperature before measure-

ments. After the measurements of background spectra, pass of the gas line was switched to the sample line and then the sample holder was heated up. The vapor of sample was delivered by carrier gas whose flow rate was controlled by the mass flow controllers, and jetted out of the glass nozzle through a pinhole (less than 0.1 mm diameter).

The vapor of sample was ionized by VUV photons at 118 nm generated by the frequency tripling in xenon. The residual third harmonic (355 nm) of a Nd:YAG laser light was separated from the VUV laser light (118 nm) by a LiF prism in a tripling cell to prevent the multiple photon ionization and separated 355 nm laser light was damped on the wall of a tripling cell. Details of this VUV generation method are described in ref.7. A mass resolution ($m/\Delta m$) of current instruments was ~ 230 at $m/z=78$.

2.2 Samples

Commercially available chemical reagents were used without any further purification. 2,3-Dinitro-2,3-dimethyl butane (DMNB) supplied by Kanto Chemical Co., Inc. was used as a sample, and benzene supplied by Wako Pure Chemical Industries, Ltd. or 5% NO diluted in argon gas were used for the calibration of a mass number.

2.3 Quantum chemical calculations

All quantum chemical calculations were performed using the Gaussian 03 series of programs⁸⁾ at the B3LYP/6-31G (d) // B3LYP/6-31G (d) level of theory. The adiabatic ionization energies of explosives and ERCs were evaluated by calculating the standard enthalpy changes between a neutral molecule and a cation with optimized structures.

3. Results

3.1 Ionization energy

First, ionization energies for ERCs and typical explosives were calculated by density functional theory calculations at the B3LYP/6-31G (d) level of theory.

Calculated ionization energies for nitromethane, nitrobenzene, 2-nitrotoluene, 4-nitrotoluene, 1,3-dinitrobenzene, 2,4-dinitrotoluene, 2,3-dinitro-2,3-dimethyl butane (DMNB), 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-tri-

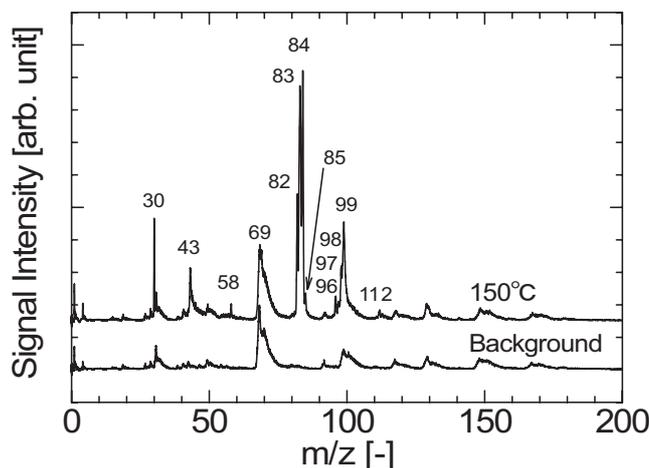
Table 1 Ionization energies for explosives and explosive related compounds

Comopunds	m/z [-]	Ionization energy [eV]	
		Exp. ^[9]	Cal. (this study)
Nitromethane	61	11.08±0.04	11.32
Nitrobenzene	123	9.94±0.08	9.43
2-Nitrotoluene	137	9.24	9.04
4-Nitrotoluene	137	9.46±0.05	9.04
1,3-Dinitrobenzen	168	10.4	10.28
2,4-Dinitrotoluene	182	–	9.61
TNT	227	10.59±0.04	10.05
DMNB	176	–	9.38
RDX	222	–	9.85
Tetryl	287	–	9.14
PETN	316	–	10.49
NTO	130	–	9.41
τ-HNIW	438	–	9.73
ψ-HNIW	438	–	9.97
ν-HMX	296	–	9.66
χ-HMX	296	–	9.75
Nitroguanidine	104	–	9.00
Nitroglycerine	137	–	9.96
MATB	228	–	9.19
DATB	243	–	8.76
TATP (D3)	222	–	8.30
TATP (C2)	222	–	7.87

nitro-1,3,5-triazine (RDX), pentaerythritol tetranitrate (PETN) and 2,4,6-trinitrophenyl-N-methylnitramine (tetryl), 5-nitro-1,2,4-triazol-3-one (NTO), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, or CL-20), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), nitroguanidine, 1-nitropropane-1,2,3-triol (nitroglycerine), 1-amino-2,4,6-trinitrobenzene (MATB), 1,3-diamino-2,4,6-trinitrobenzene (DATB) and triacetone triperoxide (TATP) are shown in Table 1.

Ionization energies for some compounds have been measured experimentally⁹⁾ and they are also shown in Table 1. Experimental values are higher than calculated values in most compounds. Maximum difference between experimental and calculated values at the B3LYP/6-31G (d) level of theory is 0.5 eV.

Ionization energies of most of explosives and ERCs in the tabulated compounds are predicted to be below 10.5 eV except for nitromethane, and these compounds are expected to be ionized by the 10.5 eV photon energy. Reported experimental values of ionization energy of nitromethane and TNT are more than 10.5 eV photon energy of 118 nm laser light. Ionization energy of PETN has not been measured experimentally, and calculated value is

**Fig. 2** Mass spectra of DMNB at 150°C of sample temperature

almost equal to the 10.5 eV. It is expected that these three compounds can not be ionized by the 10.5 eV photons on the basis of the present density functional theory (DFT) calculations.

3.2 Mass spectrum of 2,3-dinitro-2,3-dimethylbutane (DMNB)

3.2.1 Experimental results

An example of mass spectra of DMNB ($m/z=176$) obtained at around 150 °C (the vapor pressure of DMNB is 3.8 kPa⁶⁾) of sample holder and around 180 °C of sample line is shown in Fig. 2.

Though the calculated ionization energy of DMNB is 9.38 eV (<10.5 eV), a parent ion peak was not observed under various conditions. Instead, a lot of fragment ion peaks were observed at $m/z=130, 113, 112, 100, 99, 98, 97, 96, 85, 84, 83, 82, 69, 58, 43$ and 30. Relatively large background peaks were observed in our study, which may be responsible to the contamination from the vacuum grease used in the heated sampling lines or sample residues used in the previous experiments. Observed peak at $m/z=4$ is helium used as a carrier gas. The peaks with highest intensity are always at $m/z=83$ or 84. However, the ratios of the peak intensities are slightly different in different conditions. In the present study, reproducibility of the peak intensities is rather poor. This may be caused by the complicated processes of thermal decomposition and dissociation in the ionization process. In all measurements performed at different flow rates of carrier gas and different temperature, mass number sequence patterns are almost the same, therefore, it is possible to identify DMNB from the mass spectral pattern obtained using VUV-SPI-TOFMS.

3.2.2 Discussion by DFT calculation

To understand the fragmentation mechanism of DMNB with a 10.5 eV photon, DFT calculations were performed for the possible fragments. Some of the optimized structures at of fragment cation species with their minimum appearance energies are shown in Fig. 3.

Here, the minimum appearance energy is defined by (the sum of enthalpies of fragment species and other possible products) – (the enthalpy of the parent neutral mole-

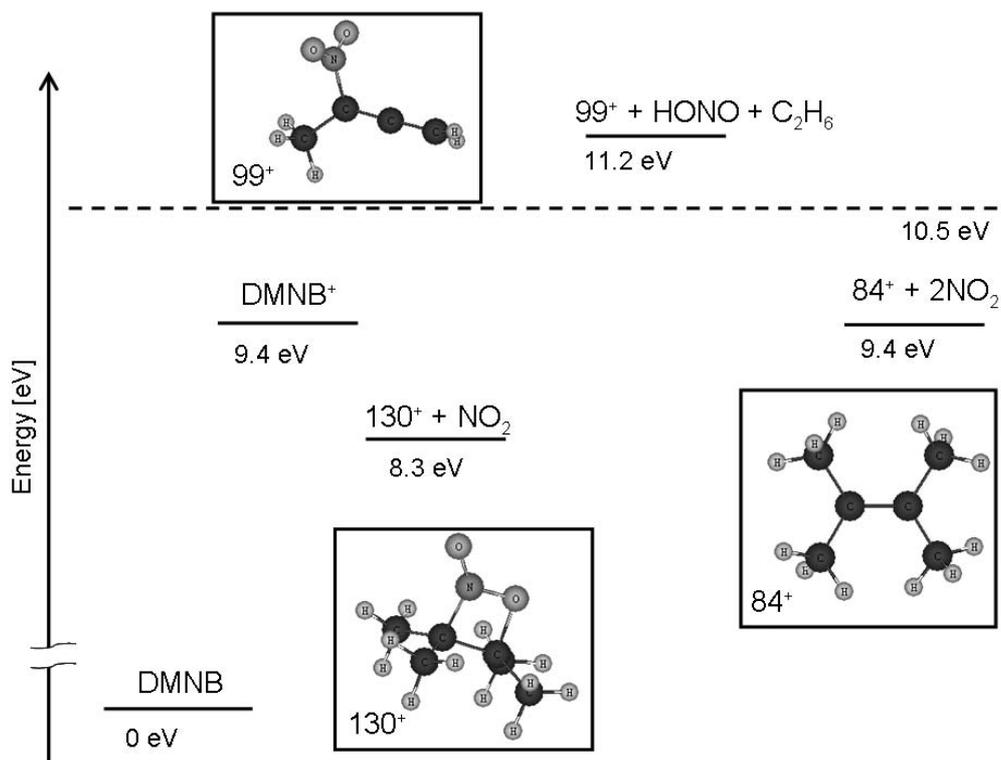


Fig. 3 Optimized structures of fragment cations (130⁺, 99⁺ and 84⁺) produced from DMNB and calculated minimum appearance energy for the fragments.

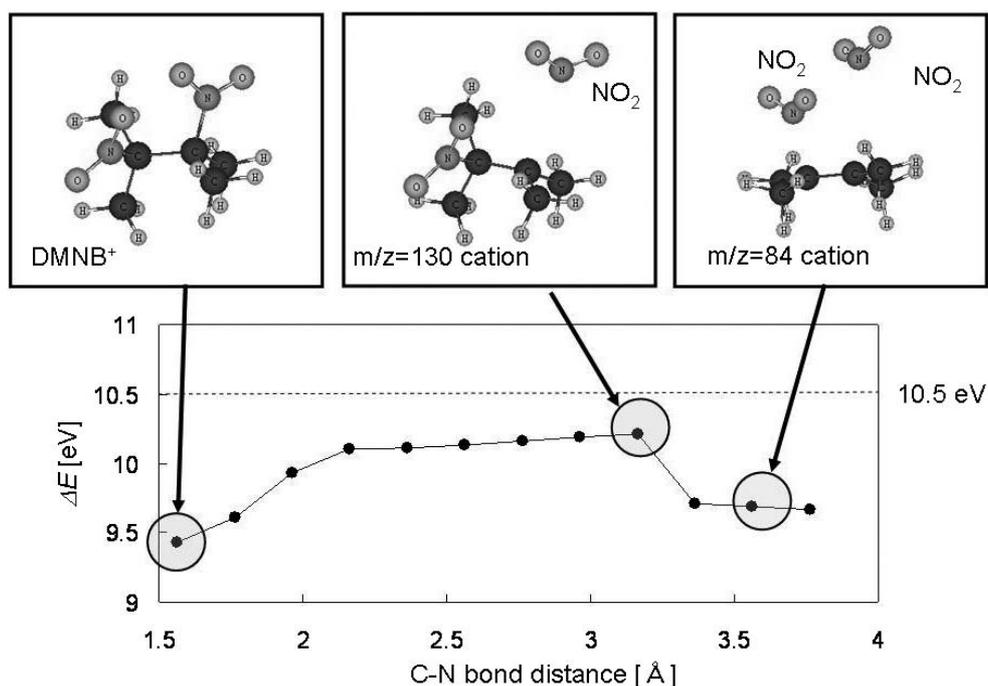


Fig. 4 Enthalpy difference ΔE for each optimized structure calculated for the NO₂ elimination from DMNB using "scan" option of Gaussian 03 program⁸.

cule). Main fragment at $m/z=84$ (84⁺) is expected to be produced by the elimination of two nitro groups which is relatively simple fragment. Fragment at $m/z=69$ could be produced by the elimination of one methyl group from $m/z=84$ species. On the other hand, the peak intensity of the fragment at $m/z=130$ is a weak even though $m/z=130$ cation (130⁺) can be produced by the dissociation of only one nitro group from DMNB parent and the calculated minimum appearance energy for the 130⁺ is 8.3 eV (<10.5 eV).

Fragment peaks at $m/z=113$ and 83 could be in the same sequences as $m/z=130$, which correspond to the mass defect of O and H from 130⁺ and further NO elimination from $m/z=113$ species, respectively. Fragment species at $m/z=100$ and 99 have several possible structures, for example C₄H₆NO₂⁺ or C₆H₁₂O⁺ for $m/z=100$ and their H loss species for $m/z=99$. One of the optimized structures of $m/z=99$ cation (99⁺) found by DFT calculation is shown in Fig. 3. The minimum appearance energy for 99⁺ is calculated at

11.2 eV, and then the 10.5 eV photon energy would not be enough to dissociate DMNB cation into 99^+ . Fragments at $m/z=58$, 43 and 30 can be assigned by CNO_2^+ , C_3H_7^+ and NO^+ , respectively.

All of these fragments are tend to be produced by elimination of at least one NO_2 group. To evaluate whether the photon energy of 10.5 eV used in this study is enough to dissociate C–N bond of DMNB into fragments, the enthalpies of optimized structures with increasing C–N bond distances by 0.2 Å step from 1.563 to 3.763 Å were calculated using “scan” option of Gaussian 03 program. C–N bond distance of DMNB cation with optimized structure (DMNB^+) is 1.563 Å, which is start point structure of “scan” calculation. Calculated enthalpy difference ΔE is defined by $\Delta E = (\text{the enthalpy of optimized structure at each C–N bond distance}) - (\text{the enthalpy of DMNB Neutral molecule})$. ΔE is plotted with optimized structures in Fig. 4.

Note that zero point energy corrections are not considered for “scan” calculations while all the other calculations in this study include zero point energy. As shown in Fig.4, when C–N bond distance is fixed at 3.156 Å, ΔE reaches to maximum and is less than 10.5 eV. At the distance longer than 3.356 Å, another C–N bond is also dissociated at the optimized structure. This result suggests that 10.5 eV photon energy could be enough to dissociate DMNB into $m/z=84$ cation and two NO_2 radicals without contribution of thermal energy.

4. Conclusions

As a real-time explosive monitoring device, a VUV-SPI-TOFMS system was investigated and mass spectra of DMNB were measured. From the DFT calculations, ionization energy values of most explosives and ERCs except for nitromethane are expected to be less than 10.5 eV photon energy used in this study. In mass spectra of DMNB which is very important species for explosive detection, a lot of peaks were detected without parent ion peak. From the results of DFT calculations, some of the fragments such as $m/z=84$ species can be produced within a photon energy of 10.5 eV, however, the complicated mass pattern in DMNB mass spectra is considered to be observed by the contribution of both photo dissociation and thermal decomposition.

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真空紫外光イオン化飛行時間型質量分析法による爆薬の検出

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近年のテロ増加に伴い、空港や駅等における爆薬のリアルタイム検知技術が必要となっている。真空紫外一光子イオン化飛行時間型質量分析 (VUV-SPI-TOFMS) は、非常に高速で選択的な検知技術となりうることが期待されている。特に、爆薬検知剤である2,3-dimethyl-2,3-dinitrobutane (DMNB) のマススペクトルパターンの情報は、実際の爆薬検出において非常に重要である。本研究ではまず、10.5 eVの光子エネルギーを持つレーザー光によるVUV-SPI-TOFMSを用いた爆薬検出の可能性を検討するため、量子化学計算により主要な爆薬及び爆薬関連物質に関してイオン化エネルギーを算出し、大部分の化合物について10.5 eV以下のエネルギーでイオン化可能であることを確認した。さらに、DMNBに関してVUV-SPI-TOFMSによりマススペクトルパターンを取得し、量子化学計算によりフラグメントの生成についての考察を行った。DMNBのイオン化エネルギーはB3LYP/6-31G(d)レベルの計算により9.38 eVと予想されたにもかかわらず明確な親ピークは検出されず、熱分解生成物と考えられるものを含むいくつかのピークのみが観測された。これらのうちピークのうち、二つのNO₂が解離したm/z=84のカチオンに関しては、10.5 eVの一光子で生成する可能性が計算により示された。

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