Multiphoton ionization mass spectrometry of nitrated polycyclic aromatic hydrocarbons

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Highlights

- The optimal wavelength for sensitive detection of NPAHs was determined to be 345 nm.

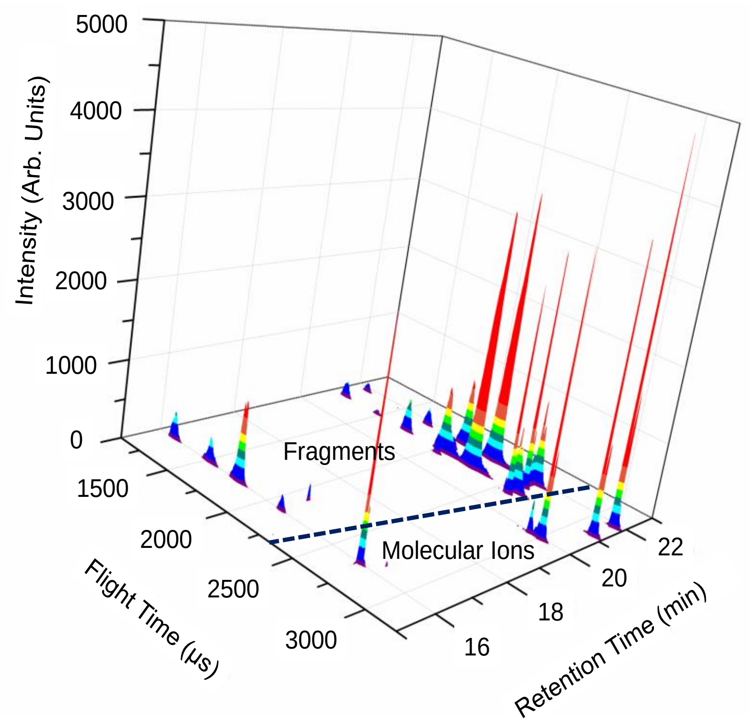
- The detection limits for NPAHs were in the subpicogram levels.

- Resonance-enhanced three-photon ionization was useful for observing molecular ions.

- Amounts of 9-nitroanthracene and 1-nitropyrene in $PM_{2.5}$ were successfully measured.

***Graphical Abstract (for review)**

Graphical Abstract



Original Papers

Multiphoton Ionization Mass Spectrometry of Nitrated Polycyclic Aromatic Hydrocarbons

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Abstract

The mechanism of multiphoton ionization was studied for the following nitrated polycyclic aromatic hydrocarbons (NPAHs), 9-nitroanthracene, 3-nitrofluoranthene, and 1-nitropyrene, using a femtosecond laser tunable in the range from 267 to 405 nm. A molecular ion was observed as the major ion and fragmentation was suppressed at wavelengths longer than 345 nm. The detection limit measured at 345 nm was at the subpicogram level. Organic compounds were extracted from a 2.19 mg sample of particulate matter 2.5 ($PM_{2.5}$), and the extract was subjected to multiphoton ionization mass spectrometry after gas chromatograph separation. The background signals were drastically suppressed at 345 nm, and a few NPAHs, including 9-nitroanthracene and 1-nitropyrene, were detected, and their concentrations were determined to be 5 and 3 pg/m^3, respectively.

Keywords: Nitrated polycyclic aromatic hydrocarbons, multiphoton ionization, mass spectrometry, particulate matter 2.5.

1. Introduction

Particulate matter 2.5 ($PM_{2.5}$) has increasingly attracted the attention of the public in recent years, since it contains polycyclic aromatic hydrocarbons (PAHs) and nitrated polycyclic aromatic hydrocarbons (NPAHs), which are highly mutagenic and carcinogenic. A few papers have reported that the content of NPAHs in $PM_{2.5}$ is 2 or 3 orders of magnitude lower than those of non-nitrated PAHs but their mutagenicity and carcinogenicity can reach 100,000 times and 10 times higher than the corresponding values for non-nitrated PAHs [1,2]. While the total amount of NPAHs and oxidized PAHs (OPAHs) is reported to exist only 8% of the total PAHs, the mutagenicity arising from these compounds can be 200% higher than the mutagenicity caused by PAHs [3]. In general, there are two main sources of NPAHs: (1) the incomplete combustion of organic matter such as fossil fuels by motor vehicles [4,5] (2) reactions of corresponding PAHs with NO_x or OH radicals in the atmosphere or heterogeneous reactions of PAHs adsorbed on ambient particles with $N_2O_5/NO_3/NO_2$ [6-9]. Due to the low concentrations of NPAHs in the environment and their high mutagenicity and carcinogenicity for human beings, it is important to develop a sensitive analytical instrument with a high selectivity for NPAHs, in conjunction with a simple pretreatment procedure before the measurement of NPAHs extracted from $PM_{2.5}$ [10,11]. It should be noted that a large amount of interfering species arising from non-nitrated PAHs is unavoidable in practical trace analysis.

Some analytical methods have been developed to date for the measurement of NPAHs. High-performance liquid chromatography (HPLC) combined with mass spectrometry (MS) and gas chromatography (GC) combined with MS are the most common techniques used for this purpose [12,13]. However, these methods suffer from limitations in sensitivity and selectivity, and the sample pretreatment process can be time consuming. Gas chromatography combined with multiphoton ionization time-of-flight mass spectrometry (GC/MPI/TOF-MS) has recently been developed and subfemtogram detection limits have been reported for PAHs by using an ultraviolet femtosecond laser as the ionization source [14]. This technique has been applied to trace analyses of dioxins [15,16], PAHs [14,17], pesticides [18,19] present in real samples. Thus, GC/MPI/TOF-MS represents a potential method for use in the trace analysis of NPAHs. Compared with other ionization techniques such as electron ionization (EI), this approach provides soft ionization and is useful for enhancing the intensity of the molecular ion and for suppressing background arising from interfering species such as PAHs [14,20]. Mass spectrometric techniques based on negativeion laser desorption ionization and nanosecond desorption followed by femtosecond ionization have been used for the measurement of NPAHs, although numerous fragments are observed in the mass spectrum [21-23].

In this study, we used an ultraviolet femtosecond laser for the efficient ionization of NPAHs. A tunable output of an optical parametric amplifier was employed to determine the optimal conditions for the sensitive as well as selective ionization and for the observation of a molecular ion to improve the reliability of the analysis. The effect of excess energy in mass spectrometry was investigated by changing the wavelength of the laser. Moreover, the background signals arising from interfering substances such as PAHs were examined using a real sample containing standard chemicals. To our knowledge, this is the first study reporting the ionization mechanism involved when a tunable ultraviolet femtosecond laser is used for trace analysis of NPAHs extracted from a $PM_{2.5}$.

2. Experimental

2.1. Apparatus

The analytical instrument used in this study has been described in detail elsewhere [24,25]. Briefly, a GC (6890GC, Agilent technologies) equipped with an auto sampler (6890N, Agilent technologies) was combined with a TOF-MS developed in our laboratory and now commercially available (HGK-1, Hikari-GK, Fukuoka, Japan). The fundamental beam of a Ti:sapphire laser (800 nm, 35 fs, 1 kHz, 4 mJ, Elite, Coherent Co.) was used as the pump source for an optical parametric amplifier (OPerA-Solo, Coherent Co.), the frequency of which was further converted into the ultraviolet (UV) region. The laser beam was introduced into the TOF-MS, the pulse energy of which was adjusted to 15 μJ using a neutral density filter at different wavelengths except 390 and 395 nm (8 μJ). A sample mixture containing NPAHs was separated using a DB-5MS column (30 m long, 0.25 mm inner diameter, 0.25 μm film thickness). The temperature program of a GC oven for separation of NPAHs was as follows: initial temperature 50 °C held for 1 min, a rate of 10 °C/min to 220 °C, then 5 °C/min to 310 °C, held for 2 min. For the measurement of a sample extracted from $PM_{2.5}$, the temperature was programed to increase from 40 °C to 120 °C at a rate of 20 °C/min, and held for 1 min, and increased to 250 °C at a rate of 5 °C/min, then held for 3 min at 250 °C. Finally, the temperature was increased to 310 °C at a rate of 5 °C/min, and held for 15 min. For both the standard sample mixture and the extract from $PM_{2.5}$, the temperature of the inlet port and the transfer line to the MS were set at 300 °C. The flow rate of helium used as a carrier gas was 1 mL/min. The ions induced by multiphoton ionization were accelerated toward a flight tube and were detected by microchannel plates (F4655-11, Hamamatsu Photonics). The signal was recorded using a digitizer (Acqiris AP240, Agilent Technologies), and the data were analyzed using a home-made software programed by LabVIEW.

2.2. Reagents and chemicals

Standard samples of 9-nitroanthracene (9-nitroANT), 3-nitrofluoranthene (3-nitroFLT), and 1-nitropyrene (1-nitroPYR) were purchased from AccStandard Inc. A standard mixture sample containing the above three NPAHs was prepared at a concentration of 1 ng/μL for each NPAH. Dichloromethane (analytical grade) and acetonitrile (LC/MS grade) used as solvents were supplied by Wako Pure Chemical Industries.

2.3. Pretreatment procedure of $PM_{2.5}$

A sample of $PM_{2.5}$ was collected on the roof of a building at the Fukuoka Institute of Health and Environmental Sciences using an instrument reported elsewhere [26]. The sampling equipment was placed 16.4 m from the ground level. The $PM_{2.5}$ was collected during a period of 1430 min on March 20, 2013 at a flow rate of 580 L/min. A quartz filter (22.8 × 17.6 cm) was placed on the equipment for the collection of $PM_{2.5}$ in ambient air. The amount of $PM_{2.5}$ trapped on the filer was 37.6 mg, the concentration of $PM_{2.5}$ in the ambient air being calculated to be 45.3 $\mu g/m^3$. The amount of $PM_{2.5}$ was evaluated from the difference in the weights of the filter measured before and after the sample collection.

Several circular filters (diameter, 4.7 cm) and rectangular filters (1.0 × 1.5 cm) were taken from the above filter. One particle-loaded circular and four rectangular filters with a total area of 23.3 cm^2 (weight of $PM_{2.5}$, 2.19 mg) were cut into small pieces using a clean stainless-steel scissors. The small pieces were then placed into a vial containing 10 mL of dichloromethane. Organic compounds such as PAHs and NPAHs were extracted three times from the filter ultrasonically with dichloromethane for 45 min. The extraction solvent was evaporated, and the residue was dissolved by adding 1 mL of acetonitrile. The sample mixture containing PAHs and NPAHs was filtered through a syringe with a membrane filter (GL-13N, pore size 0.2 μm), and was then concentrated to 70 μL using a stream of nitrogen. In order to evaluate the detection limits of the NPAHs present in the extracted sample and the effect of interference arising from other organic substances such as PAHs, the sample was measured with and without adding sufficient amounts of the standard chemicals. The sample, to which 500 pg/μL for each NPAH was added, was stored in the refrigerator in prior to the measurement.

2.4. Computational Methods

Quantum chemical calculations were performed for studies on the ionization mechanism of NPAHs using a Gaussian09 program series package. Minimum geometries were obtained using the B3LYP method based on the density functional theory (DFT) with a cc-pVDZ basis set [27]. The harmonic frequencies were calculated so as to ensure an optimum geometry providing a global energy minimum. A vertical ionization energy was evaluated from the difference between the energies of the ground and ionic states, which were obtained at the level of B3LYP/cc-pVTZ [28]. The lowest forty singlet transition energies and the oscillator strengths were calculated using time-dependent DFT (TD-DFT), and the predicted absorption spectra were generated using the Gauss View 5 software program.

3. Results and discussion

3.1. Ionization Mechanism

Resonance-enhanced multiphoton ionization (REMPI) is known to be one of the advanced techniques for the efficient ionization of organic compounds such as aromatic hydrocarbons. This approach has superior selectivity and reduces the background arising from interfering compounds. In addition, it can be utilized as a tool for soft ionization, producing a molecular ion in mass spectrometry. Although electron ionization (EI) has been applied to a few NPAHs [29], REMPI has distinct advantages with respect to high selectivity and capability of soft ionization. In the case of NPAHs, a nitro group deceases the lifetime of the singlet electronic excited state. However, the use of an ultrashort laser pulse (e.g., 35 fs) would be expected to overcome or partially compensate for the short lifetime of the excited state [30]. Therefore, the deterioration in sensitivity arising from ultrafast non-radiative energy relaxation could be minimal [31-33]. Ultraviolet-visible (UV-VIS) absorption spectra calculated by the TD-DFT method are shown in Fig. 1. The first electronic-excited states were located at energies corresponding to wavelengths of 425, 441, and 395 nm for 9-nitroANT, 3-nitroFLU, and 1-nitroPYR, respectively. Multiphoton ionization using a laser emitting in the region from near-UV to VIS would be the first choice for such an analysis. It should be noted that stronger absorption bands appear at 237, 202, and 225 nm as well for 9-nitroANT, 3-nitroFLU, and 1-nitroPYR, respectively. Ionization using a deep-ultraviolet (DUV) femtosecond laser would then be an alternate choice for achieving more sensitive detection.

The ionization energy and the scheme of ionization provided by the TD-DFT calculation are summarized in Fig. 2. Wavelengths corresponding to one-photon ionization (1PI) were 165, 155, and 163 nm for 9-nitroANT, 3-nitroFLU, and 1-nitroPYR, respectively. The boundaries between two-photon ionization (2PI) and three-photon ionization (3PI) were 330, 311, and 327 nm for these compounds, respectively. As a result, the NPAHs under consideration herein can be ionized at laser wavelengths of 267, 287, and 310 nm through a process of resonance-enhanced two-photon ionization (RE2PI), as recognized from Fig. 2. The efficiency of RE2PI is generally higher than that of RE3PI. However, a large excess energy remains in an ion when a laser emitting at 267 or 287 nm is utilized. This excess energy would accelerate the fragmentation. In the wavelength region below 350 nm, RE2PI will becomes inefficient and RE3PI will become dominant. At wavelengths below 450 nm, the energy of one photon will become insufficient for excitation to the first electronic excited state. As a result, NPAHs will be ionized through a non-resonant three-photon ionization (NR3PI) process.

3.2. Effect of Laser Wavelength

A laser emitting at 267 nm, i.e., the third harmonic emission of a Ti:sapphire laser, has been successfully employed for the detection of PAHs [17,37]. On the other hand, NPAHs have absorption bands at around 230-260 nm, 275-300 nm, and 350-405 nm [30,34-36]. In this study, the wavelength of the optical parametric amplifier was set at 267, 287, 310, 345, 375, 385, 390, 395, and 405 nm to investigate the ionization processes of the NPAHs. A two-dimensional display measured for a sample mixture at a laser wavelength of 267 nm is shown in Fig. 3. Three NPAHs were observed at the positions marked in the figure. In addition to several fragment ions, molecular ions were clearly observed for these NPAHs. Two unknown compounds are observed in the two-dimensional display at the retention times close to those of 3-nitroFLU and 1-nitroPYR, which provide signal peaks at the *m/z* values identical to some of the fragment peaks for the NPAHs. These signals likely arose from decomposition products that are produced in the injection port of the GC, since peaks corresponding to molecular ions are missing. The mass spectra of these three NPAHs can be obtained by extracting the data in the two-dimensional display at the retention times that these NPAHs are eluted. The same sample was measured at different wavelengths, and the above procedure was repeated. All of the results are summarized in Fig. 4. Molecular ions are observed as major peaks for all of these NPAHs. Some of the fragment ions could be assigned from the mass/charge (*m/z*) ratios to $[M\text{-}NO\text{-}CO]^+$, $[M\text{-}NO_2]^+$, and $[M\text{-}NO]^+$, which were further confirmed based on the data reported elsewhere [21,23,38]. In Fig. 4, the major fragment ion is $[M\text{-}NO_2]^+$ especially when measured at shorter wavelengths. It is noteworthy that other strong fragment peaks appear at m/z = 151 for 9-nitroANT and at m/z = 175 for 3-nitroFLU, when measured at laser wavelengths shorter than 345 nm. A signal peak of $[M\text{-}72]^+$ could be assigned to $[M\text{-}NO_2\text{-}C_2H_2]^+$, suggesting the efficient loss of acetylene after losing NO_2 from the molecular ion. For 3-nitroFLU, the fragment ion corresponding to $[M\text{-}NO]^+$ appeared more clearly at wavelengths longer than 390 nm, which could be explained by ionization through a process of competing nitro-nitrite rearrangement [21,38]. In addition, there are small peaks at m/z = 224 for 9-nitroANT and at m/z = 248 for 3-nitroFLU and 1-nitroPYR, which can be assigned to the isotope ions $[M+1]^+$, in which one of the ^{12}C atoms in the molecule is replaced with a ^{13}C atom.

3.3. Detection limit

In order to determine the optimal wavelength for the trace analysis of these NPAHs, the detection limits and ratios of the intensities for the molecular ion and the fragment ion of $[M\text{-}NO_2]^+$ were examined. The results are summarized in Table 1. The lowest detection limits were obtained at 345 nm due to low background signals, the values being 0.23, 0.33 and 0.31 pg for 9-nitroANT, 3-nitroFLU, and 1-nitroPYR, respectively. A detection limit of 30 pg was reported for 1-nitroPYR, which was achieved using gas chromatography combined with electron capture detection (GC-ECD) [39]. In the case of GC/MS, the detection limit can be improved to 3.14 pg (3.83 pg for 9-nitroANT) [3]. On the other hand, an analytical method based on liquid chromatography coupled with chemiluminescence detection was developed for the trace analysis of NPAHs, and the detection limit was reported to be 10 fmol (2.47 pg) for 1-nitroPYR [40]. The detection limit was further improved to 152 fg using a column that accommodated the online chemical reaction (reduction) of NPAHs [41]. In the present study, a comparable detection limit was achieved without the need for a reaction column. In addition, numerous components of NPAHs in addition to PAHs can simultaneously be determined on the two-dimensional display for comprehensive analysis, suggesting the superior performance of this method in applications to practical trace analyses of NPAHs and analogs thereof.

3.4. Measurement of NPAHs in $PM_{2.5}$

In this study, NPAHs extracted from $PM_{2.5}$ were measured at 267 and 345 nm. A two-dimensional display of the data is shown in Figs. 5 (a) and (b), respectively. Large background signals arising from interfering species appeared at 267 nm, which can be attributed to the efficient 2PI of aromatic hydrocarbons present in the actual sample. Although the pulse energy of the laser emitting at 267 nm can be increased to 300 μJ by using the third harmonic emission of the Ti:sapphire laser, it would be difficult to identify the signal peaks arising from NPAHs due to the presence of intense background signals. On the other hand, the background was substantially suppressed when a laser emitting at 345 nm was used. In order to calibrate the MS instrument, known amounts of standard NPAHs were added to the sample solution. The detection limits evaluated under the conditions used for the measurement of the real sample were 0.27, 0.60, and 0.45 pg for 9-nitroANT, 3-nitroFLU, and 1-nitroPYR, respectively. These values were not changed significantly from those obtained using the standard sample mixture dissolved in a pure solvent (see Table 1), suggesting that the effect of interference is negligible at 345 nm. By carefully checking the data shown in Fig. 5, it was possible to identify the signal peaks arising from NPAHs, the assignments for which are shown in Fig. 5 (b). In fact, the two signal peaks could be assigned to the molecular ions of 9-nitroANT and 1-nitroPYR, and their concentrations in the ambient air were determined to be 5 and 3 pg/m^3, respectively.

4. Conclusions

To evaluate the potential advantage of GC/MPI/TOF-MS especially for trace analyses of NPAHs in $PM_{2.5}$, mass spectra were obtained at different wavelengths to determine the optimal wavelength for multiphoton ionization using a tunable ultraviolet femtosecond laser. Fragment ions decreased significantly at longer wavelengths, and a molecular ion was produced as a major ion. This result is in contrast to data reporting the production of numerous fragment ions when nanosecond laser desorption/femtosecond ionization mass spectrometry was used [21,22]. In the present study, subpicogram detection limits were obtained with no or negligible effects of interference. It should be noted that NPAHs can be directly determined on the two-dimensional display of GC/MS without the need for a column for chemical reactions. Thus, this technique allows the comprehensive analysis of NPAHs contained in $PM_{2.5}$. The use of a laser with a higher pulse energy would further improve the sensitivity, since the background signal arising from interfering substances is negligible under the present conditions. Therefore, GC/MPI/TOF-MS has the potential for use in the trace analysis of NPAHs in the environment.

Acknowledgements

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Figure Captions.

Fig. 1 Calculated UV-VIS absorption spectra. (a) 9-nitroANT (b) 3-nitroFLU (c) 1-nitroPYR.

Fig. 2 Ionization schemes for 9-nitroANT, 3-nitroFLU, and 1-nitroPYR.

Fig. 3 Two-dimensional display of a standard sample mixture containing 9-nitroANT, 3-nitroFLU, and 1-nitroPYR. Concentration, 1 ng/μL for each component. Wavelength, 267 nm; pulse energy, 15 μJ.

Fig. 4 Mass spectra of NPAHs measured at different wavelengths. (a) 9-nitroANT (b) 3-nitroFLU (c) 1-nitroPYR. (1) $[M-NO_2-C_2H_2]^+$ (2) $[M-NO-CO]^+$ (3) $[M-NO_2]^+$ (4) $[M-NO]^+$

Fig. 5 Two-dimensional display of the sample extracted from $PM_{2.5}$. Laser wavelength; (a) 267 nm (b) 345 nm. Pulse energy; (a) (b) 12 μJ. The mass spectra, which were measured at the position corresponding to the molecular ions of 9-nitroANT and 1-nitroPYR, are shown as inserts in the figure.

Table

Table 1 Detection limits and M^+/F^+ ratios at different wavelengths

Wavelength (nm)	Limit of detection (LOD/pg)			M^+/F^+ *		
	9-nitroANT	3-nitroFLU	1-nitroPYR	9-nitroANT	3-nitroFLU	1-nitroPYR
267	0.78	0.48	0.35	2.8	1.1	1.4
287	0.81	0.69	0.65	2.1	1.1	1.2
310	1.05	0.51	0.54	0.8	1.0	1.1
345	0.23	0.33	0.31	1.6	1.0	1.2
375	0.55	0.53	0.40	6.7	1.7	2.4
385	1.83	1.13	0.50	10.4	2.6	3.7
390	4.61	2.85	1.17	19.6	3.9	6.5
395	87.3	34.8	29.1	14.9	7.1	17.7
405	35.0	9.18	4.35	9.6	5.2	8.1

*Calculated as a ratio of the intensities of the molecular ion and the largest fragment ion observed at a laser wavelength of 267 nm.

Figure

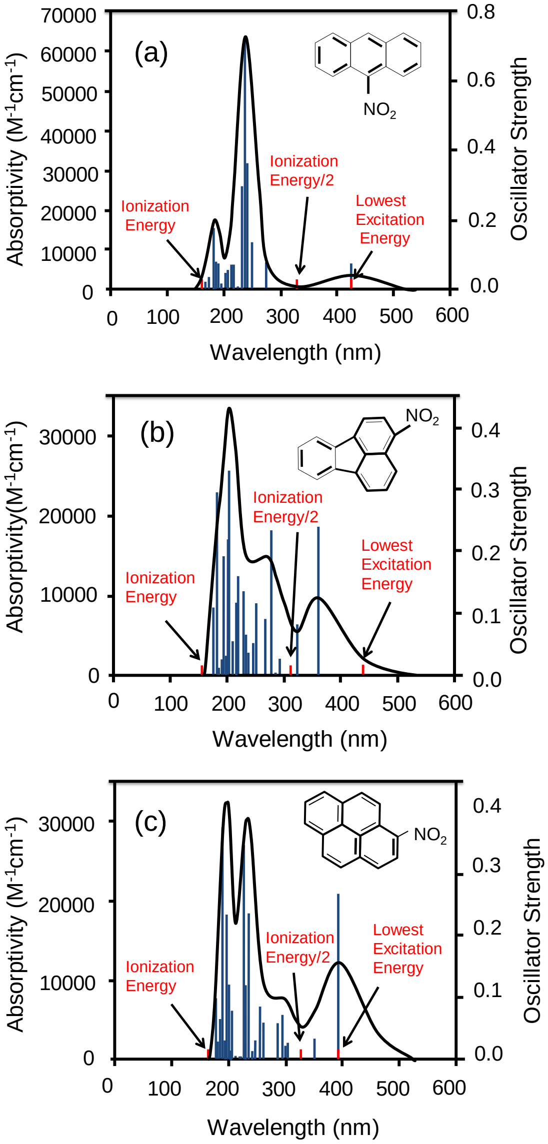


Fig. 1 Y. Tang et al.

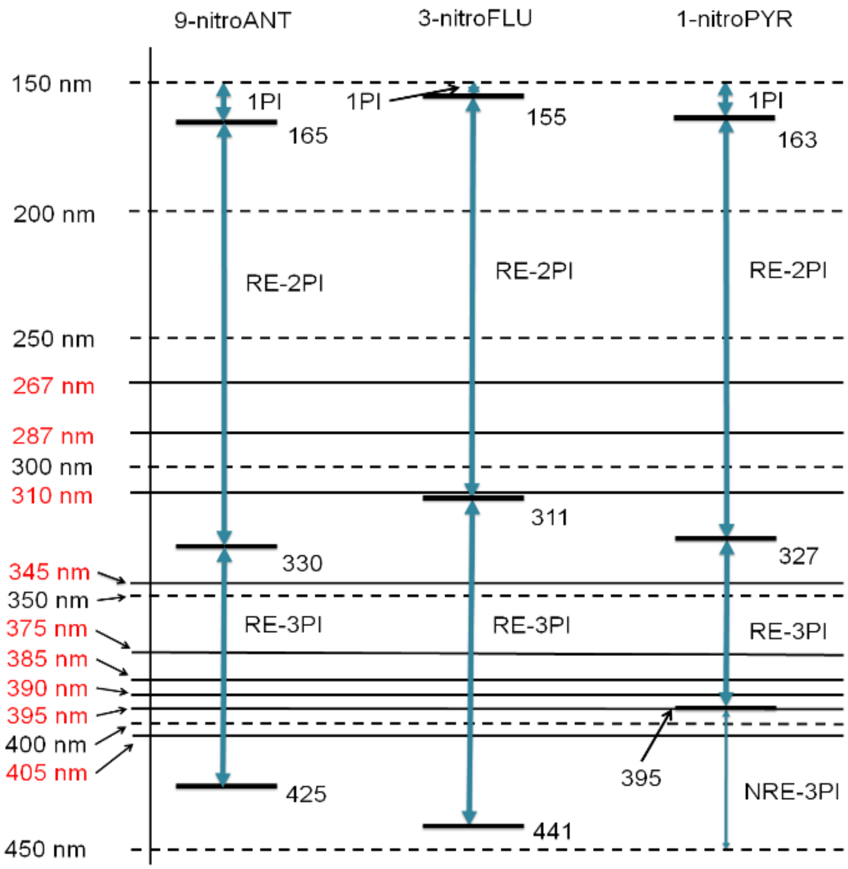


Fig. 2 Y. Tang et al.

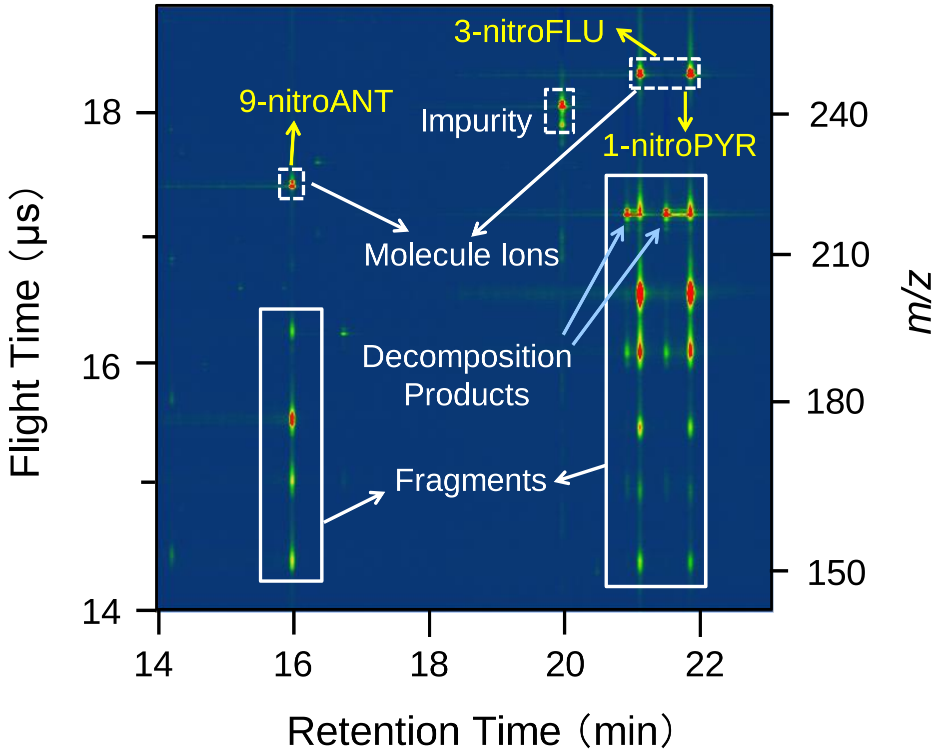
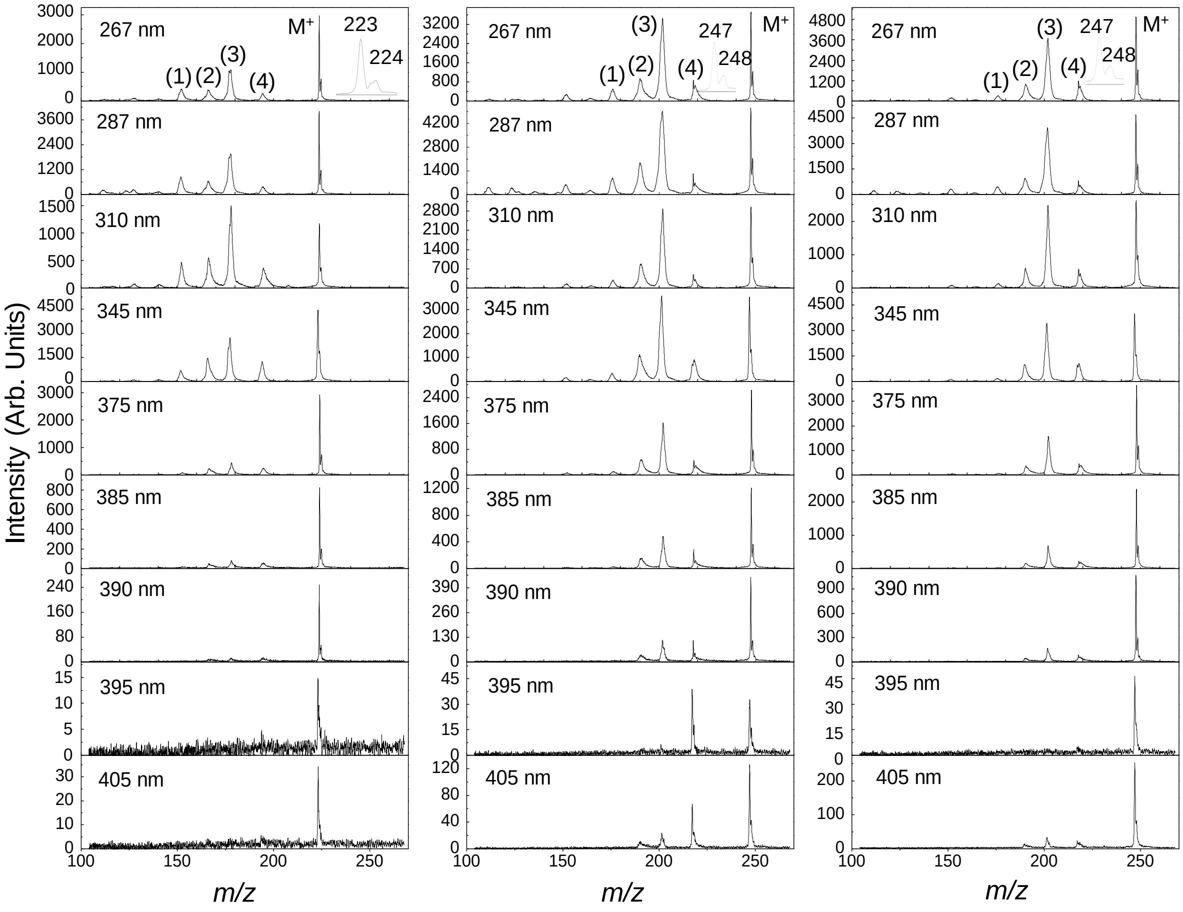


Fig. 3 Y. Tang et al.



(a) (b) (c)

Fig. 4 Y. Tang et al.

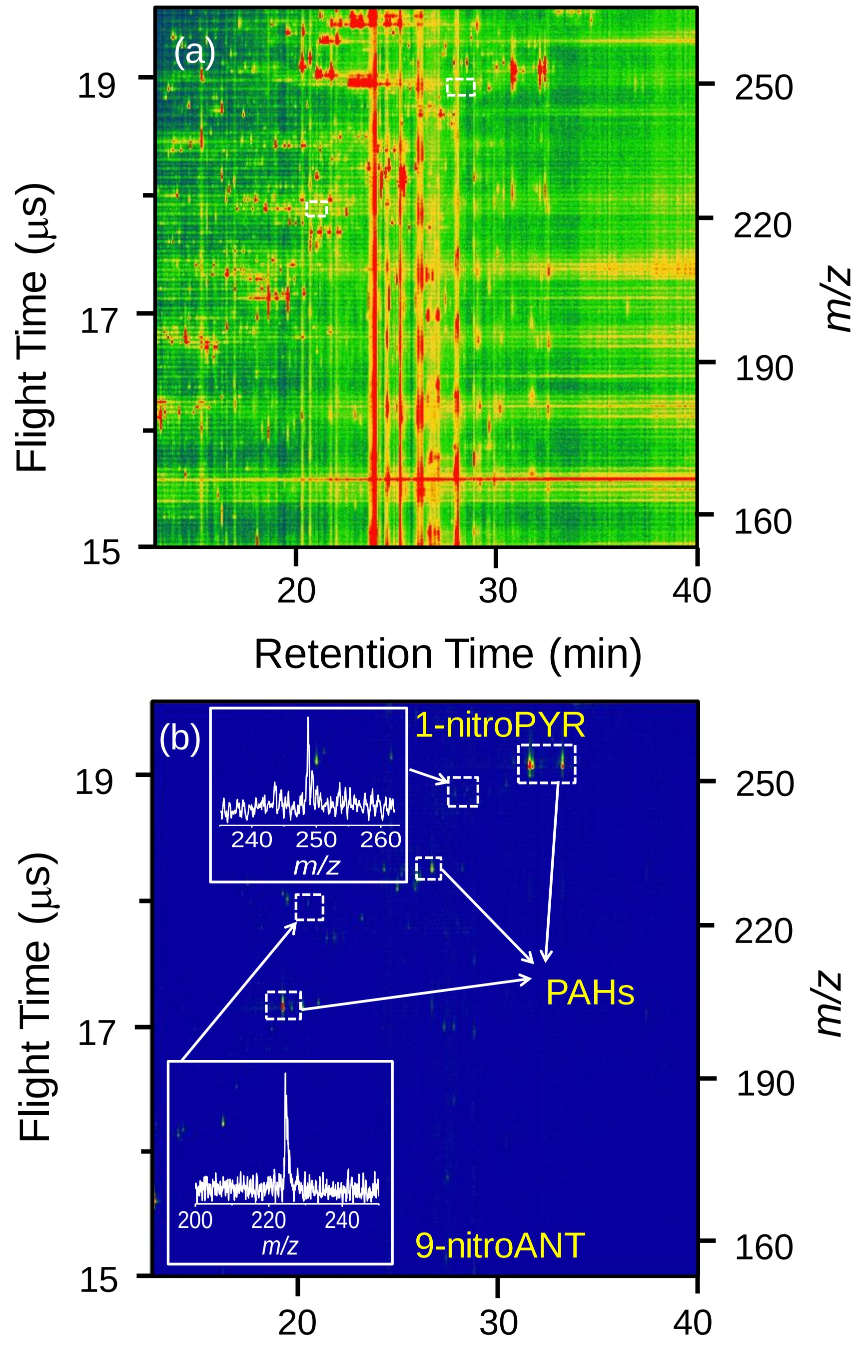


Fig. 5 Y. Tang et al.

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- E-mail address √
- Full postal address √
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- Keywords √
- All figure captions √
- All tables (including title, description, footnotes) √
- Manuscript has been 'spell-checked' and 'grammar-checked' √
- References are in the correct format for this journal √
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Cover Letter √
Novelty Statement √
Highlights √
Manuscript √
Table(s) √
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Checklist √
List of Three Potential Reviewers √