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Chemical mass shifts in quadrupole ion traps as analytical characteristics of nitro-aromatic compounds

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Dedicated to Dr. Jack Beauchamp, in recognition of his 60th birthday and in admiration of his scientific achievements.

Abstract

Chemical mass shifts of nitro-aromatic compounds were measured in a custom-modified GCQ ion trap instrument. The average normalized chemical mass shift of 0.91 ($\Delta m/m$, %) for the molecular ions of 24 nitro-aromatic compounds examined is much larger than the average value of 0.41 ($\Delta m/m$, %) measured for a group of aromatic compounds without the nitro substituent. The larger chemical mass shifts associated with the nitro group could serve as a diagnostic for identifying this class of compounds in mixtures and a simple method of implementing this test is described. Samples were examined at two different ac resonance ejection frequencies, one corresponding to the non-linear resonance frequency at $q_z = 0.80$ where chemical mass shifts are small for all compounds, the other corresponding to $q_z = 0.75$ where chemical mass shifts are in full operation. The difference in apparent mass under these two conditions is used as an easily measured criterion for recognizing compounds that satisfy the mass shift criterion for nitro-aromatic compounds. (Int J Mass Spectrom 222 (2003) 481–491)

Keywords: Chemical mass shifts; Nitro-aromatic compounds; Paul ion trap; Explosives monitoring; Collision-induced dissociation

1. Introduction

Chemical mass shifts were first observed during the early development of commercial ion trap instruments. Syka [1] observed errors as large as 0.7 Th (1 Thomson = 1 atomic mass unit per elementary charge [2]) in the measured mass/charge ratios for some ions, under experimental conditions where the measured values for other ions were in good agreement with the true mass/charge ratios. These compound-specific chemical mass shifts were eliminated empirically by adjusting the electric field in the ion trap. This was done by increasing the distance z_0 from the center of the trap to the end-cap electrodes from the theoretical value of 0.707–0.783 cm. (The theoretical value of z_0 is the value that corresponds to a pure quadrupole geometry using the relationship $r_0^2 = 2z_0^2$ for a ring electrode diameter $r_0 = 1.0$ cm.) In the stretched geometry, the value of z_0 is increased by ca. 11% without any corresponding modification to the hyperbolic shape of the ring electrode which would be required to maintain a pure quadrupole field. This adds higher-order contributions to the overall trapping field [3] that have been shown empirically [1,4] and

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theoretically [5] to offset the field imperfections caused by end-cap holes. Note that the existence of end-cap holes distorts the quadrupole field by causing *local* field faults, the effects of which can be described as adding negative higher-order fields to the quadrupole field. These negative higher-order fields result in an amplitude-dependence of the secular frequency for ion motion [6]. Stretching the trap (increasing the end-cap distance) introduces a *global* positive higher-order field. For the appropriate amount of stretching, these two different kinds of higher-order fields approximately cancel. Today, all commercial ion trap mass spectrometers adopt a stretched or otherwise altered geometry so that chemical mass shifts are almost completely removed.

Although chemical mass shifts can be successfully eliminated by changing z_0, their origin and nature remain an interesting topic that has been studied by several research groups [1,4,7–12]. This interest is sustained by the possibility that chemical mass shift measurements might have analytical significance. In addition to ion trap geometry [1,4], ion polarizability [8], dipole moment [9] and the radial distribution [11] of the ion population have all been suggested as factors that influence the magnitude of chemical mass shifts. Fragmentation was suggested by March and coworkers as a possible cause of chemical shifts [10] and Yost and coworkers have provided experimental evidence that fragile ions that show mass shifts have actually undergone dissociation [13,14] and that it is their fragments that are detected. The way in which the propensity to dissociate results in mass shifts has been explained [15,16] using the multi-particle ion trap simulation program ITSIM [5,17,18]. Both experiments and simulations indicate that the chemical mass shift is the result of the combination of two interacting factors: a delay in ion ejection during the mass scan due to field faults and compound-specific modifications of this delay due to ion collisions with the buffer gas. Ejection delay occurs for all ions, regardless of their masses or chemical structures, ions with same m/z experience the same ejection delay in the absence of collisions. In the presence of helium buffer gas, energetic collisions can cause early ion ejection. The fact that chemical mass shifts are compound-dependent arises because of the difference in the collision probabilities of individual ions, leading to different early ejection times. This affects the ejection times of the analytes and the fluorocarbon calibrant ions (perfluoro-*n*-tributylamine calibrant ions) and results in shifts in apparent masses and thus in chemical mass shift values.

In more recent work [19], correlations between chemical mass shifts and physiochemical properties of ions were sought by examining substituted acetophenone, benzophenones and pyridines in a modified ion trap mass spectrometer. Systematic changes in chemical mass shifts were found to occur with changes in the chemical structures of the ions. Brown's σ^+ constant, which is known to be correlated with the relative ease of fragmentation of substituted aromatic compounds, also correlates linearly with chemical mass shifts in *para*-substituted acetophenones and benzophenones. This correlation is evidence that the ease of dissociation of the ions is a major (but not the only) factor in determining chemical mass shifts. Therefore, compounds that are relatively easy to fragment are expected to exhibit relatively large chemical mass shifts, and this in turn suggests the possibility that the chemical mass shift phenomenon might be applied for diagnosis of particular groups of compounds, such as nitro-aromatics.

New methods for the selective detection of nitro-aromatic compounds are of great interest given their use as explosives. Compounds belonging to this group display characteristic dissociations in both EI and CI (positive and negative ion), including NO, NO_2 and OH loss processes. However, attempts to develop additional criteria for their recognition have been less successful. For example, they are remarkably difficult to recognize using ion/molecule reactions, one of the few exceptions being the work of Beauchamp and coworkers using $SiMe^+$ [20]. It is characteristic of nitro-aromatic compounds that they fragment readily due to the presence of electron-withdrawing nitro groups. As a result, some nitro-aromatic compounds have chemical mass shifts over 1 Th [15,19] although no systematic study of chemical mass shifts of these compounds has been reported, except as noted above. In this paper, a set of nitro-aromatic compounds have been examined and their mass shifts are reported. As a group they show large chemical mass shift and this characteristic is suggested as a one criterion among others that might have value in their analysis in complex mixtures. The possibility of a diagnostic test is recognized and an experiment is implemented in which the chemical mass shift is switched on or off depending on the frequency chosen for resonance activation.

2. Experimental

Experiments were performed using a modified Finnigan GCQ mass spectrometer (Thermoquest-Finnigan Cooperation, San Jose, CA). Both the hardware and software of the original commercial instrument have been modified to meet the requirements of the current study. A new set of electrode spacers was machined to maintain an ideal ion trap geometry, i.e., $z_0 = 0.707$ cm and $r_0 = 1.0$ cm. Meanwhile, a control and data acquisition module from a Finnigan LCQ mass spectrometer was used to replace the commercial data acquisition and processing system [15,19]. This module allows the instrument to be controlled with the Finnigan ion trap control language (ITCL), which provides much more versatility than the standard GCQ software.

The mass scale was calibrated using an ITCL (ion trap control language used for controlling the GCQ instrument) procedure which directly calibrated the instrument using the fragment ions of mass/charge ratio 69 and 131 generated from perfluorotributylamine (PFTBA). Each different resonance ejection working point was calibrated separately. Mass/charge values were measured at the maximum peak height and they were then compared to the exact theoretical monoisotopic values in order to calculate the mass shifts. For each data point, three measurements were made and the average values are reported. Positive mass shifts correspond to early ejection, i.e., lower than expected m/z values.

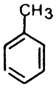
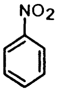
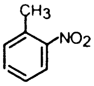
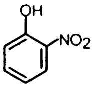
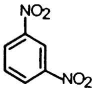
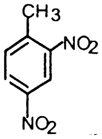
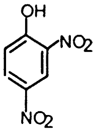
Samples were introduced by placing a small sample vial in a Cajon Ultratorr fitting located at the head of a 20 m, 250 μm i.d., deactivated column in the GC oven. The GC oven can be heated up to 350 °C so that relatively non-volatile samples can be vaporized. The headspace vapor was carried into the ion source by helium, flowing at a constant rate of 15 cm s^{-1} through a heated transfer line at a fixed temperature of 270 °C. The ion source temperature was set at 200 °C. Electron ionization (EI) was used with automatic gain control (AGC) to adjust the ionization time so that a constant number of ions was injected into the trap. By controlling the total number of ions in the trap, it is possible to minimize space–charge effects. Compressed isobutane gas was used as the chemical ionization reagent for proton transfer from the *t*-butyl cation. All chemical compounds are commercially available from Aldrich (Milwaukee, WI) and were used without further purification.

3. Results and discussion

3.1. Mass shifts for aromatic radical ions

Nitrobenzene was discovered to have a large chemical mass shift early in the development of quadrupole ion trap mass spectrometry [1]. In the present study, mass shifts for a series of nitro-aromatic compounds were compared with those for a series of non-nitro-aromatic compounds. The work was done using a custom-modified GCQ ion trap instrument with theoretical geometry, i.e., there is no compensation for the negative higher-order field contributions. Resonance ejection is performed at the GCQ default q_z value of 0.902 except as otherwise indicated when non-linear resonance and conventional resonance were compared at values of $q_z = 0.80$ and $q_z = 0.75$, respectively. Table 1 summarizes the chemical mass shifts of benzene, toluene, phenol and some of their nitro-substituted derivatives. Chemical mass shifts (Δm) are reported as the differences between the true mass and the measured apparent masses for the molecular ions. To account for a general increase in mass shifts with mass [19], a normalized value, $\Delta m/m$ (%), is also reported. Table 1 illustrates a general

Table 1
Chemical mass shifts of nitro-substituted benzene, toluene and phenol recorded at $q_z = 0.902$

Series 1	Δm (Th)	$\Delta m/m$ (%)	Series 2	Δm (Th)	$\Delta m/m$ (%)	Series 3	Δm (Th)	$\Delta m/m$ (%)
	0.05	0.06		0.19	0.21		0.16	0.17
	1.11	0.90		1.20	0.88		0.73	0.53
	1.52	0.90		1.53	0.84		1.38	0.75

observation that nitro-substituted compounds in each series have much larger normalized chemical mass shifts than their non-nitrated analogs compounds, and the absolute shifts increase with the number of nitro groups in each series.

Two major factors contribute to the increase in chemical mass shifts when the nitro group is substituted for hydrogen on the benzene ring. The first is the increase in mass. Heavier ions require higher rf amplitudes for their ejection, resulting in increases in the strength of the negative high order fields and hence in the duration of the ejection delay. Normalized chemical mass shifts ($\Delta m/m$) correct for these mass effects. As shown in Table 1, for nitrobenzene and nitrotoluene, introducing one more nitro group increases the chemical mass shifts but does not change the normalized mass shifts. The second factor is the increase in the ease of fragmentation which increases the fraction of the ejection delay observed as an actual chemical mass shift. Previous research (see Section 1) has shown that the relative ease of fragmentation during ejection delay is the major underlying factor determining the magnitude of chemical mass shifts [15,16,19,21]. For substituted aromatic compounds the ease of fragmentation is closely related to the electronic effects of the substituent groups. Nitro groups are strongly electron-withdrawing so they weaken bonds and promote lower energy fragmentation pathways, leading to a relatively large degree of dissociation and large chemical mass shifts. Table 1 shows strong electronic effects of substituents on mass shifts. Nitro-compounds with hydroxyl groups (Series 3) have much smaller chemical mass shifts than the corresponding nitro-aromatics with methyl substituents (Series 2). This is readily explained by the fact that the electron-donating hydroxyl group stabilizes the positively charged ion leading to less dissociation. However, the substituent effects are not the only features contributing to the ease of dissociation and good correlations with chemical mass shifts were observed only in the same class of compounds [19].

Table 2 summarizes the chemical mass shifts for 24 nitro-aromatic compounds, while Table 3 illustrates the chemical mass shifts for 22 aromatic compounds which do not contain nitro substituents. The percentage of fragmentation (% Frag) is presented as a measure of the degree of dissociation for each compound and calculated using literature data [22] associated with 70 eV electron impact mass spectra using the equation:

$$\%\,\mathrm{Frag} = \frac{\sum \text{Fragment ion abundance}}{\sum \text{Fragment ion abundance} + \text{molecular ion abundance}}$$

In general, nitro-aromatic compounds as a group display a larger degree of dissociation and larger chemical mass shifts than do non-nitro aromatic compounds. The average mass shift is 1.46 Th for the former but only 0.60 Th for latter (average normalized values are 0.91 and 0.41%, respectively).

Table 2
Chemical mass shifts of nitro-aromatic compounds recorded at $q_z = 0.902$

Compound	Monoisotopic mass (Th)	Chemical mass shift (Th)	% Frag	Normalized mass shift (%)
o-Nitrophenol	139.03	0.73	0.76	0.53
4-Methoxy-2-nitroaniline	168.05	0.94	0.81	0.56
p-Nitrobenzaldehyde	151.03	0.94	0.77	0.62
p-Nitrophenol	139.03	1.01	0.82	0.73
2,4-Dinitrophenol	184.01	1.38	0.78	0.75
1-Chloro-4-nitrobenzene	156.99	1.29	0.87	0.82
1-Methyl-2,4-dinitrobenzene	182.03	1.53	0.97	0.84
o-Nitrotoluene	137.05	1.20	0.99	0.88
m-Nitrobenzophenone	227.06	2.04	0.93	0.90
Nitrobenzene	123.03	1.11	0.88	0.90
m-Dinitrobenzene	168.02	1.52	0.81	0.90
1-Fluoro-4-nitrobenzene	141.02	1.31	0.74	0.93
p-Nitrobenzophenone	227.06	2.12	0.92	0.93
1-Nitronaphthalene	173.05	1.63	0.75	0.94
4-Nitro-*m*-xylene	151.06	1.43	0.95	0.95
4-Nitro-*o*-xylene	151.06	1.46	0.81	0.97
p-Nitrotoluene	137.05	1.33	0.80	0.97
1-Fluoro-2-nitrobenzene	141.02	1.38	0.76	0.98
o-Dinitrobenzene	168.02	1.69	0.84	1.01
2-Nitrobenzoic acid	167.02	1.72	0.72	1.03
3-Nitrobenzyl alcohol	153.04	1.69	0.79	1.10
m-Nitroacetophenone	165.04	1.87	0.94	1.13
p-Nitroacetophenone	165.04	1.89	0.94	1.15
2-Nitro-*m*-xylene	151.06	1.86	0.94	1.23
Average		1.46	0.85	0.91

3.2. Identification of nitro-aromatics

The characteristically large chemical mass shifts of nitro-substituted aromatic compounds might be useful as a diagnostic for these compounds, including some explosives. The multiple nitro substituents in many explosives are expected to cause very large chemical mass shifts while other compounds typically present in air and water matrices will often have much smaller chemical mass shifts. The criterion is not expected to be an absolute rule—rather it is expected to function as one analytical test among others for nitro-compound recognition. One way to quickly recognize large mass shifts is to record spectra under two conditions, one chosen so as to give large compound-dependent mass shifts (the chemical mass shift is "switched on"); the other using operating conditions that give small or no chemical mass shifts (the chemical mass shift is "switched off"). By comparing the mass spectra of the same sample recorded successively under the two conditions, it is easy to distinguish which peaks are shifted. For any given peak observed in each of the two scans, the difference in measured apparent mass can be used as a diagnostic for the presence of compounds of interest, specifically for easily dissociated ions. A criterion for a significant mass shift can be chosen so that only ions which are likely to be nitro-aromatics (or other large shifters) are marked. In addition, the mass spectrum recorded with the shift "switched off" can also provide normal *m*/*z* information for ion and compound identification.

There are several ways to switch the chemical mass shift on and off. Here we do so by using two different ac resonance ejection frequencies in an ion trap with negative higher-order field contributions to the quadrupole rf trapping field. One frequency

Table 3
Chemical mass shifts of non-nitro aromatic compounds recorded at $q_z = 0.902$

Compound	Monoisotopic mass (Th)	Chemical mass shift (Th)	% Frag	Normalized mass shift (%)
Pyridine	79.04	0.05	0.60	0.06
Benzene	78.05	0.05	0.53	0.06
Pyrene	202.08	0.20	0.50	0.10
2,3-Dihydro-2-methylbenzofuran	134.07	0.20	0.67	0.15
2,5-Dimethylfuran	96.06	0.15	0.81	0.16
Phenol	94.04	0.16	0.54	0.17
Phenanthrene	178.08	0.33	0.51	0.19
Toluene	92.06	0.19	0.71	0.21
9-Methyl-anthracene	192.09	0.46	0.65	0.24
2-Methylfuran	82.04	0.26	0.76	0.32
Dihydrobenzofuran	120.06	0.43	0.43	0.36
3-Ethylaniline	121.09	0.46	0.72	0.38
2,6-Dimethyl-naphthalene	156.09	0.71	0.69	0.45
2,7-Dimethoxy-naphthalene	188.08	0.95	0.57	0.51
9,10-Dihydro-anthracene	180.09	0.96	0.73	0.53
(*E*)-stilbene	180.09	0.96	0.77	0.53
Diphenyl ether	170.07	0.94	0.67	0.55
2-Ethylaniline	121.09	0.71	0.83	0.59
4-Ethylaniline	121.09	0.84	0.84	0.69
Benzophenone	182.07	1.55	0.86	0.85
N-Butylbenzene	134.11	1.23	0.90	0.92
Acetophenone	120.06	1.31	0.89	1.09
Average		0.60	0.69	0.41

corresponds to a non-linear resonance and the other one corresponds to a nearby frequency which does not coincide with a non-linear resonance. When the mass scan is performed using resonance ejection under non-linear resonance conditions, ions are excited by the dipolar ac field as they approach resonance, oscillate with large amplitudes, and are ejected quickly by the non-linear resonance effect [6]. A study of

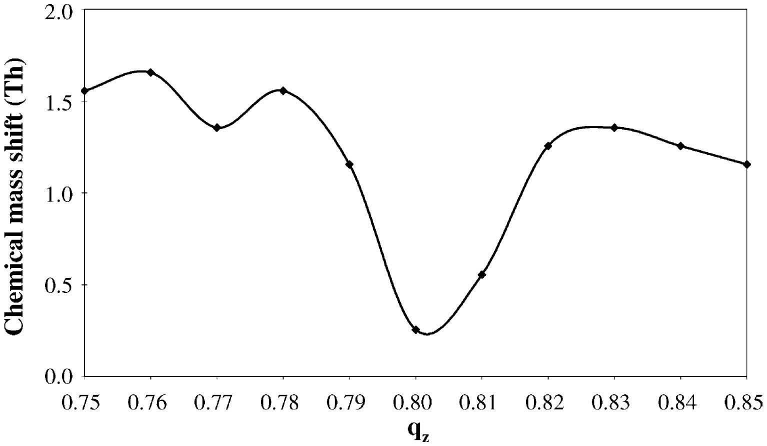


Fig. 1. Chemical mass shift of *o*-nitrotoluene as a function of resonance ejection q_z recorded in an ion trap with $z_0 = 0.707$ cm ($r_0 = 1.000$ cm).

the effect of resonance ejection on chemical mass shifts in the ion trap [21] revealed strong minima in chemical mass shifts at ac frequencies corresponding to non-linear resonance points. As shown in Fig. 1, the chemical mass shift of the radical cation of *o*-nitrotoluene is almost removed when resonance ejection is performed at the non-linear resonance working point $q_z = 0.80$ ($\beta_z = 0.69$). The non-linear resonance significantly reduces the ion ejection delay for all ions regardless of their chemical structure. Under these conditions, ions are ejected rapidly and there is not sufficient time for them to be differentiated by collisions; this leads to the marked decreases in the chemical mass shifts. However, when resonance ejection is performed at a nearby frequency which does not coincide with a non-linear resonance, for example at $q_z = 0.75$ ($\beta_z = 0.62$), no such non-linear resonance effect occurs. The ejection delay caused by field faults operates and thus large, compound-specific chemical mass shifts are observed. The position of the minimum of chemical mass shifts as a function of resonance ejection parameter q_z is compound

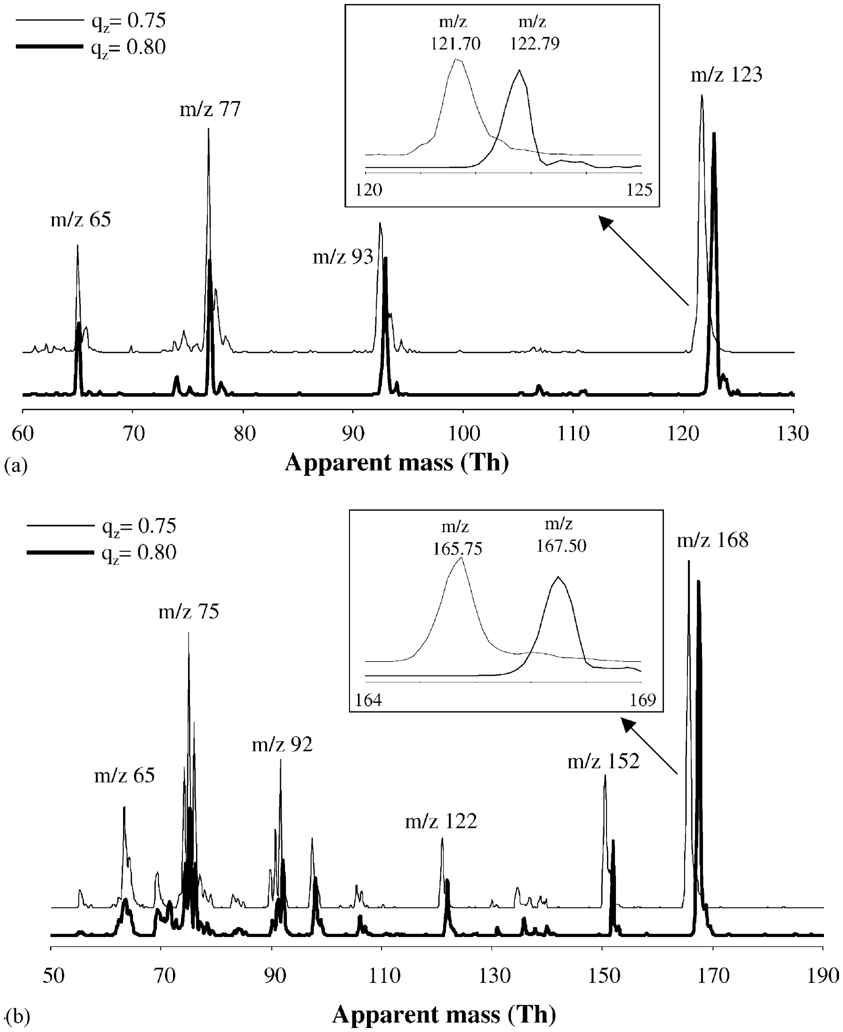


Fig. 2. Mass spectra (EI) of nitro-aromatic compounds with resonance ejection at $q_z = 0.75$ and at $q_z = 0.80$. (a) Nitrobenzene; (b) *m*-dinitrobenzene.

independent. However, the magnitude of this feature is compound dependent.

EI mass spectra of nitrobenzene recorded at $q_z = 0.75$ and at $q_z = 0.80$ are displayed in Fig. 2a. The measured apparent mass/charge ratios for the molecular ion of nitrobenzene are 121.70 and 122.79 Th, respectively, under the shift-on and shift-off conditions. The corresponding chemical mass shifts are 1.33 and 0.24 Th and their difference is 1.09 Th. The change in normalized mass shift upon switching resonance frequencies is 0.88 ($\Delta m/m$, %). Low mass fragments such as *m*/*z* 65 and *m*/*z* 77 do not show differential chemical mass shifts while the *m*/*z* 93 fragment ion displays only a small shift and hence a small difference between the two scans.

Similar data were obtained for *m*-dinitrobenzene (Fig. 2b). The important feature is that the chemical mass shift of *m*-dinitrobenzene molecular ion is significantly increased due to the second nitro group. The measured apparent masses for the molecular ion are 165.75 and 167.50 Th, respectively, which correspond to chemical mass shifts of 2.27 and 0.52 Th under the two operating conditions, making the apparent mass difference 1.75 Th ($\Delta m/m = 1.04\%$). Fragment ions which contain a nitro group, such as *m*/*z* 122 and *m*/*z* 152, also show large mass shifts.

In contrast to the behavior of the nitro-aromatics just discussed, the molecular ions of phenanthrene, naphthalene and pyrene display negligible chemical mass shifts under all operating conditions: these chemically stable structures do not easily fragment.

3.3. Chemical ionization

Although molecular radical cations generated by electron ionization (EI) carry valuable chemical mass shift information, EI is not always the best method for the characterization of nitro compounds. In the case of complex mixtures, EI might lead to too much fragmentation and so obscure the information of interest in a congested mass spectrum. In addition, many nitro-aromatics, especially those bearing methyl substituents, often have molecular ions of very low abundance. This difficulty is evident in the data for 2,4-dinitrotoluene (Fig. 3) recorded under the same conditions used for Fig. 2. Even though the *m*/*z* 182 molecular ion displays a large chemical mass shift, the peak intensity is too small to be useful for qualitative analysis in mixture.

In order to simplify mass spectra and to increase molecular ion abundances by minimizing fragmentation, chemical ionization (CI) can be used. Proton

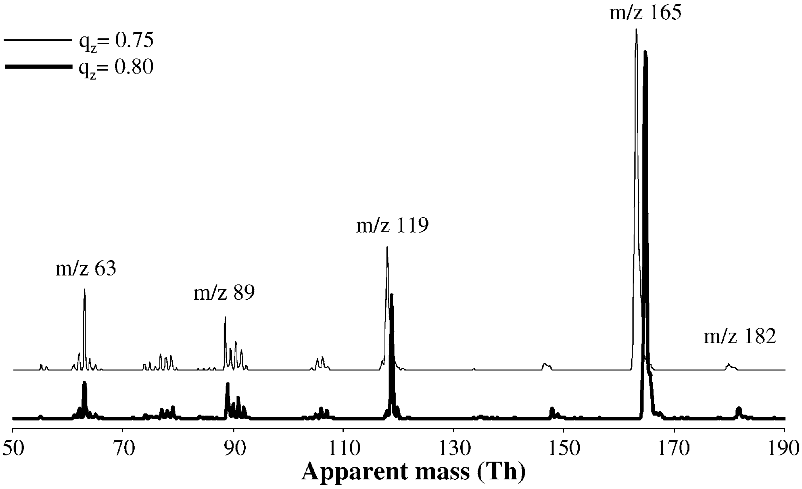


Fig. 3. Mass spectra (EI) of 2,4-dinitrotoluene with resonance ejection at $q_z = 0.75$ and $q_z = 0.80$.

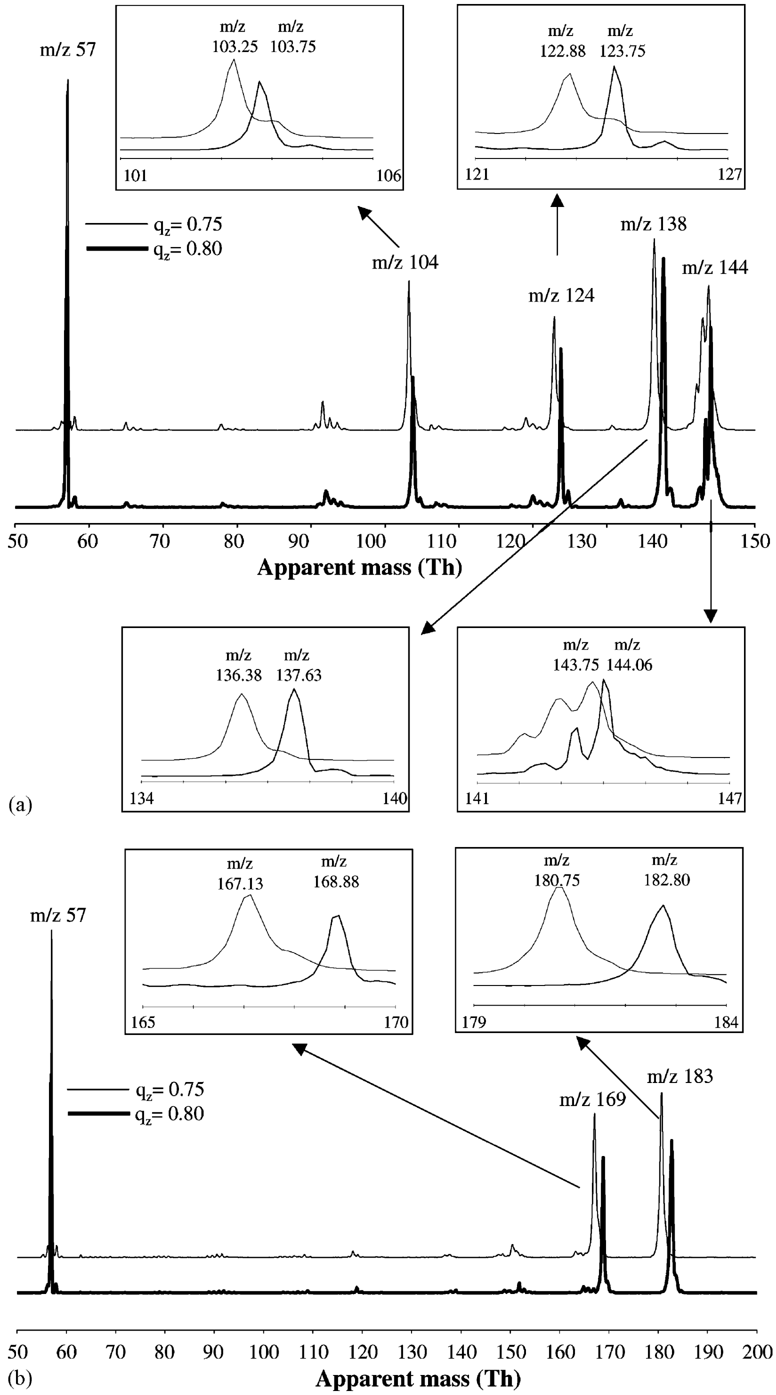


Fig. 4. Mass spectra (proton transfer CI) of nitro-aromatic compound mixtures with resonance ejection at $q_z = 0.75$ and $q_z = 0.80$. (a) A mixture of benzonitrile (*m/z* 104), nitrobenzene (*m/z* 124), nitrotoluene (*m/z* 138) and 8-methylquinoline (*m/z* 144); (b) a mixture of *m*-dinitrobenzene (*m/z* 169), 2,4-dinitrotoluene (*m/z* 183).

transfer reaction mass spectrometry (PTR-MS) is a promising method for on-line monitoring of volatile organic compounds at the ppb levels, for example, for air analysis [23]. We therefore studied the chemical mass shift behavior of protonated aromatic ions and found that protonated nitro-aromatic compounds demonstrate similar chemical mass shift behavior to the corresponding molecular radical cations generated by EI. In particular, they display characteristically large chemical mass shifts, the mass spectra are much simpler and less fragmentation occurs. The molecular ion is the base peak for all tested nitro-aromatic compounds under the chosen experimental conditions, however, this is not because the ions are more stable than the molecular radical cations but rather because of the mild conditions of CI. The large mass shifts observed indicate that fragmentation is facile in the course of ion ejection, as shown below.

Fig. 4a illustrates the proton transfer CI mass spectrum of a four-component mixture of benzonitrile, nitrobenzene, *o*-nitrotoluene and 8-methylquinoline and Fig. 4b shows the mass spectrum of a mixture of *m*-dinitrobenzene and 2,4-dinitrotoluene obtained using the same ionization method. In both cases, resonance ejection was performed at $q_z = 0.75$ and $q_z = 0.80$. All four nitro-aromatic compounds display large shifts in apparent mass at $q_z = 0.75$. The observed mass/charge differences are 0.87, 1.25, 1.65 and 2.05 Th for protonated nitrobenzene (*m*/*z* 124), nitrotoluene (*m*/*z* 138), *m*-dinitrobenzene (*m*/*z* 169) and 2,4-dinitrotoluene (*m*/*z* 183), respectively. By contrast, only small shifts are observed for protonated benzonitrile (*m*/*z* 104) and 8-methylquinoline (*m*/*z* 144) at this q_z value. Both groups of compounds show small shifts under the non-linear resonance conditions encountered when the spectra are recorded at $q_z = 0.80$ and this serves as a standard condition for comparing chemical shifts. The simplified mass spectra recorded by proton transfer CI facilitate mixture analysis, ideally converting each aromatic compound present in a mixture into a separate $(M + H)^+$ peak in the mass spectrum. In practice, high mass hydrocarbon compounds can undergo incomplete protonation which leads to multiple peaks such as in the group associated with *m*/*z* 144 in the 8-methylquinoline spectrum (Fig. 4a). This might be due to the inefficient ionization of hydrocarbons because of the relative stable *t*-butyl cation [24]. One must be careful either to avoid misassignments of chemical mass shifts in such cases or use a better CI reagent gas.

Since nitro-aromatic compounds as a group have large chemical mass shifts, false negatives are easily avoided provided the mass spectrometer has enough sensitivity. However, false positives could occur in a complex mixture due to the presence of other types of ions with large chemical mass shifts. Chemical mass shifts are characteristic but not infallible indicators of specific classes of compounds. As shown in Table 3, some non-nitro-aromatic compounds, such as benzophenone and *n*-butylbenzene, show large mass shifts. This means that the method of testing for nitro-aromatic compounds is recommended only for initial screening. Negative ion formation has been suggested as another selective method of detecting nitro-aromatic compounds due to their large electron affinities or gas phase acidities, and this allows confirmation through characteristic fragmentation behavior. Negative ion formation also greatly reduces matrix interferences and false positives. Chemical mass shifts in the negative ion experiment would add an additional characteristic but they remain to be measured.

4. Conclusion

Characteristically large chemical mass shifts are observed for all nitro-aromatic compounds, and the shifts increase with the number of nitro substituent groups. This characteristic behavior is suggested as the basis for a test for recognizing the presence of nitro-aromatic compounds. Nitrobenzene, *o*-nitrotoluene, *m*-dinitrobenzene and 2,4-dinitrotoluene, which are simulants for explosives, all show large shifts in apparent mass when comparing data taken at two ac resonance ejection frequencies, one chosen to correspond to a non-linear resonance which greatly reduces the chemical mass shift. Molecular radical cations $M^{\bullet +}$ and protonated molecular ions $(M + H)^+$ can both be used to implement this diagnostic method, and both show advantages and limitations. The chemical mass shifts yield an additional property that is characteristic of nitro-aromatic compounds and, with further development, these results might provide the basis for a method of qualitative analysis for nitro-aromatic explosives. Future work will cover the chemical mass shift behavior of negative ion species such as $M^{\bullet -}$ or $(M - H)^-$ and apply the diagnostic method to air samples containing explosives.

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