

# Real time measurement of PAN using SIFT-MS

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## Abstract

The on-line detection of gaseous peroxyacetyl nitrate (PAN) using SIFT-MS has been investigated using a synthetic sample of PAN in air at a humidity of ~30%. Using the H<sub>3</sub>O<sup>+</sup> reagent ion, signals due to PAN at  $m/z$  122, 77 and 95 have been identified. These are the protonated PAN, protonated peracetic acid and its water cluster respectively. These products and their energetics have been probed through quantum mechanical calculations. The H<sub>3</sub>O<sup>+</sup> rate coefficient has been estimated to be  $4.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  leading to a PAN sensitivity of 138 cps/ppbv. This gives a limit of detection of 20 pptv in 10 s using the  $m/z$  122 product ion.

Peroxyacetyl nitrate (PAN) is a multifunctional organic molecule produced by the atmospheric photo-oxidation of reactive hydrocarbons. It was first identified by Stevens et al.<sup>1</sup> as the compound responsible for many of the irritative properties of photochemical smog. Its highly temperature dependent decomposition rate<sup>2,3</sup> means it is capable of being a vehicle for the transport of radicals and nitrogen oxides over large distances in cooled air masses<sup>4</sup>. In fact PAN is a major odd nitrogen species in arctic environments<sup>5</sup>. Measurement of PAN concentrations are normally performed by gas chromatography with electron capture detection (GC-ECD)<sup>6,7</sup>. This is a very sensitive technique that is capable of low detection limits and relatively high sampling frequencies<sup>8,9</sup>. However, the high temporal and spatial variability of PAN concentrations has continued to fuel the development of faster analytical methods.

Mass spectrometric methods would appear to be a viable option for PAN detection but the inherent instability of PAN means that most ionization techniques result in high degree of fragmentation which complicates detection. Thermal decomposition followed by chemical ionization mass spectrometry of the resulting acylperoxy radical has been shown to be a specific technique for PAN type compounds<sup>10</sup>. Hansel and Wisthaler have examined the use chemical ionization using  $\text{H}_3\text{O}^+$  and drift tube mass spectrometric analysis methods, both in the laboratory and in the field using the proton transfer mass spectrometry (PTR-MS) technique for PAN analysis<sup>11</sup>. They found that while ionization of PAN produces a protonated parent ion  $\text{PAN.H}^+$ , this ion reacts with water in the drift tube to produce the protonated peracetic acid  $\text{CH}_3\text{COOH.H}^+$ . They used this assignment to show a detection limit of 70 pptv with a time resolution of 15s. There was some background assigned to the acetone water cluster and the protonated peracetic acid impurity. In a ship borne field study, de Gouw et al.<sup>12</sup> found a strong correlation between the protonated peracetic acid signal from a PTR-MS and independent PAN measurements, although the acetone interference was more marked in a subsequent study<sup>13</sup>.

In this paper we examine the potential use of selected ion flow tube-mass spectrometry (SIFT-MS) for the detection of PAN. SIFT-MS utilizes chemical ionization under thermal conditions with three chemical ionization agents ( $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$ , and  $\text{O}_2^+$ ) and we demonstrate that this makes it an attractive option for fast PAN analysis.

## **EXPERIMENTAL**

### **SIFT-MS**

The SIFT-MS instrument used in this study was a Voice200® manufactured by Syft Technologies Ltd. (Christchurch, New Zealand). The Voice200® is similar to the Voice100™ described earlier in some detail<sup>14</sup> except that the flow tube reactor is pumped by a dry scroll pump (S35 Edwards, Crawley, West Sussex U.K.) and not a Roots-type blower with a corresponding reduction in weight, size and flow rate. In brief, target compounds are identified by chemical ionization reactions taking place within a flow tube reactor. Three reagent ions  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$  are generated by a microwave discharge and then selected by mass using a quadrupole mass filter. The pure chemical ionization reagents are then introduced into the flow tube reactor where they react with the trace volatile species in the sample forming product ions. No sample work-up is required as the chemical ionization agents are unreactive with the major components of air. The sample is simply a small amount of air (~10%) leaked directly into the flow tube. The ions, both product ions and unreacted reagent ions, are carried along the flow tube in a stream of inert gas and exit the reaction region through a small orifice at the far end. The flow tube pressure is maintained at 0.78 Torr and the reaction time between the ionization agents and the analytes is around 5ms. After traversing through the orifice, the ions are focused by a lens array into a second quadrupole mass filter located at the downstream end of the instrument where they are identified by mass and counted by a continuous dynode-type particle multiplier. Reagent ion signals of  $10^7$  cps are typical and corrections to the raw ion intensities were made using a certified standard containing gases which create single products spanning the mass range of the downstream quadrupole. The concentrations of the trace species of interest are found by measuring the ratios of the product ion signals to the reagent ion signals providing the relevant kinetic parameters are known.

### **PAN Synthesis**

PAN was prepared by the nitration of peracetic acid in undecane using nitric acid, with the peracetic acid in turn being prepared by the reaction of acetic anhydride with hydrogen peroxide<sup>6,15</sup>. The organic solution was double washed with iced water. The undecane solution is expected to contain PAN, as well as traces of organics not completely removed by

washing, and perhaps the water insoluble diacetyl peroxide, an expected by-product in the peracetic acid synthesis. To aid in assigning mass spectral peaks to PAN and possible impurities, a blank preparation was performed by working through the preparation but excluding the nitration step.

## **THE SIFT-MS SPECTRA OF PAN AND THE IDENTIFICATION OF TARGET PEAKS**

A 1mL sample of the headspace gas above a room temperature sample of the synthesized PAN solution was diluted with 1 L of cylinder air (Southern Gas Ltd, Christchurch) in a Tedlar® (SKC Inc, Eighty Four, PA, USA) sample bag. This sample was then admitted directly to the Voice200® SIFT-MS inlet which is a short length (approximately 5cm) of thin bore tubing to control the leak of air into the flow tube. This tubing and the associated connections (up to 50cm of 1/8"OD passivated stainless steel tubing) are usually heated to 100°C to prevent condensation and sample loss. The thermal decomposition of PAN at temperatures above room temperature is rapid, so at these elevated temperatures the PAN would be expected to be entirely decomposed in the sample inlet prior to entering the flow tube<sup>11,16</sup>. The initial decomposition produces peroxyacetyl radicals and NO<sub>2</sub>, but the radical would be expected to follow one of a number of reaction pathways to give methyl radicals and CO<sub>2</sub> as carbon containing products. Thus a viable protocol for PAN measurements, with this instrument, is to maintain the inlet at room temperature (~25°C) for PAN measurements and revert to a heated inlet to provide a PAN and essentially organic free background.

Figures 1-3 show the chemical ionization mass spectra obtained for a PAN sample. Each reagent ion spectrum is shown separately with the PAN spectrum and the background spectrum, obtained by heating the sample, overlaid.

Of the three reagent ions used in the study, the clearest indication of PAN is observed in the H<sub>3</sub>O<sup>+</sup> ionization spectrum. The PAN spectrum shows the ion from proton transfer at  $m/z$  122, a major ion at  $m/z$  77, likely protonated peracetic acid<sup>11</sup> CH<sub>3</sub>C(O)OOH.H<sup>+</sup>, and a water cluster of this molecular ion at  $m/z$  95. Fragment ions at  $m/z$  43 (CH<sub>3</sub>CO<sup>+</sup>) and  $m/z$  46 (NO<sub>2</sub><sup>+</sup>) are also observed. Other major peaks observed are from known impurities in the PAN namely:  $m/z$  119 and 137 from protonated diacetyl peroxide and its water cluster; and  $m/z$  61, 79, and 121 corresponding to protonated acetic acid, its water cluster, and the protonated

dimer respectively. On heating the sample, the  $m/z$  122 ion disappears and the  $m/z$  77 and 95 ions decrease by an order of magnitude when referenced to the acetic acid peaks. They are also present in the preparation blank suggesting this background concentration results from peracetic acid that is not completely washed from the organic phase. Some contribution to the  $m/z$  95 peak could be from phenol which is present in Tedlar® bags<sup>17,18</sup>.

These observations are in general agreement with those from the selected ion flow drift tube (SIFDT) study of PAN with  $\text{H}_3\text{O}^{+11}$  where observed ions at  $m/z$  122, 46 and 43 were attributed to the products from the desired reaction and ions at  $m/z$  77, 61 and 64 (protonated nitric acid) to products from reactions with impurities. Water clusters of acetic and peracetic acids were not reported presumably because the higher energy of the ions in the drift tube is sufficient to dissociate them.

Thus the ion products that appear to be sufficiently specific for the on-line analysis of PAN by SIFT-MS are at  $m/z$  122, 77 and 95.

The protonated molecule at  $m/z$  122 is the most promising for analytical measurements as its production is simply related to PAN and, since it retains the nitrogen, its even  $m/z$  separates it from the protonated molecules of most of the organic molecules in the atmosphere. However the reaction of this ion with water to produce peracetic acid has been reported to have a rate constant of  $1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at  $\text{KE} = 0.11 \text{ eV}$  in the SIFDT<sup>11</sup>. Under these instrumental conditions 95% of the protonated molecule would be reacted to give the protonated peracetic acid molecule at 0.2% water in the drift tube. In a PTR-MS, leakage of water from the ion source into the drift tube generally exceeds this value and so this reaction precludes the use of the  $m/z$  122 for PAN measurements.

This reaction with water should also occur in the SIFT-MS. The spectra in Figure 1 show that high concentrations of water are present even in the laboratory system. The three major protonated water peaks at  $m/z$  19, 37 and 55 have ion counts of 5.3, 2.9 and  $0.5 \times 10^6$  cps. In addition the protonated acetic acid, peracetic acid and diacetyl peroxide all show water clusters. This water is likely coming from the sampling bag as no attempt was made to control the water concentration. Bags were not dried prior to being filled and neither was the air or the PAN solution used to make the sample. The effect of humidity on the ratio between the  $\text{H}_3\text{O}^+$  ion and its water clusters allowed the determination of the relative humidity in the bag sample as 30 (+/- 4)%. At this water concentration the continued presence of the

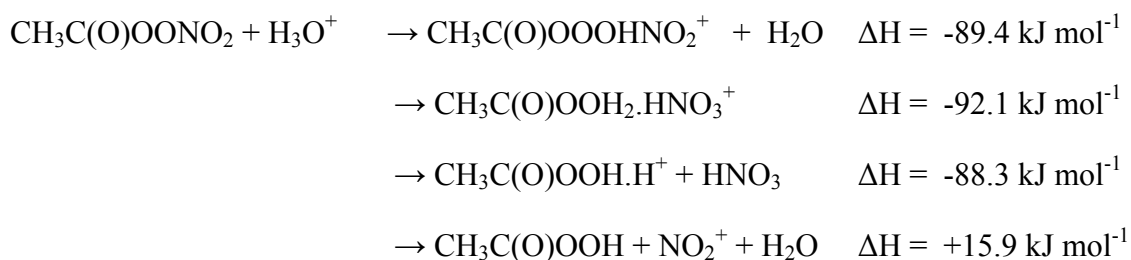
protonated PAN molecule at  $m/z$  122 in the flow tube can only be explained if the rate constant for the reaction with water is less than  $5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . The discrepancy with the published value must reflect the thermalized ion energy in the flow tube of the SIFT compared with that in the SIDT. The comparatively slow reaction also indicates that the  $m/z$  77 ion observed in this study must come directly from the reaction of PAN with  $\text{H}_3\text{O}^+$ .

The major products of the  $\text{NO}^+$  chemical ionization reaction with PAN are  $\text{CH}_3\text{CO}^+$  ( $m/z$  43) and  $\text{NO}_2^+$  ( $m/z$  46). It should be noted that  $\text{NO}^+$  (ionization energy 9.2 eV) will not form  $\text{NO}_2^+$  directly from gaseous  $\text{NO}_2$  (ionization energy = 9.59 eV)<sup>19</sup> and thus this peak is the result of ionic fragmentation of PAN and not electron transfer from  $\text{NO}_2$ . The peaks at  $m/z$  90 and 155 are the acetic acid adduct  $\text{CH}_3\text{COOH}.\text{NO}^+$ , and the  $(\text{M-H})^+$  from the undecane respectively.

Chemical ionization from  $\text{O}_2^+$  of PAN produces mainly the  $\text{CH}_3\text{CO}^+$  ion with a smaller amount of the  $\text{NO}_2^+$  ion. There is an appreciable amount of  $\text{H}_3\text{O}^+$  produced by the reaction of  $\text{O}_2^+$  with water in the system, as evidenced by the peaks at  $m/z$  19, 37 and 55. Thus reaction of these ions with PAN gives rise to the small peaks at  $m/z$  61, 79, 95 and 122 that mirror the  $\text{H}_3\text{O}^+$  spectrum. The higher mass peaks are predominantly hydrocarbon fragments from the undecane. By comparing the cold to hot inlet spectra one can see that the  $\text{NO}_2^+$  signal is higher in the hot inlet spectra, this is assigned to the direct formation of  $\text{NO}_2$  via the thermal dissociation of PAN<sup>16</sup>.

### Computational Study

Calculations on the thermochemistry of the reaction of PAN with  $\text{H}_3\text{O}^+$  were performed at the G3MP2<sup>20</sup> level of theory using the Gaussian 03 program<sup>21</sup>. Curtiss et. al.<sup>20</sup> give average absolute deviations of  $4.9 \text{ kJ mol}^{-1}$  for enthalpies of formation,  $5.9 \text{ kJ mol}^{-1}$  (0.061 eV) for ionization energies, and  $4.3 \text{ kJ mol}^{-1}$  (0.044 eV) for proton affinities for this method. PAN can be potentially protonated at three positions: (i) The carbonyl oxygen (PA = 761 kJ/mol), the peroxy oxygen bound to the carbon (PA = 724 kJ/mol), and the peroxy oxygen bound to the nitro group (PA = 779 kJ/mol). These values are in good agreement with previous calculations<sup>22,23</sup> and are lower than the experimental bracketing study of the PA of PAN<sup>24</sup>. The observed reaction appears to involve an association reaction with some rearrangement. The four channels examined and the thermochemical results are given below and in Figure 4.



The last reaction has a high entropy change so would have a small negative free energy ( $-28.7 \text{ kJ mol}^{-1}$ ), but significantly more positive free energy change than the reaction to form nitric acid ( $-90.9 \text{ kJ mol}^{-1}$ ). These results confirm that the observed ions  $\text{PAN}\cdot\text{H}^+$  and  $\text{PAA}\cdot\text{H}^+$  are thermodynamically feasible. We do not see the addition product  $\text{CH}_3\text{C}(\text{O})\text{OOH}_2\cdot\text{HNO}_3^+$ . The proton affinity of peroxyacetic acid is calculated to be  $783 \text{ kJ/mol}$  which is in reasonable agreement with a previous calculation<sup>25</sup>.

The polarizability and dipole moments of PAN were calculated at the MP2(FU)/6-31G\* level of theory at  $3.81\text{D}$  and  $6.18 \text{ \AA}^3$  respectively. These values are used in the later calculation of the collision limited rate coefficient.

## APPLICATION TO THE MEASUREMENT OF PAN CONCENTRATION

The expected collision-limited rate coefficients have been calculated using the polarizability and dipole moments calculated above and the theory of Su and Chesnavich<sup>26</sup> one can calculate the expected collision-limited rate coefficients. These are  $4.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ,  $3.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , and  $3.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$ , and  $\text{O}_2^+$  respectively. As a proton transfer product is observed for the  $\text{H}_3\text{O}^+$  reagent ion, this reaction is expected to be exothermic and thus the rate coefficient will be equal to the collision-limited rate coefficient. By comparing the magnitude of the reagent and product ions for  $\text{NO}^+$  and  $\text{O}_2^+$  we can see that both are also expected to proceed at or near the collision-limited rate.

As the concentration of PAN above the sample is unknown we cannot directly relate the observed signal levels to a limit of detection. However typical sensitivities on the Voice200 for reactions with similar reaction rate coefficients are typically  $150 \text{ cps/ppbv}$ . As the

reactions of the reagent ions do not give a single product ion, this sensitivity will be spread across all the products. The cold inlet scans can be used to estimate the relative branching ratios for each reaction channel and from this partition the overall sensitivity. Using these values and the measured background counts at the appropriate mass from the Voice200 we calculate the 10 s limits of detection and quantitation<sup>27</sup> for PAN that are shown in Table 1.

## CONCLUSION

We have examined the use of SIFT-MS for the detection of peroxyacetyl nitrate (PAN) in ambient air. Using  $O_2^+$  and  $NO^+$  as reagent ions do not give sufficiently specific product ions to be useful as an analytic method. However several PAN related ion products have been observed using  $H_3O^+$  as the reagent ion, in particular the PAN protonated molecular ion at  $m/z$  122. This ion was observed for a sample with 30% relative humidity showing that the lower reaction energy in the SIFT flow tube gives less reaction with water compared to SIFDT and PTR-MS methods. A fragment ion at  $m/z$  77, likely protonated peracetic acid, and its water cluster at  $m/z$  95 were also observed to result from the PAN reaction with the reagent ion. The thermalized rate constant for the reaction of the  $m/z$  122 ion with water is too slow to produce significant  $m/z$  77 ions in this system. The use of the  $m/z$  122 ion is more specific to PAN than the other ions because of its simple relationship to the analyte and the potential interference of a water cluster of acetone with the ion at  $m/z$  77. By altering the temperature of the inlet to the SIFT-MS instrument it can be confirmed that the ions assigned to PAN are truly due to PAN as they are not observed when the inlet temperature is 100°C and thermal decomposition of PAN is expected.

Using theoretical parameters the  $H_3O^+$  rate coefficient can be calculated and from this the sensitivity of the SIFT-MS technique can be estimated to be 138 cps/ppbv. This gives a limit of detection of 20 pptv in 10 s using the  $m/z$  122 product ion.

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Table 1: Limits of Detection (LoD) and Limits of Quantitation (LoQ) for PAN with various reagent ions in pptv. Limits of Detection are for a 10 second scan and the Limits of Quantitation are for an acceptable relative standard deviation of 20%.

<b>Reagent Ion</b>	<b>Product ion <math>m/z</math></b>	<b>LoD</b>	<b>LoQ</b>
<b>H<sub>3</sub>O<sup>+</sup></b>	77	80	138
	95	120	210
	122	20	170
<b>NO<sup>+</sup></b>	43	700	1200
	46	345	590
<b>O<sub>2</sub><sup>+</sup></b>	43	420	710

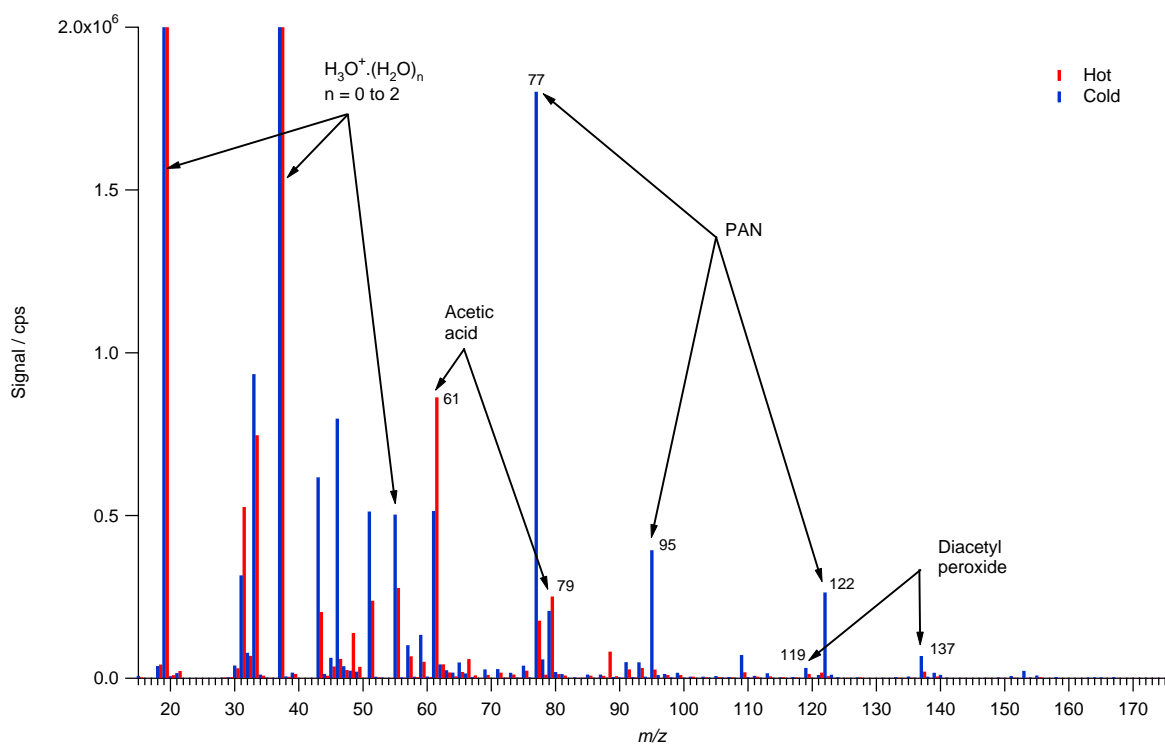


Figure 1: The mass spectra of PAN (blue) and the background obtained by heating the sample (red), using H<sub>3</sub>O<sup>+</sup> as the reagent ion.

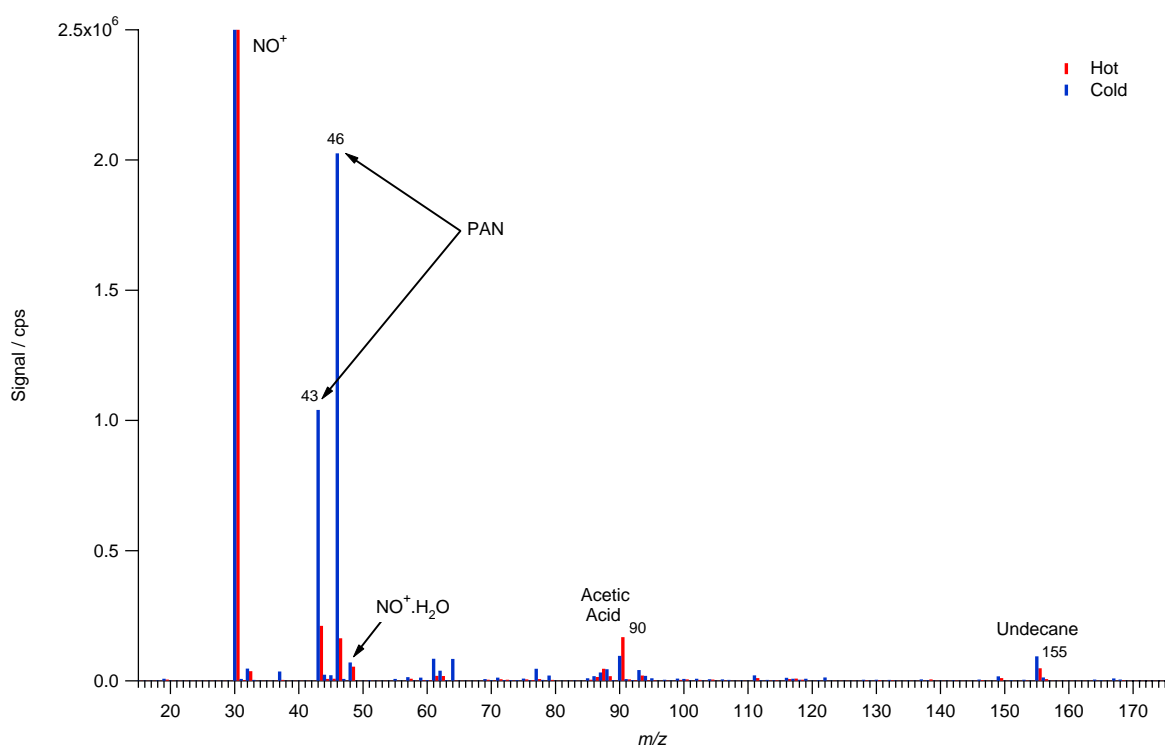


Figure 2: The mass spectra of PAN (blue) and the background obtained by heating the sample (red), using NO<sup>+</sup> as the reagent ion.

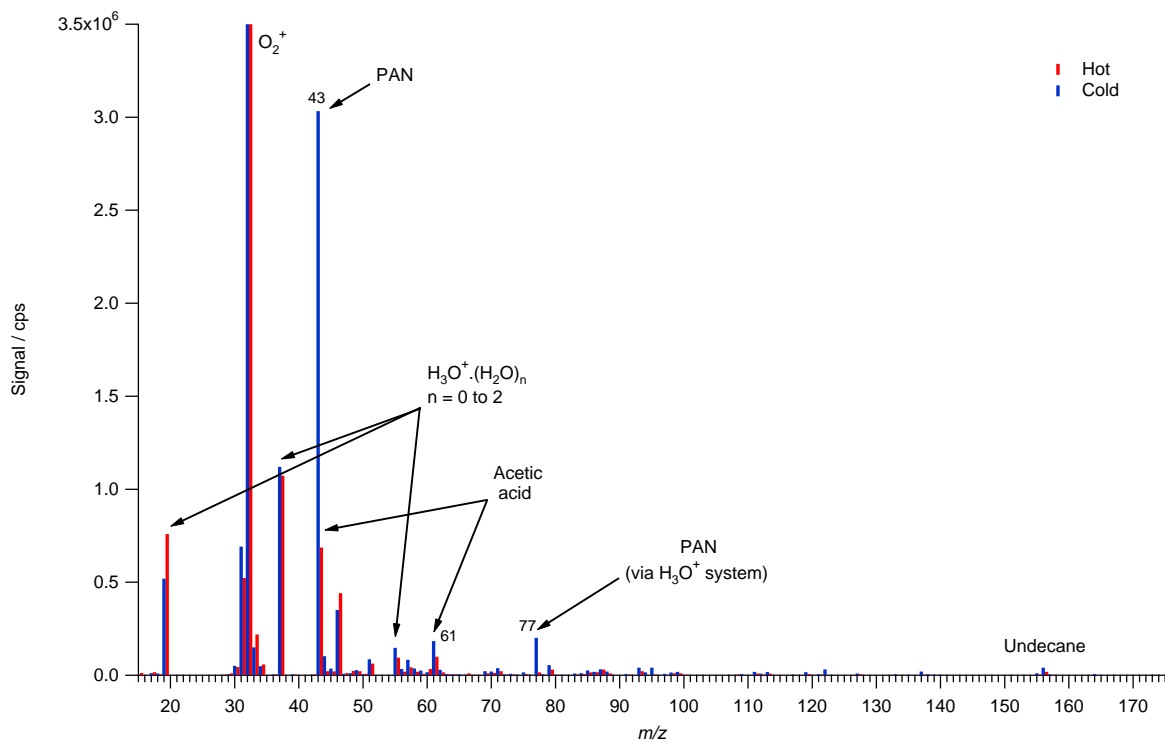


Figure 3: The mass spectra of PAN (blue) and the background obtained by heating the sample (red), using  $O_2^+$  as the reagent ion.

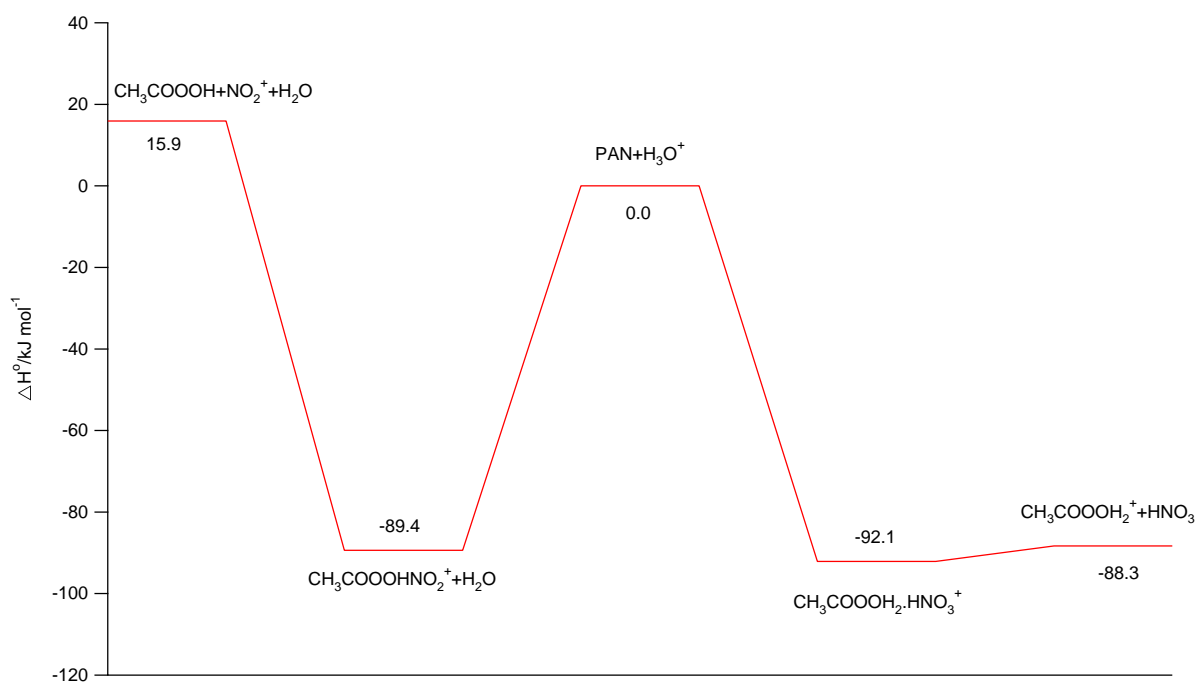


Figure 4: Results of the calculations on the thermochemistry of the reaction of PAN with  $H_3O^+$ .