

# Sensitive Atmospheric Pressure Detection of Nitroaromatic Compounds and NO<sub>x</sub> (x = 1,2) Molecules in an Ionization Chamber Using Resonance-enhanced Multi-photon Ionization

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Nitrobenzene and *o*-nitrotoluene were detected in trace concentrations in gas mixtures at atmospheric pressure in a simple unity-gain ionization chamber. The detection procedure relies on tunable ultraviolet laser radiation that identifies the characteristic wavelength dependence of the NO<sup>+</sup> ion fragment. Sensitivity levels are  $0.25 \pm 0.05$  ppm for nitrobenzene and  $0.75 \pm 0.1$  ppm for *o*-nitrotoluene, with the current limitations being background ionization, laser power and small sampling volume. Additionally, nominally 1 ppm NO and NO<sub>2</sub> gas samples were analysed and the saturation fluence (via a resonant two-photon process at 226.3 nm) for NO<sup>+</sup> production from NO gas was determined. Sensitivity levels of 120 and 50 ppb were estimated from the data on NO<sub>2</sub> and NO, respectively. It is shown that an increase in sensitivity of an order of magnitude is possible in all instances if the experimental parameters are optimized.

**Keywords:** Resonance-enhanced multi-photon ionization; nitroaromatic vapour; ionization chamber detection; sensitivity; NO<sub>x</sub> molecule

## Introduction

The detection and identification of environmentally sensitive vapours at trace levels in the atmosphere is an issue of great importance. In the area of vapour phase explosives monitoring there is a requirement for real-time analysis of air samples so that rapid response can be effected.

The use of atmospheric pressure ion mobility spectrometers has demonstrated the sensitive detection of explosive species, where reactant ions created by a <sup>63</sup>Ni source<sup>1-6</sup> interact with the analyte molecules in a charge-transfer reaction that allows the analyte to become charged and drawn down the drift region to the detector. Interpretation of spectra can be hindered by a variety of possible chemical reactions involving the analyte molecules and the inherent diffusion-limited resolution. An additional drawback to high sensitivity arises because of interference from the reactant ions, which also drift to the detector. Consequently, the spectrometers are often coupled to a quadrupole mass filter in order to allow for more detailed analysis.<sup>2,6</sup>

Coupling a laser ionization source to the atmospheric pressure ion mobility spectrometer has the advantage of more selective ionization and/or fragmentation of the analyte molecules over and above the background species, and hence

produces a cleaner spectrum.<sup>7</sup> Tunability of the laser wavelength would also aid identification of species of interest by virtue of their wavelength-dependent ionization yield.

It has been shown that a simple ionization chamber at atmospheric pressure can also be used with advantage to detect environmentally sensitive gases.<sup>8,9</sup> In view of this, a simple ionization chamber has been constructed and coupled to a gas dilution flow system. This arrangement has been used to monitor the presence of the NO<sup>+</sup> ion, which is efficiently produced from the photofragmentation/photoionization of nitroaromatic compounds in the wavelength region around 226 nm.<sup>10,11</sup> By scanning the laser wavelength over this region it is possible to identify the presence of the NO<sup>+</sup> ion in addition to detecting background resonances originating from molecular oxygen Rydberg transitions.<sup>12</sup> These spectral features serve as calibration markers and also verify system functionality. The purpose of the sample dilution apparatus is to determine sensitivity levels for the prevailing operating parameters.

NO and NO<sub>2</sub> samples at 1 ppm in nitrogen and air balances, respectively, have also been studied to yield information about fluence levels required to form NO<sup>+</sup> ions. This might aid the understanding of the process by which the NO<sup>+</sup> ion is formed from some of the larger explosives molecules. It is also perceived that the laser ionization technique is well suited to detecting NO<sub>x</sub> molecules in general.

## Experimental

A detailed description of the laser system and data acquisition procedure has been given previously.<sup>13</sup> Coumarin 47 (LC4700) dye was used in the dye laser and the shot-to-shot data are presented after normalization to the laser pulse energy (typically 300 μJ). The spectra are composed of 600 laser shots per nanometre, which means that at 10 Hz a 2 nm scan over the NO<sup>+</sup> band takes 2 min (operating at 1 kHz would take just over 1 s). Fig. 1 shows a schematic diagram of the experimental set-up, including the sample dilution system. The sample dilution system consists of a sample arm and a large flow rate dilution arm operating at a flow rate of 1000 ml min<sup>-1</sup>. Flow through the sample arm is restricted to about 30 ml min<sup>-1</sup> in an attempt to maintain a saturated vapour pressure of sample in the sample arm air stream. The saturated vapour pressures of nitrobenzene and *o*-nitrotoluene at 300 K are 0.36 and 0.24 Torr (48 and 32 Pa), corresponding to 470 and 315 ppm, respectively. With a flow rate of saturated vapour of around 2 ml min<sup>-1</sup> being diluted into the 1000 ml min<sup>-1</sup> line, a sample concentration of about 1 ppm of nitrobenzene is produced, whereas for nitrotoluene a saturated vapour flow rate of around 3 ml min<sup>-1</sup> is required. These sample concentrations are upper limits, as the sample

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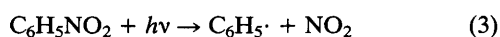
vapours cannot attain a greater number density than that of the saturated vapour pressure.

The sample and dilution arms are combined prior to introduction to the chamber and an exhaust system removes the mixture after sampling has been carried out. With NO<sub>x</sub> samples, the 1 ppm samples were admitted directly to the chamber and exhausted as before.

Samples were used as supplied by the manufacturer. Nitrobenzene was obtained from BDH-Merck (Poole, Dorset, UK) and *o*-nitrotoluene from Aldrich Chemical (Gillingham, Dorset, UK). Bottled air, 1 ppm of NO in nitrogen and 1 ppm of NO<sub>2</sub> in air were obtained from BOC (Glasgow, UK). The actual concentrations of the 1 ppm samples were 0.96 ppm NO in N<sub>2</sub> and 0.79 ppm NO<sub>2</sub> in air.

### Results and Discussion

Sensitive detection is best achieved where there is the strongest analyte signal and smallest background interference. Of the wavelength regions studied to date, the largest laser-induced signal from the nitroaromatic samples occurs at 226.3 nm and originates from the ionization of neutral NO molecules. A detailed discussion of the various fragmentation pathways has been presented by Kosmidis *et al.*,<sup>14</sup> the main routes in this wavelength range being



Only route (2) contributes significantly to NO<sup>+</sup> production from nitrobenzene directly, but further absorption of photons by photodissociation products of nitrobenzene also leads to NO<sup>+</sup> production *via* the other pathways.

Analysis of the bottled air sample (Fig. 2) shows that there are no vapour species that absorb strongly around 226 nm, thus making this a suitable wavelength region for detection of the NO<sup>+</sup> component from nitroaromatic and NO<sub>x</sub> molecules in the atmosphere. The ionization yield recorded in Fig. 2 constitutes the background ionization referred to in the remainder of the discussion. Close examination of the 226 nm region shows the presence of a very small background NO<sup>+</sup> signal, which arises from previous use of the chamber for

experiments involving nitroaromatic compounds. When this wavelength region is scanned with the nitroaromatic samples in the atmospheric pressure ion chamber, we see that the characteristic rotational-vibrational structure of the NO<sup>+</sup> ion is still very prominent in both cases (Fig. 3). It is important to note that the atmospheric pressure does not cause the detailed rotational structure in the ionization yield to be lost.

When performing the sensitivity measurements for the nitroaromatic molecules, the dilution flow was held constant while the sample arm flow rate was increased, the assumption here being that the liquid sample maintains a saturated vapour pressure in the headspace, which is then forced downstream by the air flow and is diluted before entry into the ion chamber. Figs. 4 and 5 show wavelength scans for bottled air flows to which are added nitrobenzene and *o*-nitrotoluene, respectively, for a range of analyte concentrations. The ion yield has been normalized to the laser pulse energy to make comparisons between spectra more accurate. This is a valid procedure as the laser pulse energy profile did not vary appreciably from sample to sample.

The spectra for nitrobenzene and *o*-nitrotoluene (Figs. 4 and 5) show increasing intensity of the NO<sup>+</sup> ion signal as the analyte concentration is increased, while the other spectral features remain constant. When the area under the NO<sup>+</sup> features for nitrobenzene is measured and allowance is made for non-NO<sup>+</sup> ion contributions (see Fig. 4, where the shaded areas correspond to these values), a relationship between signal size and vapour concentration that is approximately linear is obtained [Fig. 6(a)]. Deviations from linearity reflect the determination of the NO<sup>+</sup> component above the background. A similar procedure is carried out for *o*-nitrotoluene [Fig. 6(b)]. The projected limit of sensitivity for a pulse-to-pulse scan can be calculated to be 0.25 ± 0.05 ppm for nitrobenzene and 0.75 ± 0.1 ppm for *o*-nitrotoluene. These figures are obtained by examining the wavelength spectra and calculating the smallest signal that could be distinguished above the background, and fall in the same range as the 0.2 ppm detection achieved by Proctor *et al.*<sup>3</sup>

A study of the effect of laser fluence on NO<sup>+</sup> ion production was carried out on NO and NO<sub>2</sub> samples. The rate equation model developed by Singhal *et al.*<sup>15</sup> was used with an absorption cross-section of 5 × 10<sup>-18</sup> cm<sup>2</sup> (ref. 16) and an ionization cross-section of 7 × 10<sup>-19</sup> cm<sup>2</sup> (ref. 17) to predict

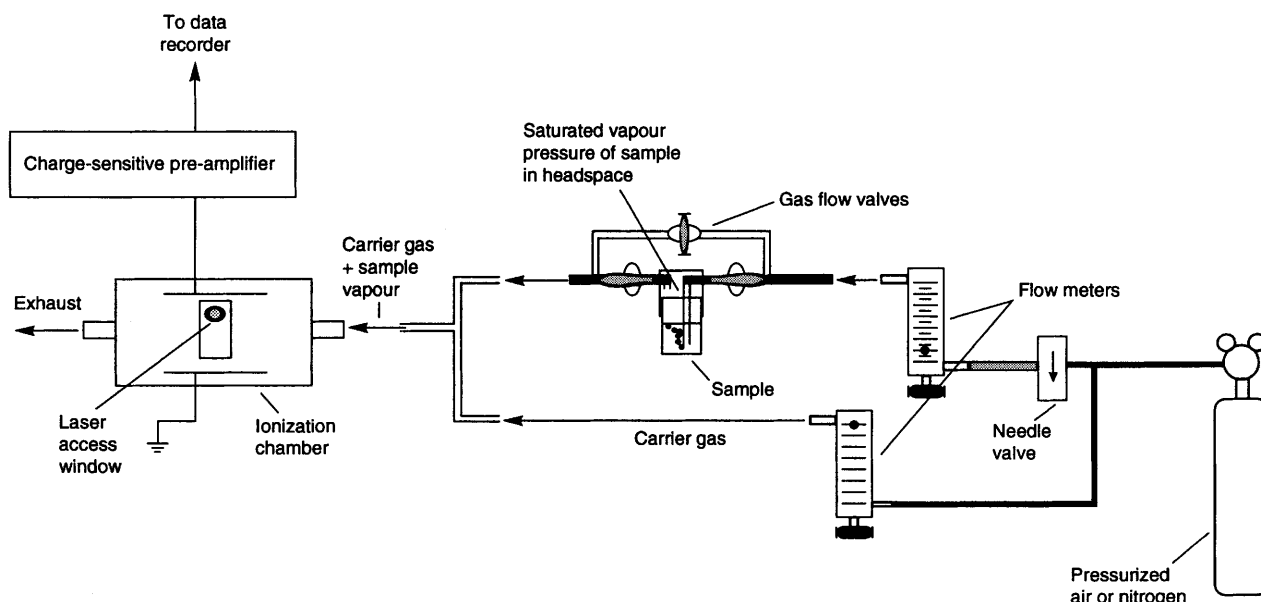


Fig. 1 Schematic diagram of the detector and gas flow system.

the effect of increasing laser fluence on  $\text{NO}^+$  ion yield. The experimental data for 1 ppm NO in nitrogen sample are compared with this model in Fig. 7. Calculation of laser fluence relies on measurement of the beam diameter using a travelling microscope to observe the impression caused by multiple laser shots on burn paper. A value of  $40\ \mu\text{m}$  for the diameter was obtained using this approach, and the fluence was calculated accordingly. The dependence of the  $\text{NO}^+$  signal on the fluence is also displayed for beam diameters of 35 and  $32\ \mu\text{m}$ . Also shown is the theoretical fit for absorption and ionization cross-sections of  $5 \times 10^{-18}$  and  $9 \times 10^{-19}\ \text{cm}^2$ , respectively. With a laser fluence of  $100\ \text{mJ mm}^{-2}$ , the  $\text{NO}^+$  signal is almost completely saturated; at around  $20\ \text{mJ mm}^{-2}$  there is a 50% yield.

When the 1 ppm samples of NO in nitrogen and  $\text{NO}_2$  in air are compared (Fig. 8), there is a significant difference in the yield. This reflects the additional dissociation step required in

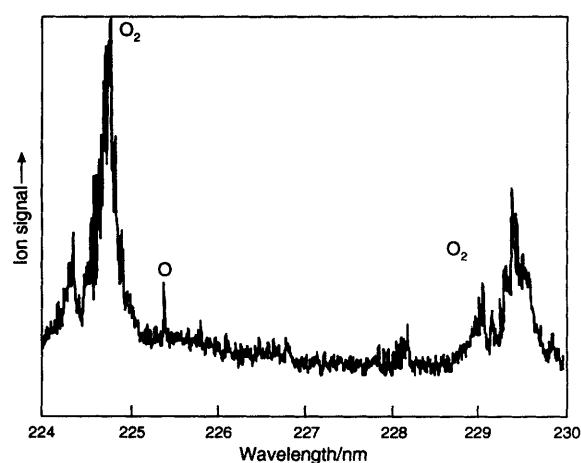


Fig. 2 Ionization spectrum from 224 to 230 nm of bottled air (carrier gas) with no analyte added. The contributions from REMPI of atomic and molecular oxygen are indicated.

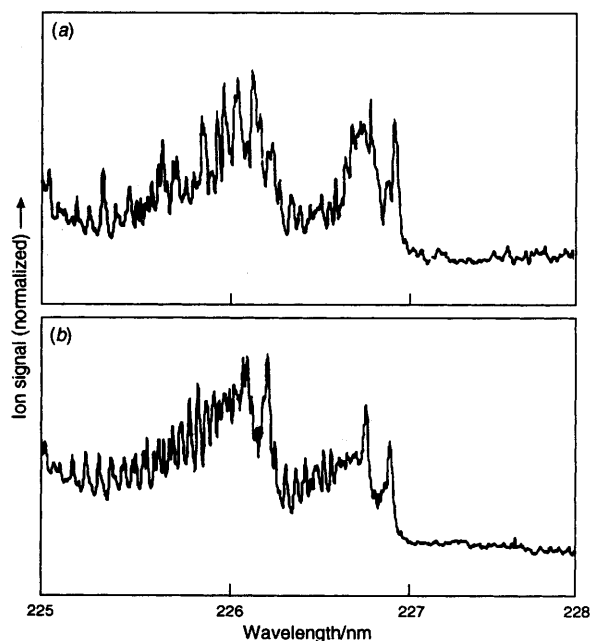


Fig. 3 Wavelength dependence of the ionization yield from the carrier gas plus analyte for (a) nitrobenzene and (b) *o*-nitrotoluene samples between 225 and 228 nm. The spectra have been normalized to laser pulse energy.

the  $\text{NO}_2$  molecule to produce the neutral NO molecule and also the different populations of the ground-state rotational-vibrational levels in the  $\text{NO}_2$  dissociated NO molecules.<sup>13,18</sup>

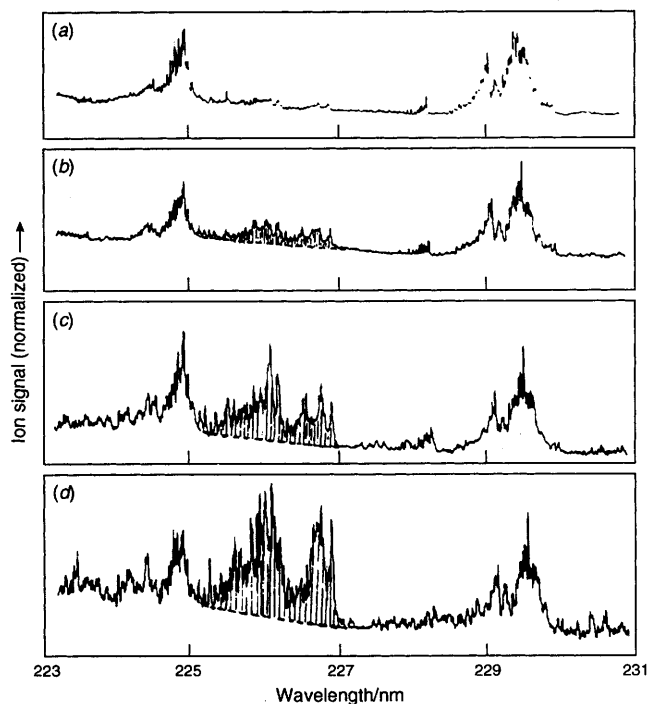


Fig. 4 Wavelength dependence of the normalized ionization yield for a variety of concentrations of nitrobenzene sample over the wavelength range 223–231 nm. (a) Background; (b) 1 ppm; (c) 5 ppm; and (d) 10 ppm.

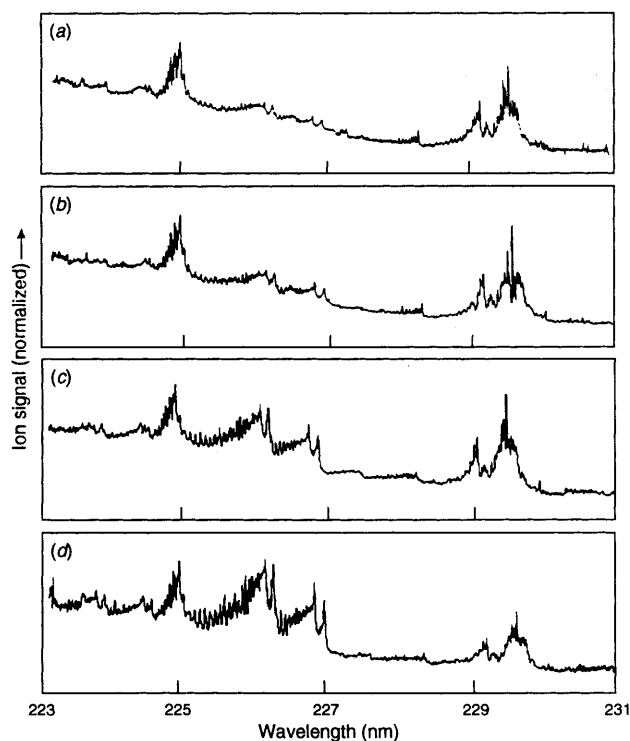


Fig. 5 Wavelength dependence of the normalized ionization yield for a variety of concentrations of *o*-nitrotoluene sample over the wavelength range 223–231 nm. (a) 1.5 ppm; (b) 3 ppm; (c) 6 ppm; and (d) 7.5 ppm.

Earlier work<sup>10</sup> has demonstrated sensitivity levels at the 150 ppb level for the detection of NO<sub>2</sub>. Fig. 9 shows the spectrum of 1 ppm of NO in nitrogen, where the signal-to-noise ratio is 20:1, with an estimated sensitivity level of 50 ppb. These levels can be compared with 240 ppb for NO<sub>2</sub> and 8 ppb for NO reported by Lemire *et al.*<sup>19</sup> at 226.3 nm using a mass spectrometer system.

The issue of ion collection efficiency in the ionization chamber in the two situations is unclear because it is not

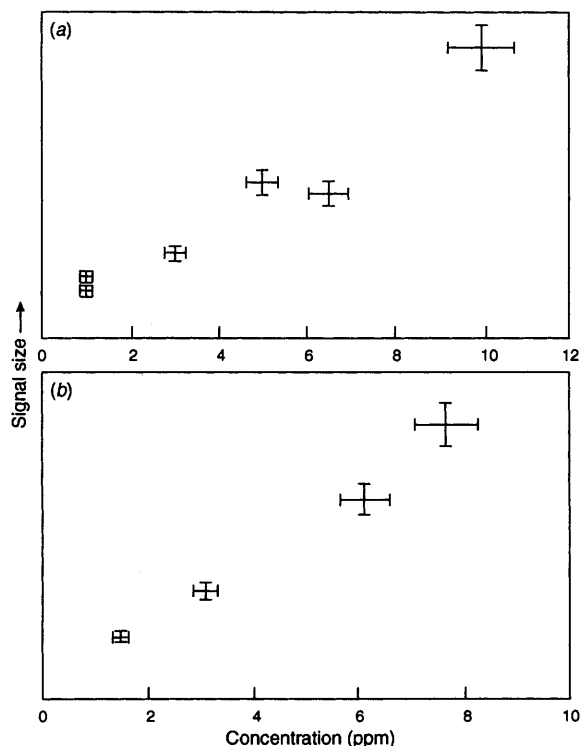


Fig. 6 Graph of the NO<sup>+</sup> ion signal size as a function of concentration for (a) nitrobenzene and (b) *o*-nitrotoluene.

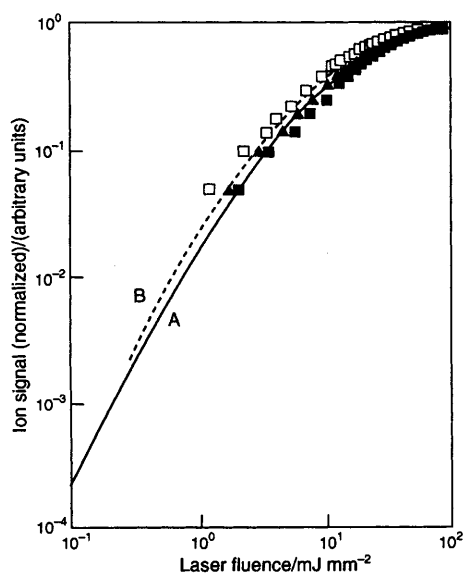


Fig. 7 Theoretical versus experimental graph of NO<sup>+</sup> yield from 1 ppm NO gas as a function of laser fluence. Diameter spot size: ■, 32  $\mu$ m; ▲, 35  $\mu$ m; and □, 40  $\mu$ m. A,  $7 \times 10^{-19}$  cm<sup>2</sup> ionization cross-section; and B,  $9 \times 10^{-19}$  cm<sup>2</sup> ionization cross-section. The excitation cross-section was  $5 \times 10^{-18}$  cm<sup>2</sup>.

possible to obtain NO<sub>x</sub> samples with the same balance gas owing to sample stability problems. However, the two power dependences show that the NO<sup>+</sup> yield from the NO<sub>2</sub> sample is still increasing linearly with laser fluence at the maximum value, whereas that of the NO sample has almost saturated. This identifies the photodissociation of the NO<sub>2</sub> molecule as the rate-limiting step. The same is true for nitrobenzene, where the step of producing neutral NO determines the NO<sup>+</sup> yield.

One issue that is currently unresolved in studies of the nitroaromatic species is that of the residual hydrocarbon fragments. For every NO<sup>+</sup> ion detected there is necessarily either a parent minus NO/NO<sub>2</sub> molecule, or some smaller fragment. In experimental work carried out in vacuum conditions,<sup>11</sup> hydrocarbon fragments were observed albeit in small proportion to the NO<sup>+</sup> signal. Zhu *et al.*<sup>20</sup> using atmospheric pressure ionization mass spectrometry (at 213 nm) and Simeonsson *et al.*<sup>21</sup> ionizing *o*-nitrotoluene and *m*-nitrotoluene in vacuum (at 193 nm) demonstrated much greater hydrocarbon ion yields. This suggests that the wavelength regions around 205 and 215 nm [where there are strong absorption bands in the NO molecule (Fig. 10)] would yield additional information via ionized hydrocarbon components. An ability to analyse the background ionization components could well serve as a means of discriminating

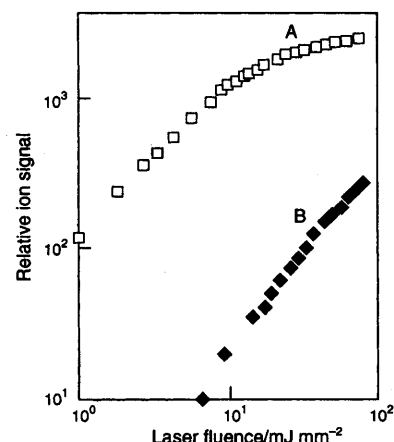


Fig. 8 Comparison of NO<sup>+</sup> ion yield from A, 1 ppm NO in nitrogen and B, 1 ppm NO<sub>2</sub> in air as the laser fluence is varied.

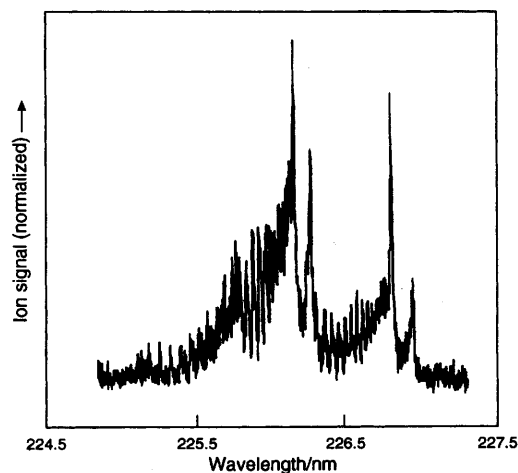


Fig. 9 Wavelength dependence of the NO<sup>+</sup> ion production from the 1 ppm NO in nitrogen sample where the ion signal has been normalized to take into account fluctuations in laser fluence.



between  $\text{NO}^+$  contributing species. This would not be particularly practical using an ionization chamber configuration, but could be feasible using an atmospheric pressure ion mobility spectrometer (IMS). Here, the  $\text{NO}^+$  ion would be separated from the other ions as it travels along the drift region towards the detector and so could be monitored as before, while other fragment ions will arrive with different mobilities and their peak intensities can also be marked and monitored. Ideally, the ionic species would be further analysed using mass spectrometric techniques.<sup>3,22</sup>

Although for the nitroaromatics these levels of detection sensitivity are not at the 'ultra-trace' level, they can be detected without sample preconcentration and with a short (1 min) sampling time. This time is dictated by the pulse repetition rate of the laser (10 Hz) and the scan speed. By increasing the laser repetition and scanning rates, it will be possible to decrease the analysis time by at least one order of magnitude.

Inspection of the dependence of  $\text{NO}^+$  ion production from nitroaromatic molecules on the fluence (Fig. 11) shows that the laser fluence is not sufficient to saturate the molecular transitions in the photodissociated neutral NO fragments. This means that an increase in laser fluence will cause an increase in both the analyte and background signals leading to improved signal-to-background statistics and greater detection sensitivity.

Possibly the greatest gain could be made by increasing the laser interaction volume to sample a greater population of analyte molecules. Currently, the rectangular cross-section of the laser beam is focused to provide a high enough fluence for

ionization. Considering that the cross-sectional area of the laser beam is focused from approximately 6 to 0.04 mm<sup>2</sup>, a factor of 150 increase the number of analyte ions could be expected if sufficient fluence could be maintained across the 6 mm<sup>2</sup> cross-section. As the background also increases by a similar amount, the signal-to-noise ratio only increases by the square root of this number, giving an increase in sensitivity of about one order of magnitude.

The final source of improvement would come about if the background level in the spectra could be lowered. As the statistical fluctuation of a signal varies as the square root of the number of events contributing to that signal, a decrease in the number of ions recorded would lower the level of fluctuation. By using an IMS detector, the background ion contribution due to non- $\text{NO}^+$  producing molecules could be separated from the signal of interest, thus decreasing the level of fluctuation on the  $\text{NO}^+$  signal. In addition, if the wavelength scanner was operated in the burst mode and a boxcar averager was used to average the signal per wavelength increment, the fluctuation in the background level in the spectra could be further decreased.

### Conclusions

Detection of the nitroaromatic compounds *o*-nitrotoluene and nitrobenzene has been demonstrated at 1.5 and 1 ppm levels, respectively. Given the recorded spectra, levels of  $0.75 \pm 0.1$  and  $0.25 \pm 0.5$  ppm, respectively, could be detected with the current configuration. At present, the detection levels for NO and  $\text{NO}_2$  are 50 and 150 ppb, respectively. Laser beam geometry and fluence levels, together with on-line signal averaging, are factors that could be expected to increase the detection levels by an order of magnitude.

A further improvement would be to separate the various ion species using an IMS, not only for identification purposes, but also to decrease the statistical noise contribution from the large background ion signal.

Varying the laser wavelength to ionize more of the hydrocarbon neutral species will be investigated in the future. The NO absorption bands at 215 nm (1-0) and 205 nm (2-0) would be expected to produce a similar  $\text{NO}^+$  yield to maintain or even improve current sensitivity levels. In addition, an increased hydrocarbon ion yield would also be expected, which would provide a considerably increased selectivity for the various  $\text{NO}^+$ -producing species.

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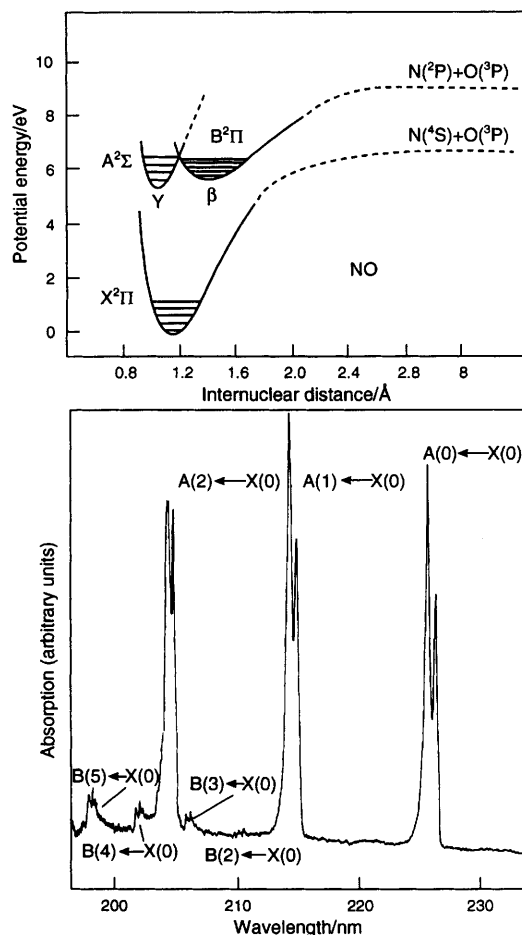


Fig. 10 Absorption spectrum of NO gas showing the various absorption bands in the wavelength region of 195–250 nm.

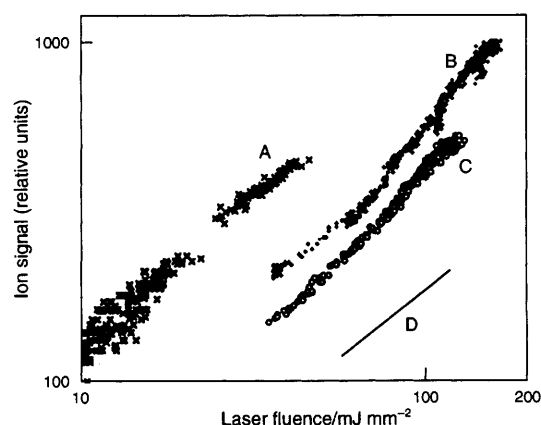


Fig. 11 Fluence dependence of the  $\text{NO}^+$  signal from A nitrobenzene and B, *o*-nitrotoluene compared with C, the background. Also indicated is a linear dependence D.

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